FINNISH METEOROLOGICAL INSTITUTE

DAYTIME AND NIGHTTIME AGING OF LOGWOOD COMBUSTION AEROSOLS

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20th ETH-Conference on Combustion Generated Nanoparticles, Zürich, 13.–15.6.2016

Motivation

- Emissions from small-scale wood combustion have a significant contribution to the atmospheric particulate matter (black carbon, primary and secondary organic aerosol)
- Aging processes alter the physical and chemical properties of the emissions:

  What kind of differences are there in daytime and nighttime aging?
- What factors may influence on, e.g. secondary organic aerosol formation and SOA type?

This presentation is based on

Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging

Tiitta, P.[1], Leskinen, A.[2,3], Hao, L.[2], Yli-Pirilä, P.[1,2], Kortelainen, M.[1], Grigonyte, J.[1], Tissari, J.[1], Lamberg, H.[1], Hartikainen, A.[1], Kuuspalo, K.[1], Kortelainen, A.[2], Virtanen, A.[2], Lehtinen, K. E. J.[2,3], Komppula, M.[3], Pieber, S.[4], Prévôt, A. S. H.[4], Onasch, T. B.[5], Worsnop, D. R.[5], Czech, H.[6], Zimmermann, R.[6,7,8], Jokiniemi, J.[1], and Sippula, O.[1,8]

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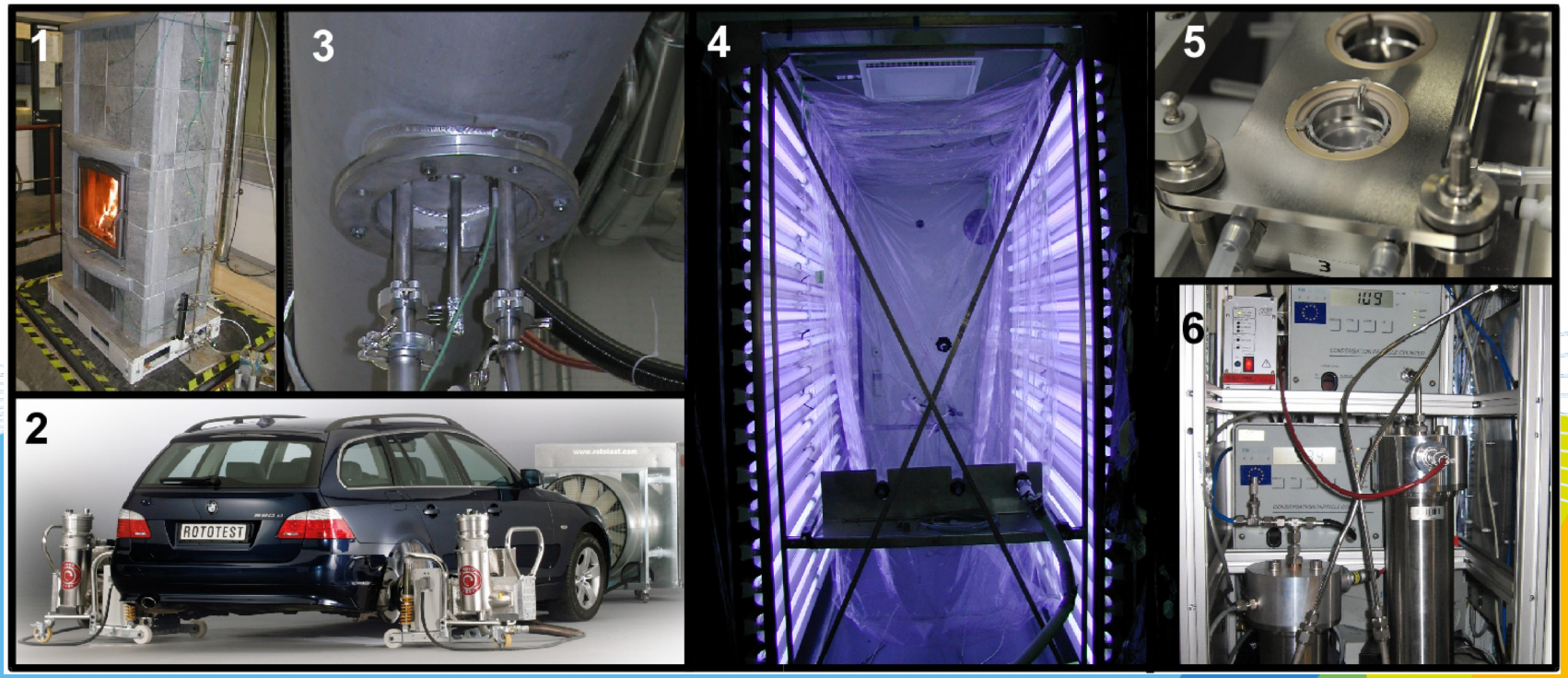
[8]HICE-Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health–Aerosols and Health (www.hice-vi.eu)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-339, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 2 May 2016

The research unit “ILMARI” at UEF

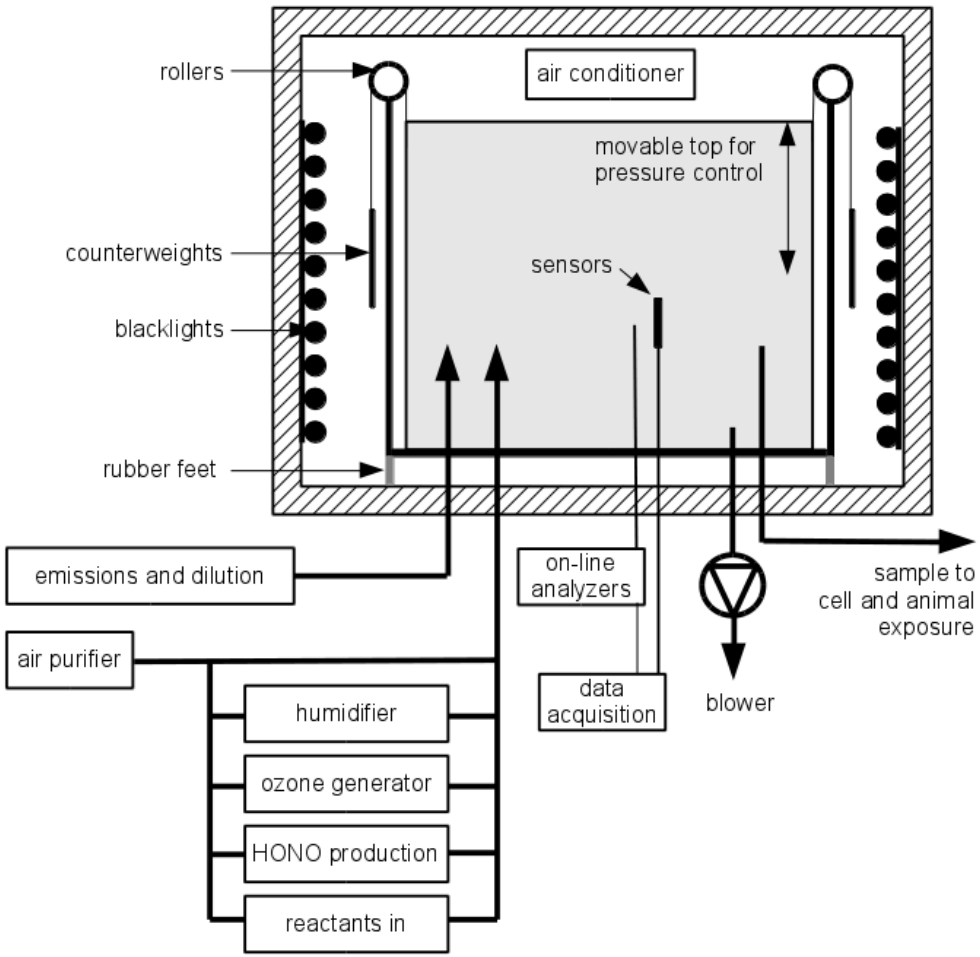
- Emission sources (**stoves**, burners, vehicles) and **dilution**
- **Environmental chamber**
- On-line cell exposure (air-liquid interface) and animal whole body exposure units



The emission source and dilution

- Wood logs (spruce) were burnt in a modern heat-storing masonry heater with a staged combustion air supply
- The emission was drawn from the **stack** through a **PM10 cyclone**, a **porous tube dilutor**, and a heated (100 °C) line into an **ejector dilutor** which pushed the diluted sample into the **chamber** (pre-filled with purified air)
- Total dilution rate (porous tube and ejector dilutors and chamber), based on [CO_2], was ~ 250

The environmental chamber at ILMARI



- Made of **125 µm FEP Teflon** film
- 3.5 m × 3.5 m × 2.4 m (**29 m^3**)
- **Movable top**, lines and cables through the floor, maintenance hatch
- **Purified air source** ~170 lpm
- **Blacklight lamps**, spectra centered at 365 nm, 350 nm, and 340 nm
- An **air-conditioned** enclosure with **reflective walls**

Leskinen et al., AMT, 8, 2267–2278, 2015

Experiments: combustion procedure

- In each experiment **2.5 kg of wood logs** (spruce) were burned (main batch 2.35 kg, **kindlings 0.15 kg**) with combustion initiated from **“cold start”**
- Different ignition speeds (**“fast” and “slow”**) were applied by using kindlings of different sizes on top of the main batch
- The emissions from burning **one batch** with all combustion phases (ignition, flaming, char burning) were introduced into the environmental chamber

IGNITION:

”FLAMING”:

CHAR BURNING:

Experiments: aging procedure

- **Injection of emission** (35 min), **stabilization** (10–40 min)
- **Injection of ozone** in order to convert NO to NO_2 and reach an atmospheric level of $[O_3]$ (40 ppb) in the chamber
- **Injection of butanol-d9** (OH exposure from its decay)
- **4 hours of dark aging** ("nighttime": oxidation by ozone and nitrate radical) **+ 3 hours of UV light exposure** ("daytime": oxidation by (ozone and) OH radicals at $(0.5–5)\times10^6$ molecules cm^{-3} concentration corresponding to atmospheric age up to 18 h) **OR 4 hours of UV light exposure**
- Mean wavelength of UV lights **350 nm**
- One experiment with HONO (OH radical source) + propene

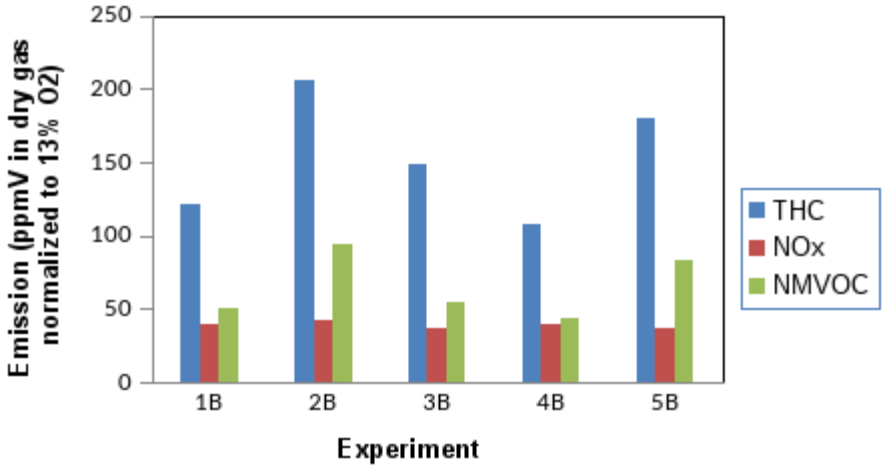
Measured properties (instruments)

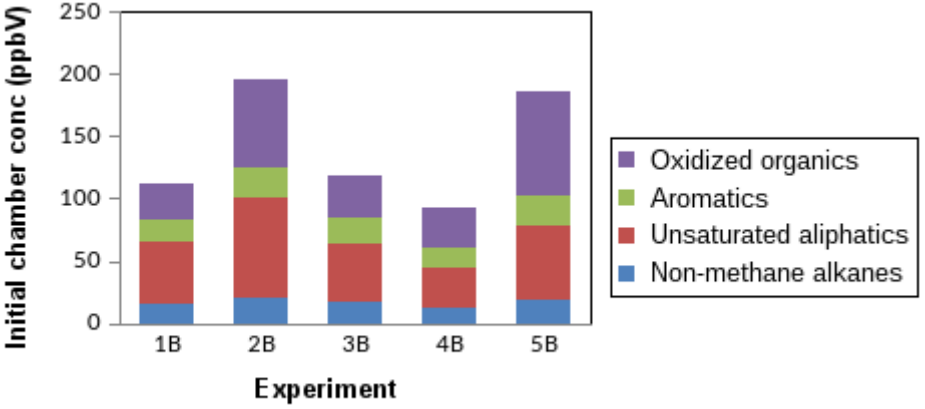
- Nitrogen oxides, ozone, sulphur dioxide, organics (FTIR)
- Gas phase chemical composition (PTR-MS)
- Particle size distribution (SMPS)
- Particle mass concentration (TEOM)
- Particle chemical composition (SP-HR-ToF-AMS)

FTIR: Fourier transformation infrared spectroscopy, PTR-MS: Proton transfer reaction - mass spec.
SMPS: Scanning mobility particle sizer, TEOM: Tapered element oscillating microbalance,
SP-HR-ToF-AMS: Soot particle - high resolution - time-of-flight - aerosol mass spectrometry

Emission characterization (gas phase)

- Slow ignition experiments (2B and 5B) produced more organic compounds than fast ignition experiments
- Greatest difference in concentrations of oxidized organics and unsaturated aliphatics
- VOC:NOx ~ 5 in slow ignition and ~ 3 in fast ignition

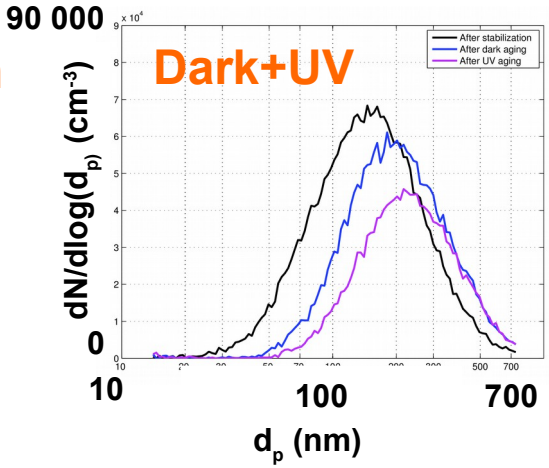


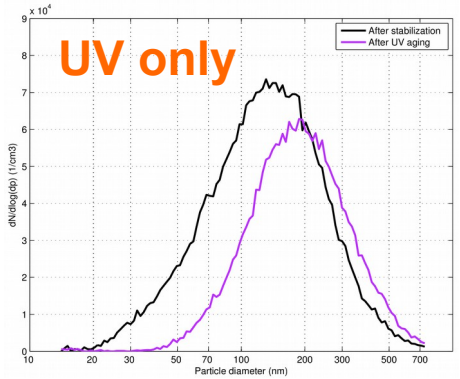


THC: Total hydrocarbons,
NO_x ($NO+NO_2$): Nitrogen monoxide and dioxide
NMVOC: Non-methane volatile organic compounds

Particle size distributions in the chamber

Slow ignition

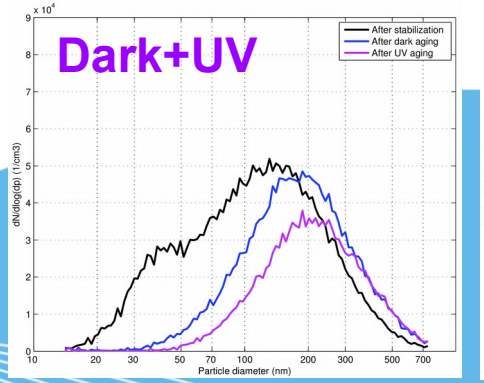


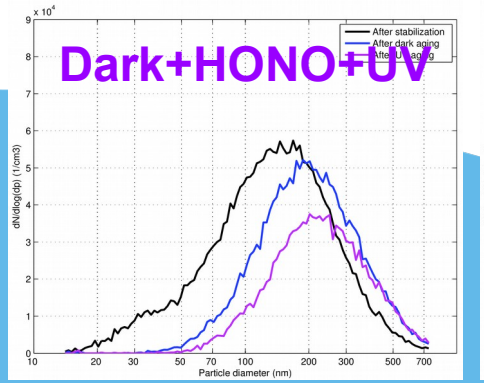


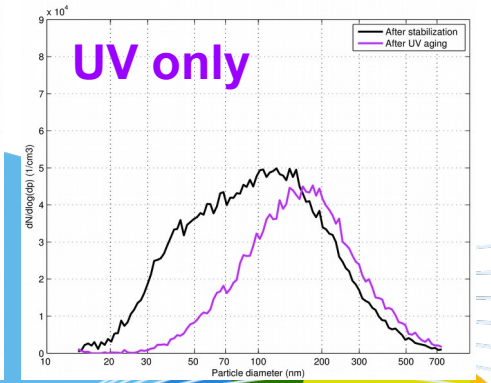
After stabilization
After dark aging
After UV aging

All corrected for wall losses

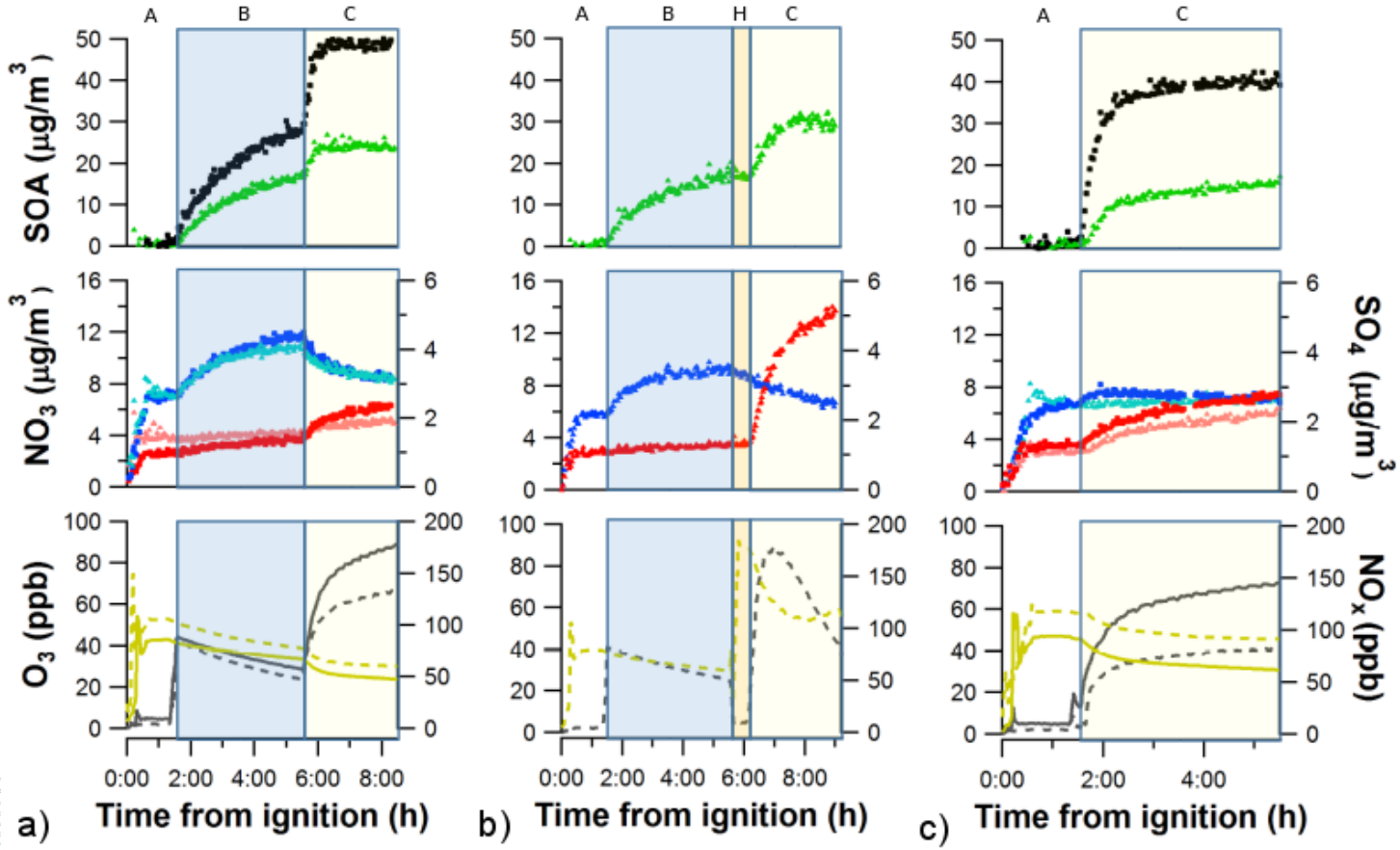
Fast ignition







Evolution of SOA, NO3, O3, SO4, and NOx



Black: slow ignition

Green: fast ignition

Blue: NO_3

Red: SO_4

Black: O_3

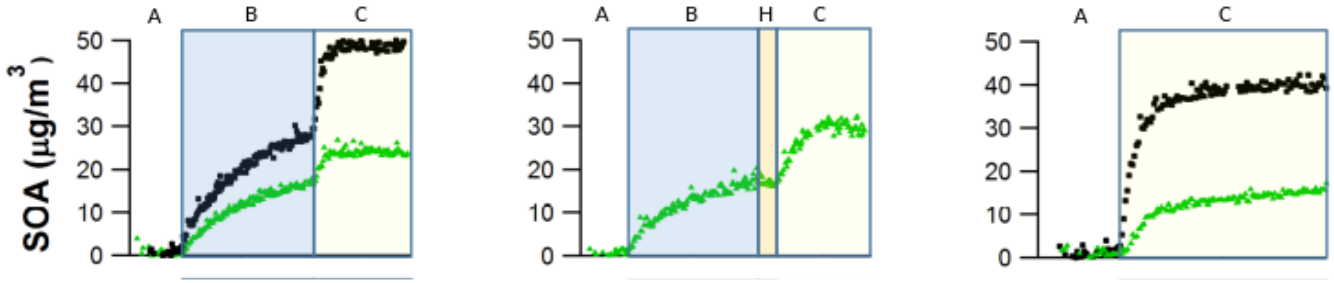
Yellow: NO_x

Solid: slow ign.

Dashed: fast ign.

SOA mass and its increase rate

SOA is secondary organic aerosol



Black: slow ignition
Green: fast ignition

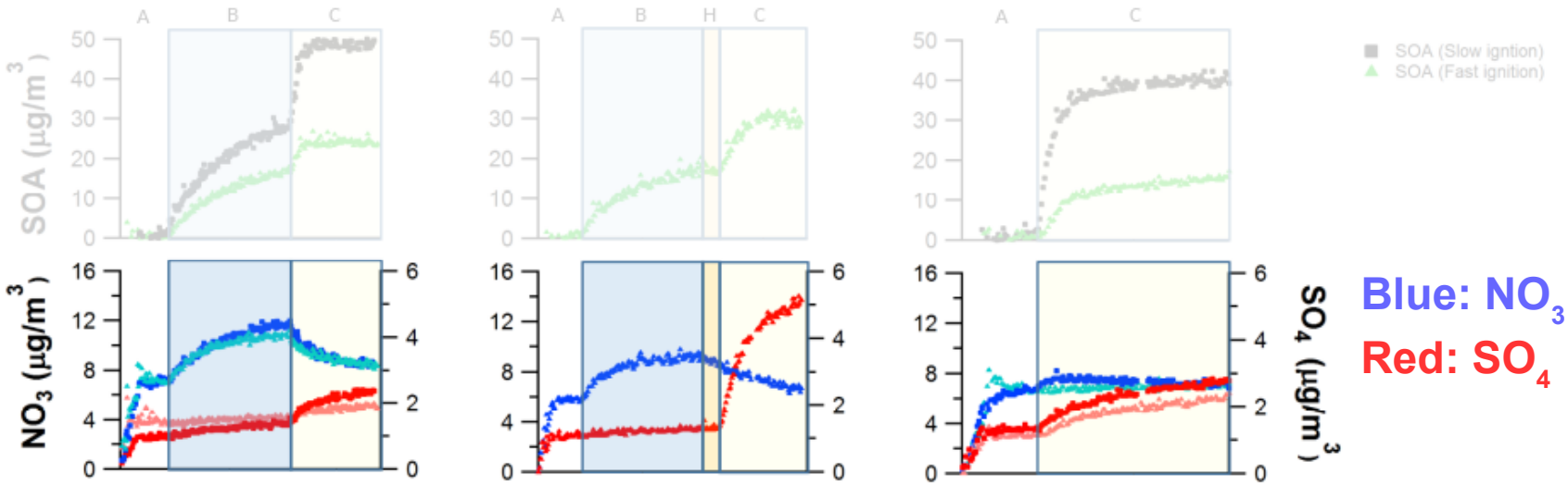
SOA mass increase rate (µg/h) and total SOA mass (µg):

	DARK			UV (after dark)			UV only		
	1st hr	2nd hr	SOA m.	1st hr	2nd hr	SOA m.	1st hr	2nd hr	SOA m.
SLOW	15	6	26	21	0	+21	32	2	39
FAST	8	3	17	5	0	+5	10	2	16
FAST+HONO	8	3	17	12	2	+14	–	–	–

- Slow ignition produces more SOA than fast ignition
- SOA mass increase is faster in UV aging than in dark aging
- More than half of the SOA is produced during the first hour
- Dark aging produces a remarkable amount of SOA
- HONO addition enhances SOA formation

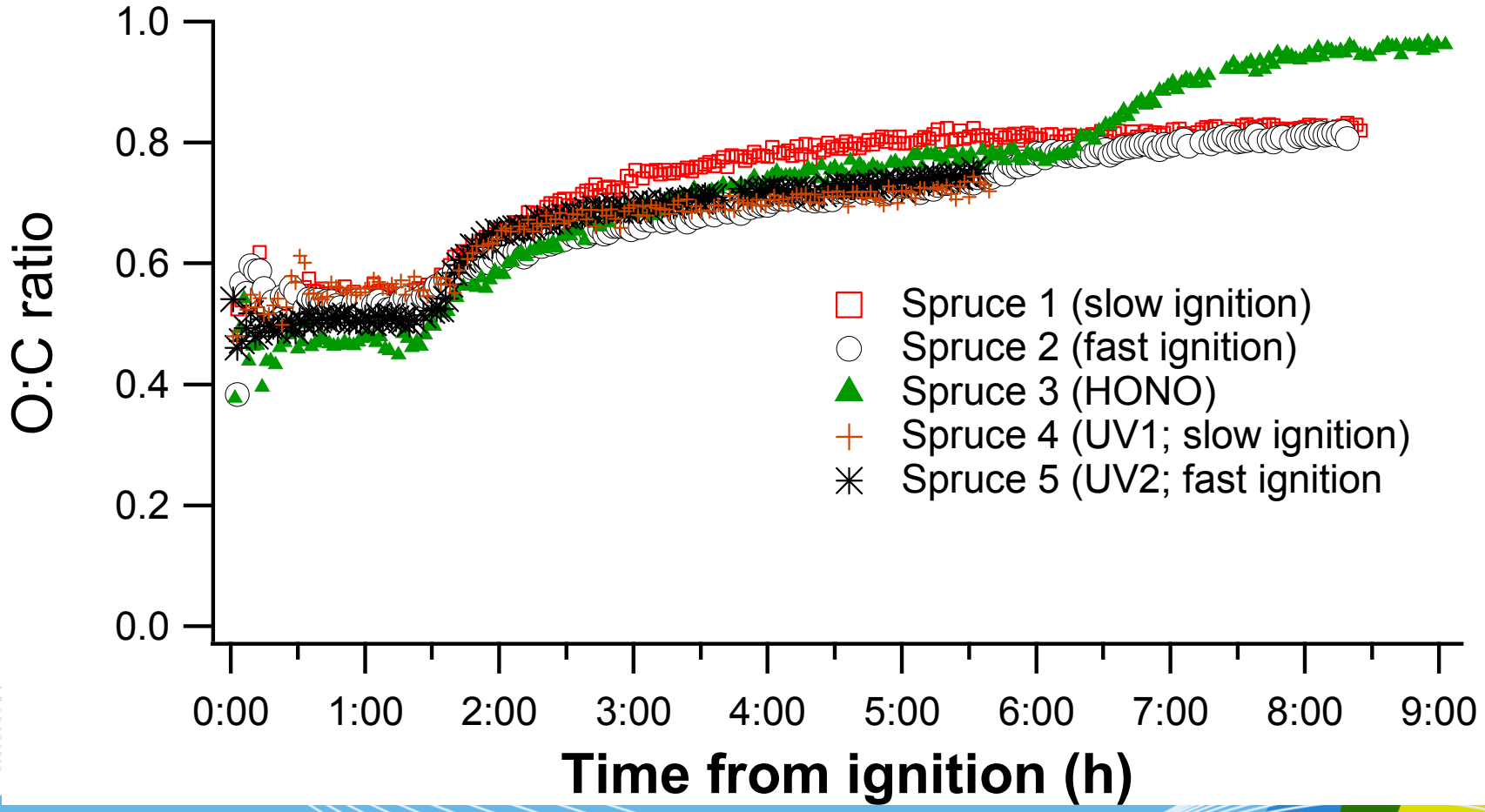
HONO is a source for OH radicals

Nitrate (NO_3) behaviour



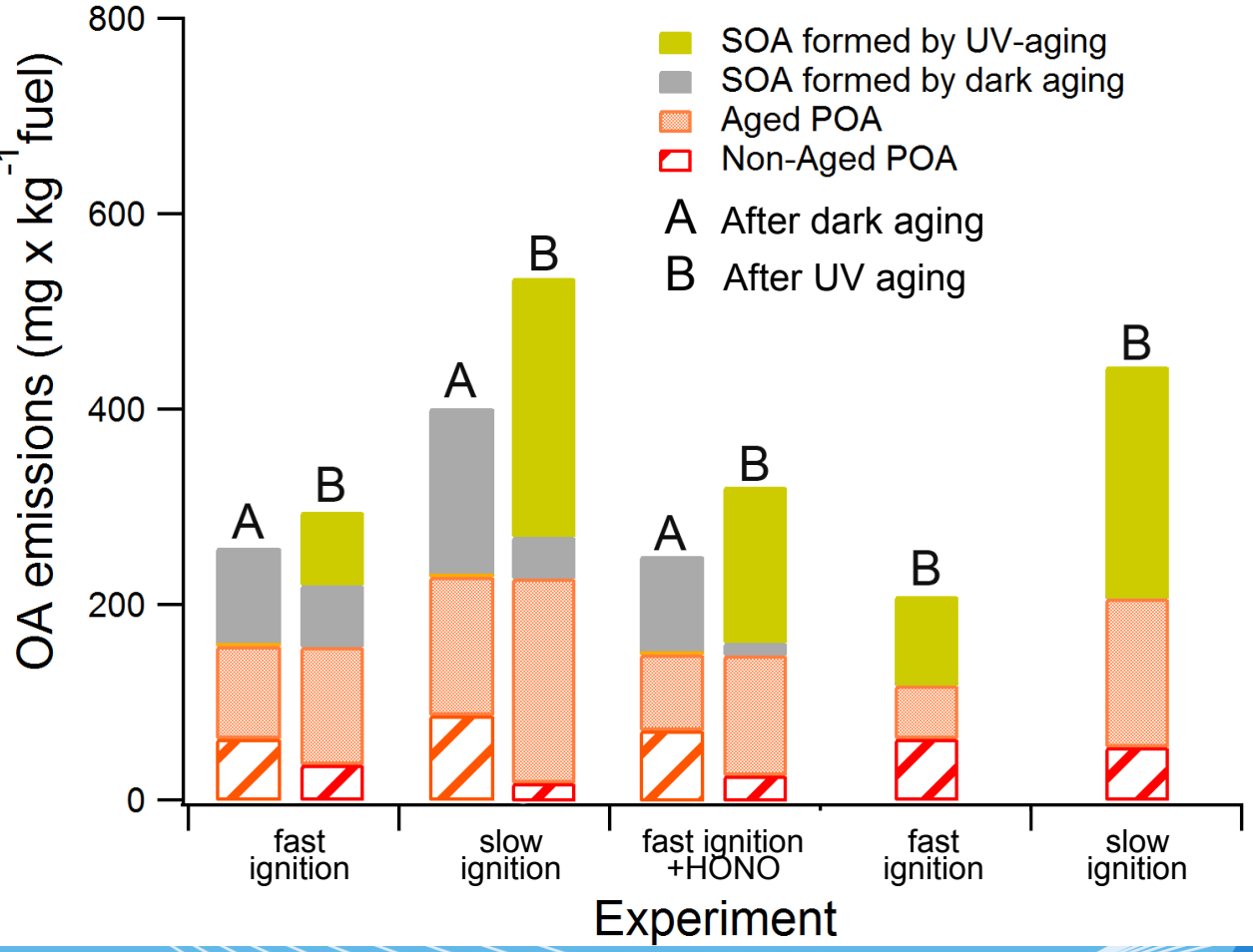
- During dark aging nitrate (NO_3) concentration increased
- The observed nitrate was identified as organonitrates
- Nitrate concentration decreases during UV aging because organonitrates decompose in UV light

Oxidation of particulate organic matter



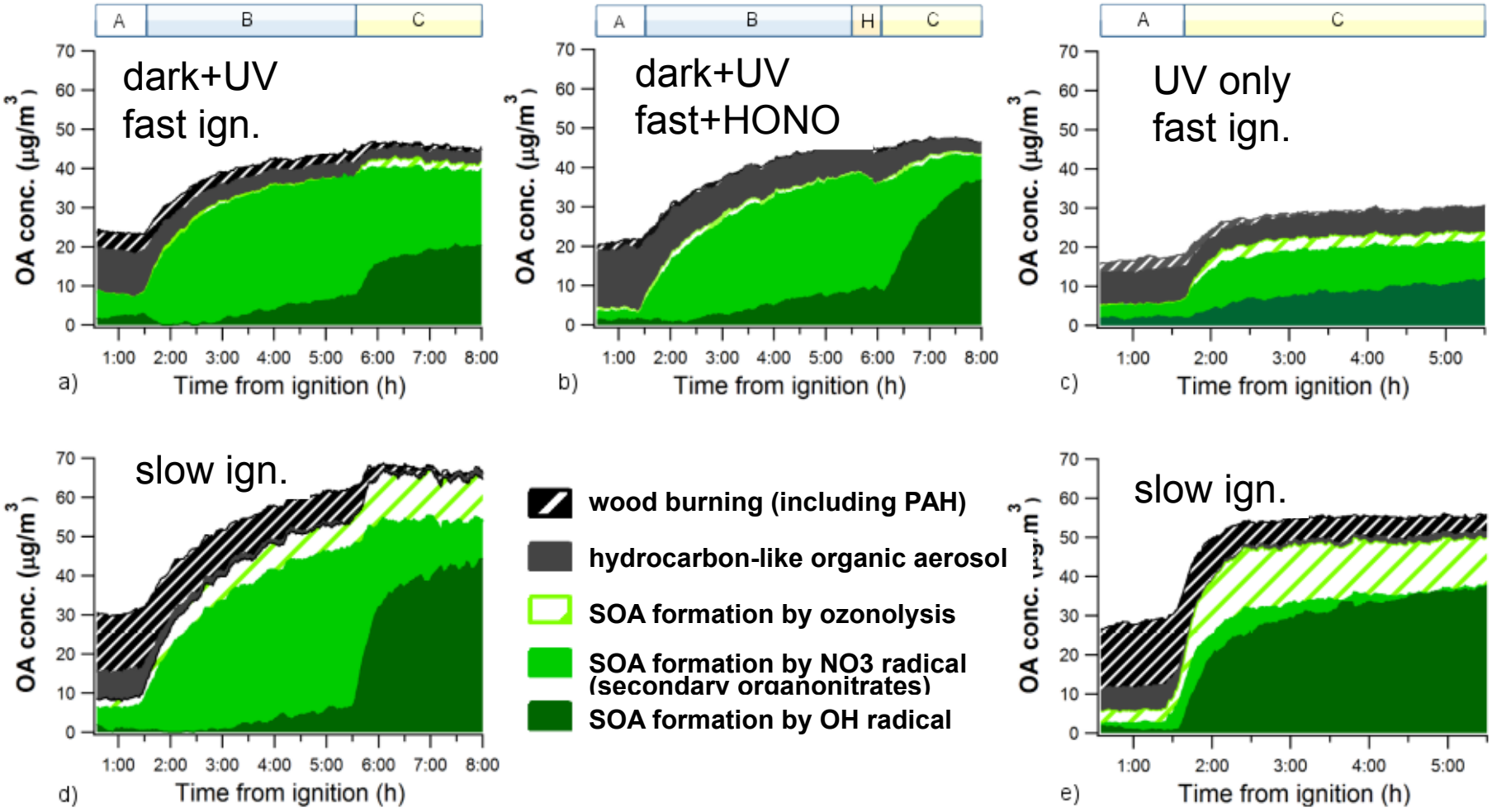
- No matter whether the ignition is slow or fast, we end up with similar O:C ratio
- Additional HONO injection produces secondary compounds with more oxygen

Emission factors of organic aerosol



- Primary organic aerosol was also oxidized (evaporation and homogeneous gas-phase oxidation, heterogeneous oxidation of particulate matter)

Evolution of organic aerosol (PMF)



- The concentration of primary organic aerosol decreases during dark aging
- The concentration of organonitrates increases remarkably during dark aging and decreases during UV aging

Summary

- Emissions from spruce log combustion with slow ignition contained more organic compounds (VOC:NOx ~ 5) than from that with fast ignition (VOC:NOx ~ 3)
- 50–60 % of the primary organic aerosol had been oxidized after dark aging, 77–92 % after (subsequent) UV aging
- SOA mass increased both during UV aging (“daytime”) and dark aging (“nighttime”); the increase was faster in UV aging
- SOA was produced more from slow ignition emissions than from fast ignition emissions
- HONO addition enhanced SOA formation
- Most of the SOA was produced during the first hour of aging

Conclusions

- Logwood burning emissions are subject to intensive chemical processing in the atmosphere
- Small changes in burning conditions (e.g., ignition speed) may have a big effect on secondary organic aerosol formation
- Time scale for the transformations is relatively short
- **Wood combustion is a significant source of organonitrates and their precursors**
- **Not only UV aging but also dark aging plays an important role in secondary organic aerosol formation**

Thank you for your attention !

See also Tiitta et al. (2016)

http://www.atmos-chem-phys-discuss.net/acp-2016-339/
DOI: 10.5194/acp-2016-339

Perhaps also post a comment... (by 27 June 2016)

Visit also poster by Olli Sippula here at ETH

Or come and discuss with us (I, Olli, and Jorma are here)

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