SOA (trans)formation through aqueous phase guaiacol photonitration: Chemical characterization of the products

Irena Grgić[1], Zoran Kitanovski[2], Ana Kroflič[1] and Alen Čusak[3]

[1]Analytical Chemistry Laboratory, [2]Laboratory for Food Chemistry, National Institute of Chemistry, Ljubljana, Slovenia
[3]EN-FIST Center of Excellence, Ljubljana, Slovenia

European Geosciences Union
General Assembly 2014
Vienna | Austria | 27 April – 02 May 2014

Introduction

- Biomass burning (BB) is one of the largest primary sources of OA in the atmosphere.
- Many different products are formed via thermal degradation of wood lignin:
  - Hardwood burning produces mainly *syringol* (2,6-dimetoxyphenol) deriv.; softwood exclusively *guaiacol* (2-methoxyphenol) and its derivatives.
- Taking into account physical properties of methoxyphenols only, their concentrations in atmospheric waters might be underestimated.
- Aqueous phase reactions can be an additional source of SOA, especially in regions under significant influence of wood combustion.

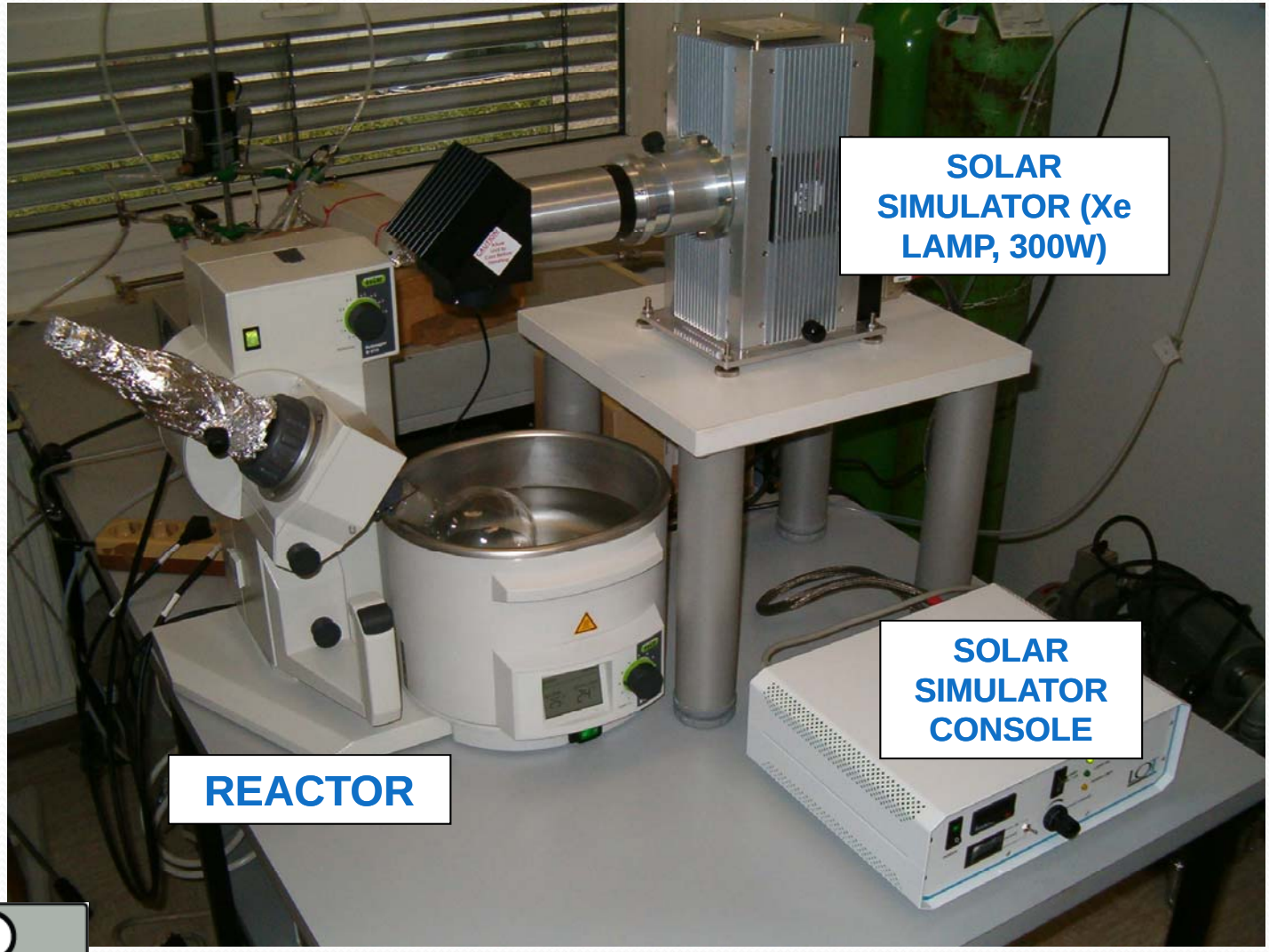
Objectives

The aim was to study the aqueous-phase reactivity of guaiacol as a source of SOA in the atmosphere.

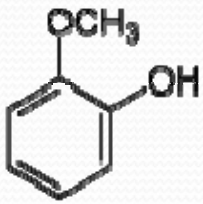
The main objectives:

- to isolate and identify the main products with semi-prep. HPLC-UV/Vis, NMR, and MS/MS,
- to identify several guaiacol products in ambient aerosols by HPLC-ESI-MS/MS.

Experimental setup



Simulation of aqueous-phase reactions



0.1 mM GUAIACOL IN AQUEOUS PHASE (pH = 4.5)

+

1 mM H_2O_2 + 1 mM $NaNO_2$

+

UV/VIS SUNLIGHT

↓

REACTION PRODUCTS (yellow solution)

For product isolation and identification:
10 mM G + 100 mM H_2O_2 + 100 mM $NaNO_2$

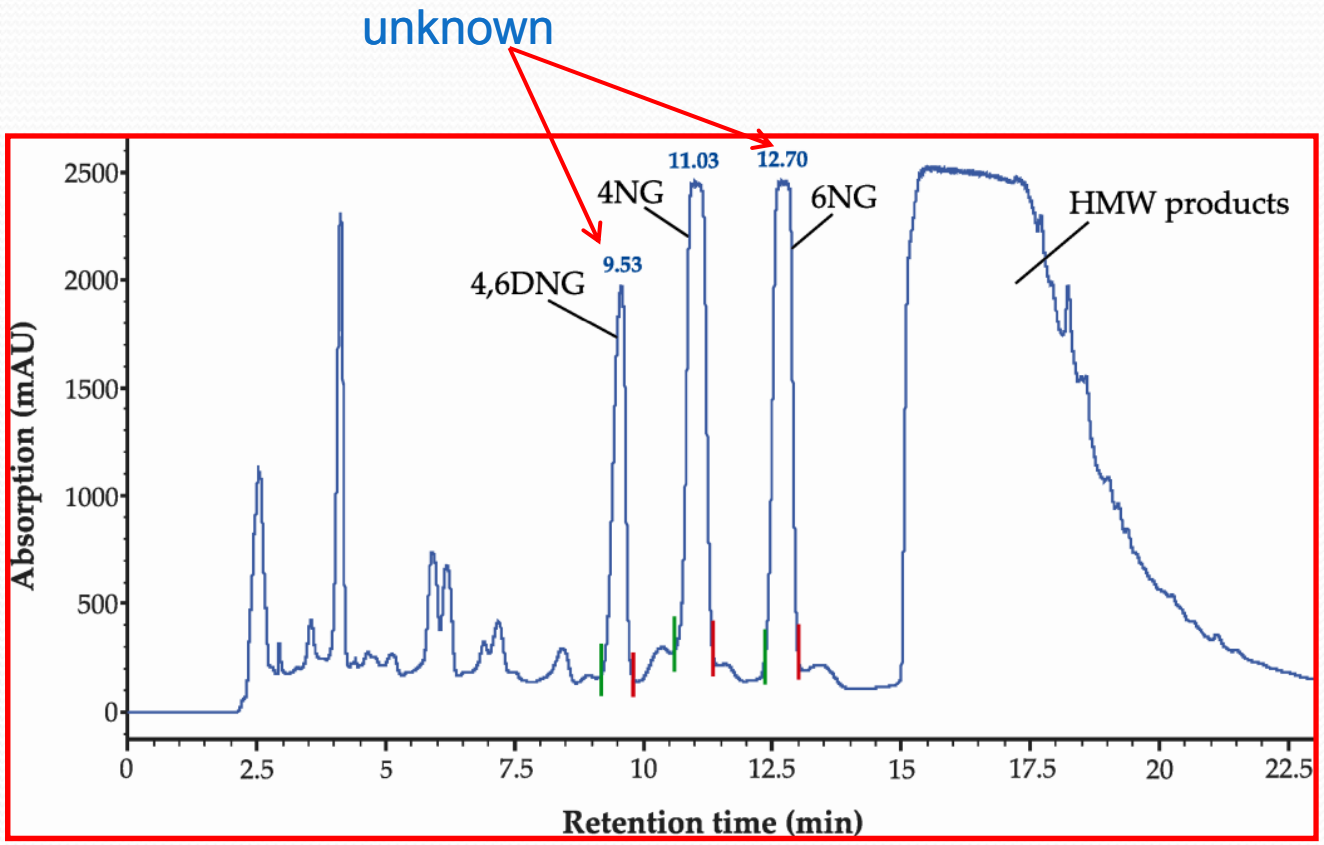
EXTRACTION + CONCENTRATION (SPE)

SEMI-PREP RP-HPLC PURIFICATION

Agilent 1100 HPLC with analytical-scale fraction

Column: Atlantis Prep T3 (250 x 10 mm i.d., 5 µm) with guard column (10 x 10 mm i.d., 5 µm)
Mobile phase: ACN/THF/aqueous amm. formate pH 3 = 30/4/66 (v/v/v), 5 mM buffer conc.
Flow rate: 5.0 mL min^{-1}; Injection volume: 100 µL; Column temperature: 30 °C
DAD triggered peak collection @ λ = 300 and 345 nm

Semi-prep chromatogram of guaiacol product extract



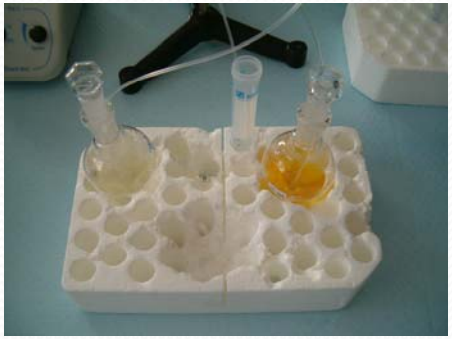
4NG and the two main unknown peaks were first purified by semi-preparative HPLC and then isolated as pure solids by SPE.

HPLC/UV-SPE-MS-NMR workflow

ISOLATION AND CONCENTRATION (SPE-RP)

SEMI-PREP RP-HPLC PURIFICATION

PEAK COLLECTION



REMOVAL OF M.Ph. ORG. SOLVENT FROM FRACTIONS

FRACTION COMPOUND ISOLATION (SPE-RP)

COMPOUND IN PURE CRYSTALINE FORM

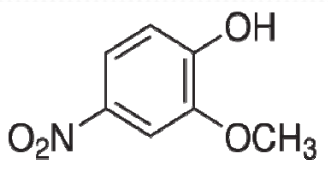
STRUCTURE DETERMINATION

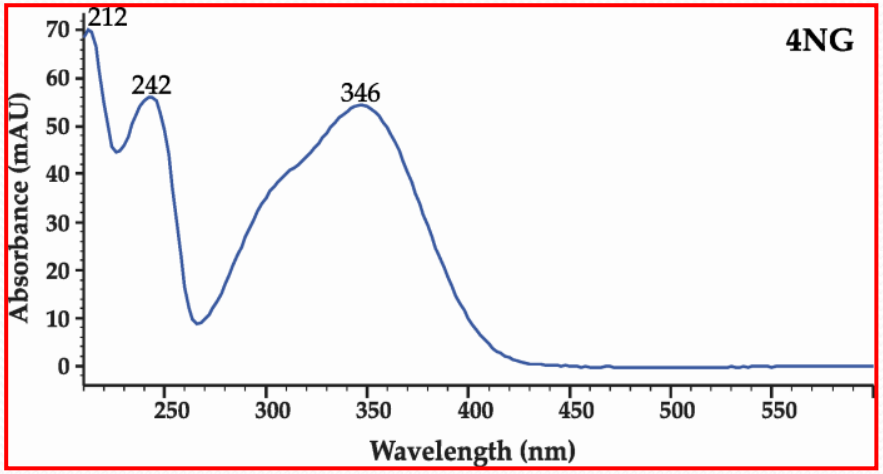
DIRECT INFUSION-MS or MS/MS

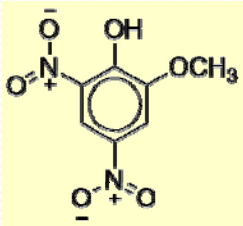
^{1}H-NMR, ^{13}C-NMR, 2D-NMR (COSY, HMBC, HSQC)

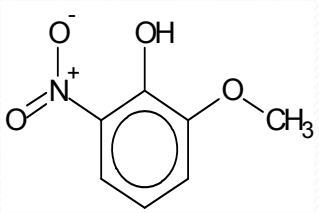
LC-MS^{2} (PRODUCT ION SCAN)

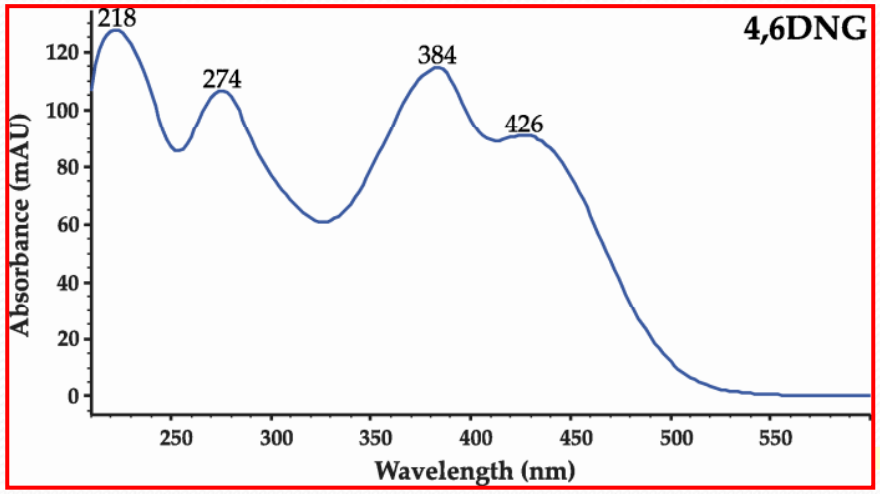
UV/Vis spectra of 4,6-DNG, 4-NG and 6-NG

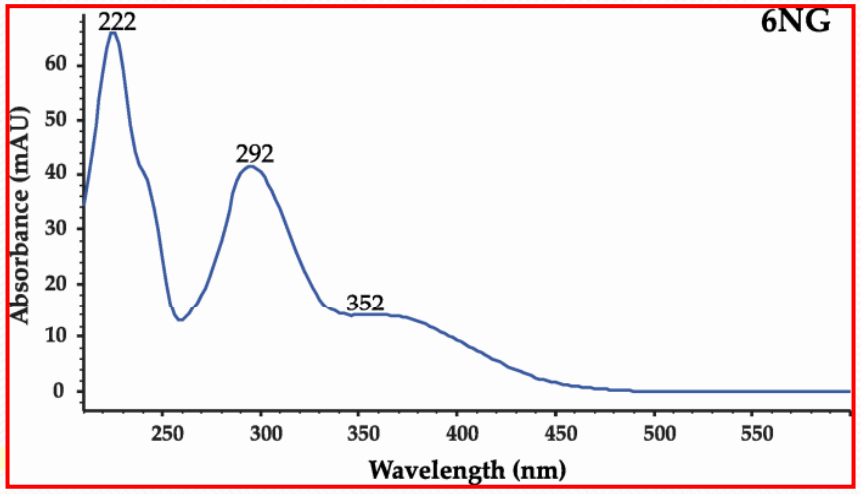




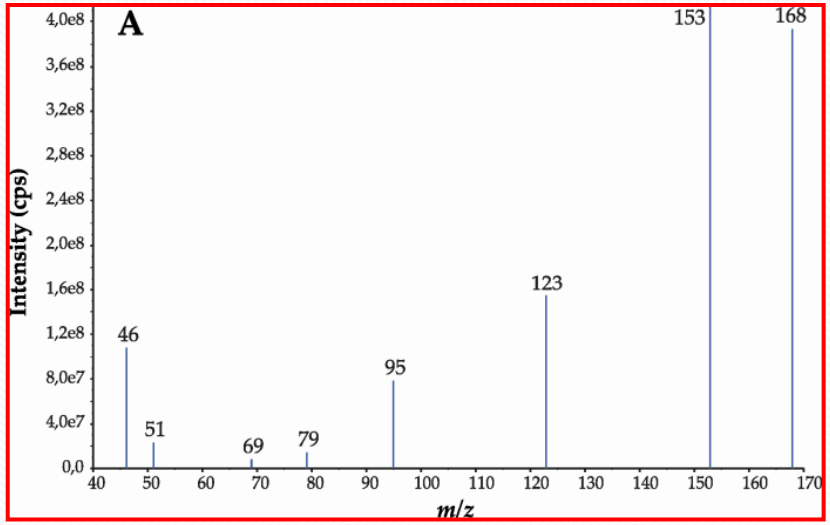


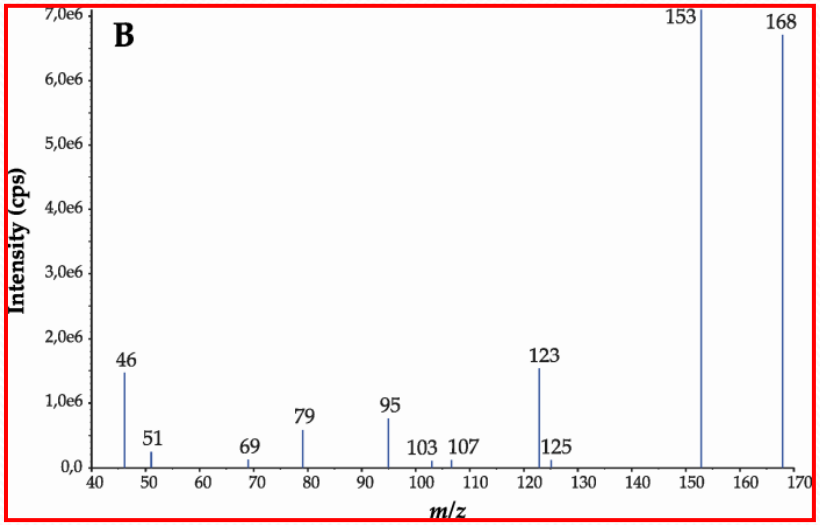


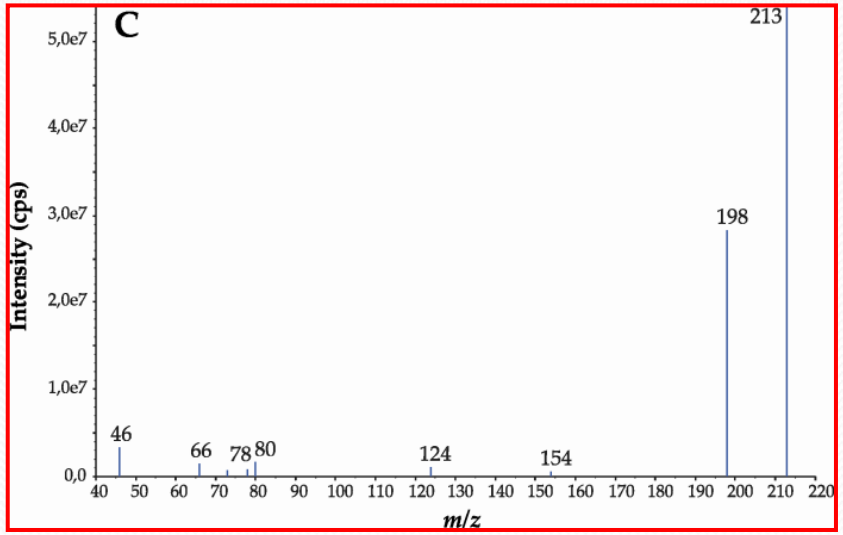




ESI-MS^2 spectra of 4NG, 6NG and 4,6DNG



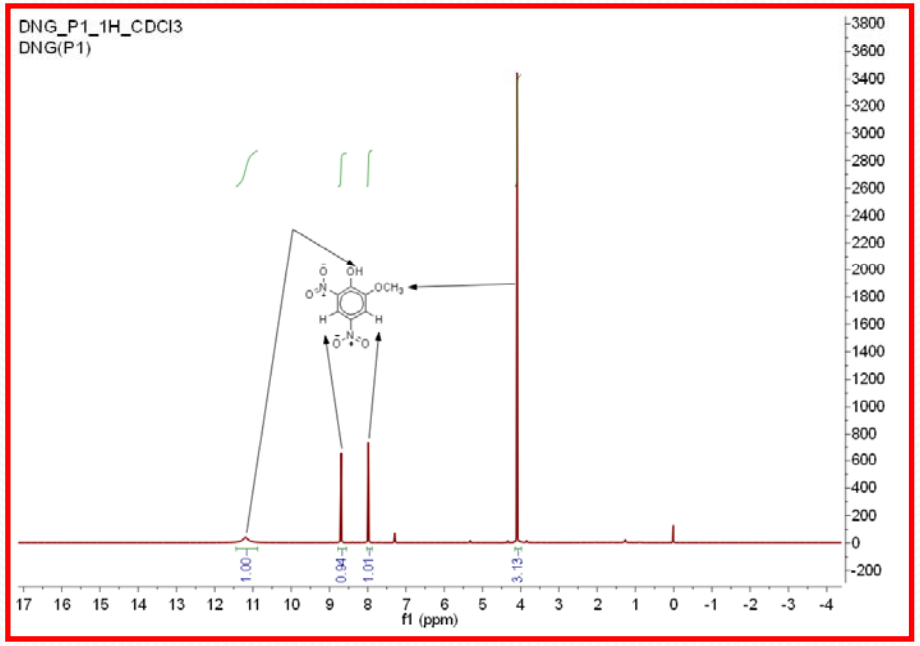




Direct infusion (−)ESI−MS^2 product ion spectra of $[M - H]^-$ for *4NG (A), 6NG (B)* and *4,6DNG* (C) standards obtained on the 4000 QTRAP instrument .

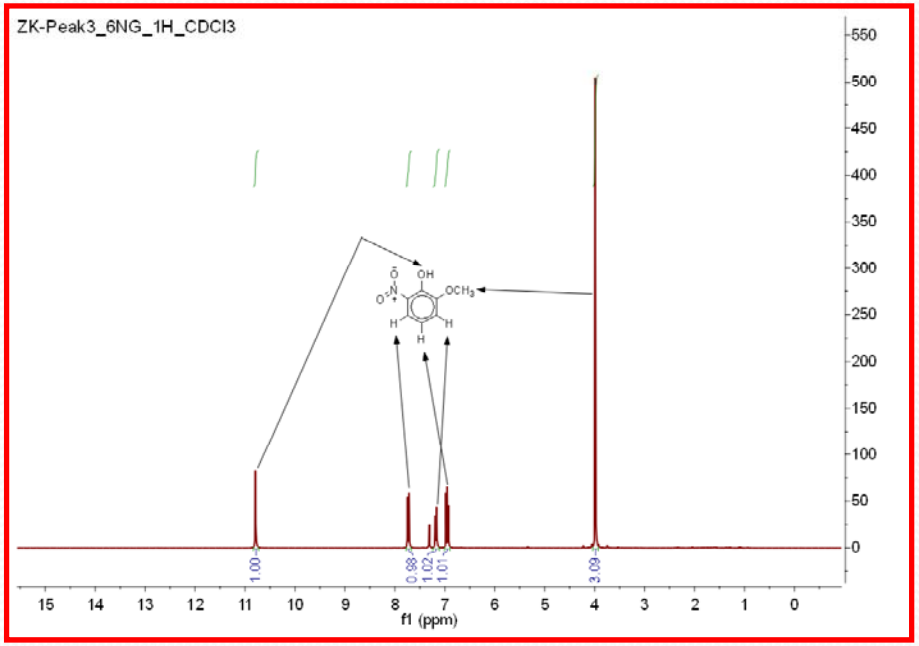
^{1}H-NMR spectra of 4,6DNG and 6NG

4,6DNG



Yellow crystalline solid

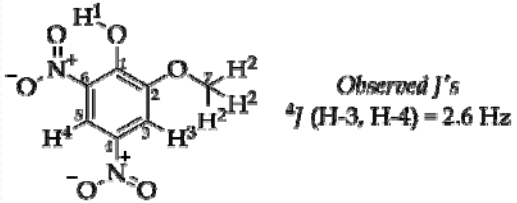
6NG

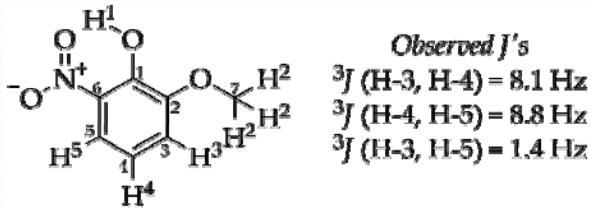


Pale yellow solid

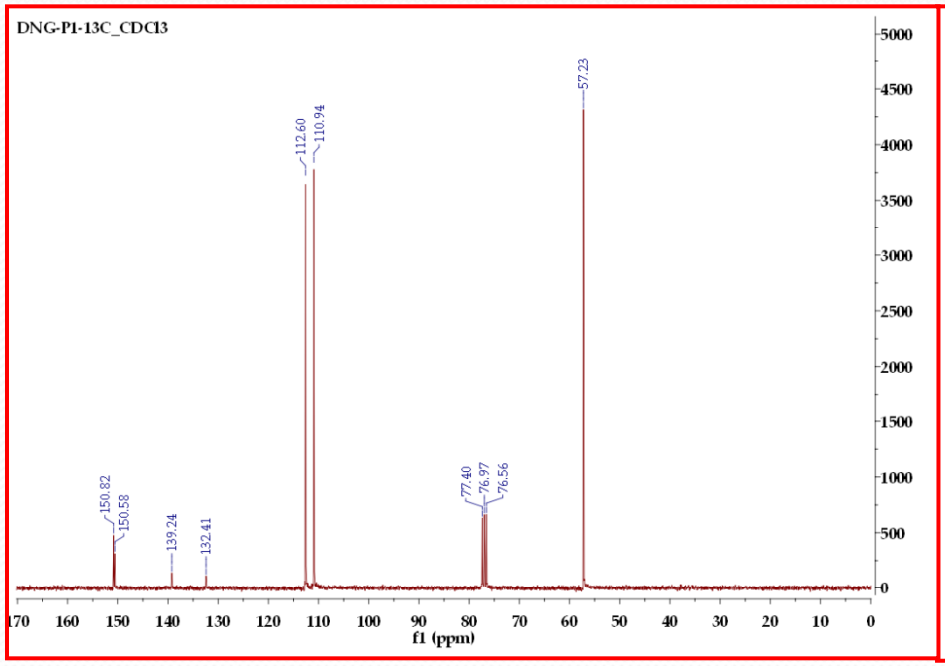
^{13}C NMR spectra of 4,6DNG and 6NG

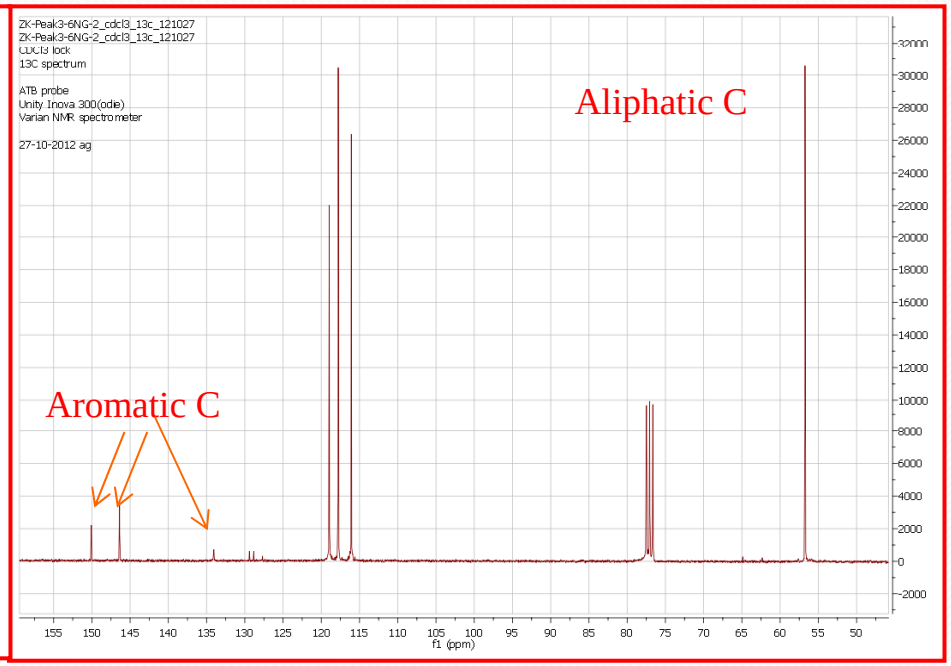
4,6DNG





6NG





Identification of guaiacol SOA compounds in atmospheric aerosols

The main photonitration products of guaiacol, 4NG, 6NG and 4,6DNG, were examined for their presence in PM10 with an optimized LC-(–)ESI-MS/MS (SRM).

To reduce the possibility of false positive identification, two characteristic SRM transitions were monitored:

- *m/z* 168 → *m/z* 153 (SRM1) and *m/z* 168 → *m/z* 79 (SRM2) for 4NG, 5NG and 6NG,
- *m/z* 213 → *m/z* 198 (SRM1) and *m/z* 213 → *m/z* 124 (SRM2) for 4,6DNG

SRM1 / SRM2 ratios obtained by using LC-MS/MS elution method I*

Analytes	SRM1 / SRM2 ratio				
	Standard (± SD; n=3)	23/12/10 PM10	Identified (by SRM1 / SRM2)	Rt match (std *vs.* sample)	
4NG	59.4 (± 1.5)	50.0	**Yes**	**Yes**	✔
5NG	68.3 (± 4.8)	not detected	**No**	**No**	✘
6NG	7.4 (± 0.1)	88.7	No	Yes	**?**
4,6DNG	33.6 (± 0.9)	33.1	**Yes**	**Yes**	✔

Elution order: 6NG→5NG→4NG

*(methanol/THF/water (30/15/55, v/v/v) mixture with 5 mM amm. formate buffer pH 3)

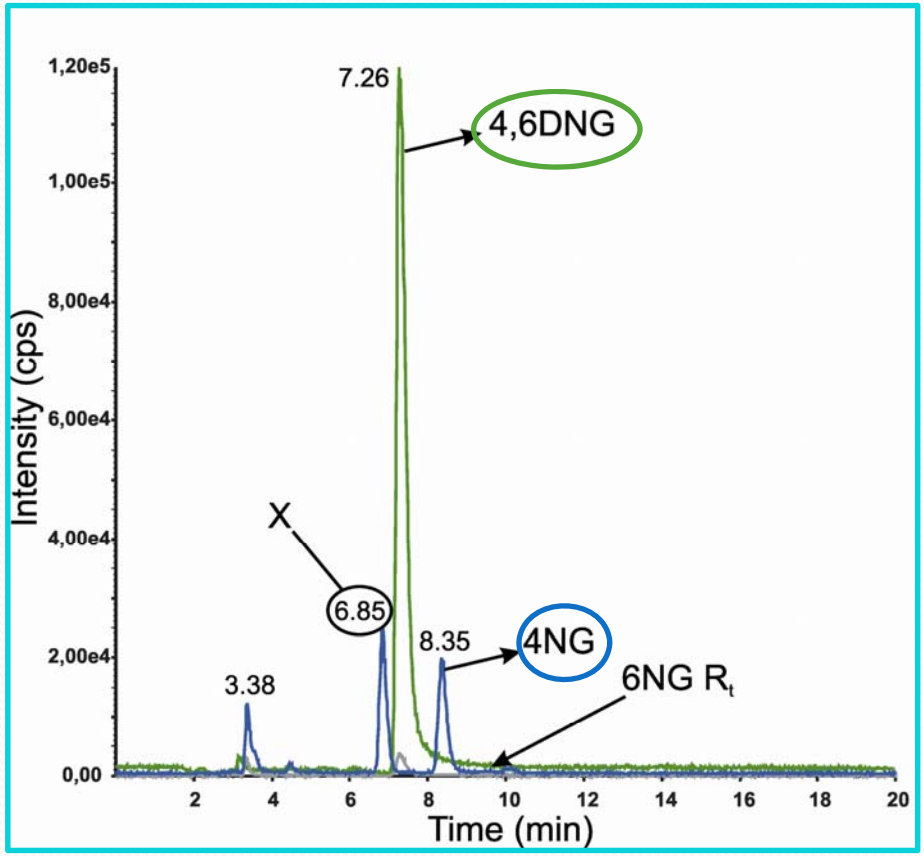
SRM1 / SRM2 ratios obtained by using the LC/MS/MS elution method II*

Analytes	SRM1 / SRM2 ratio			
	Standard (± SD; n=3)	23/12/10 PM10 sample	Identified (by SRM1 / SRM2)	Rt match (std *vs.* sample)
4NG	61.1 (± 0.9)	58.7	**Yes**	**Yes** ✔
5NG	68.8 (± 3.8)	not detected	**No**	**No** ✖
6NG	7.2 (± 0.1)	not detected	**No**	**No** ✖
4,6DNG	28.0 (± 0.6)	32.9	**Yes**	**Yes** ✔
Peak at Rt = 6.84 min	/	89.2		

Elution order: 5NG→4NG→6NG

*(ACN/THF/water (30/4/66, v/v/v) mixture of 5 mM amm. formate buffer pH 3)

Identification of guaiacol SOA compounds in atmospheric aerosols



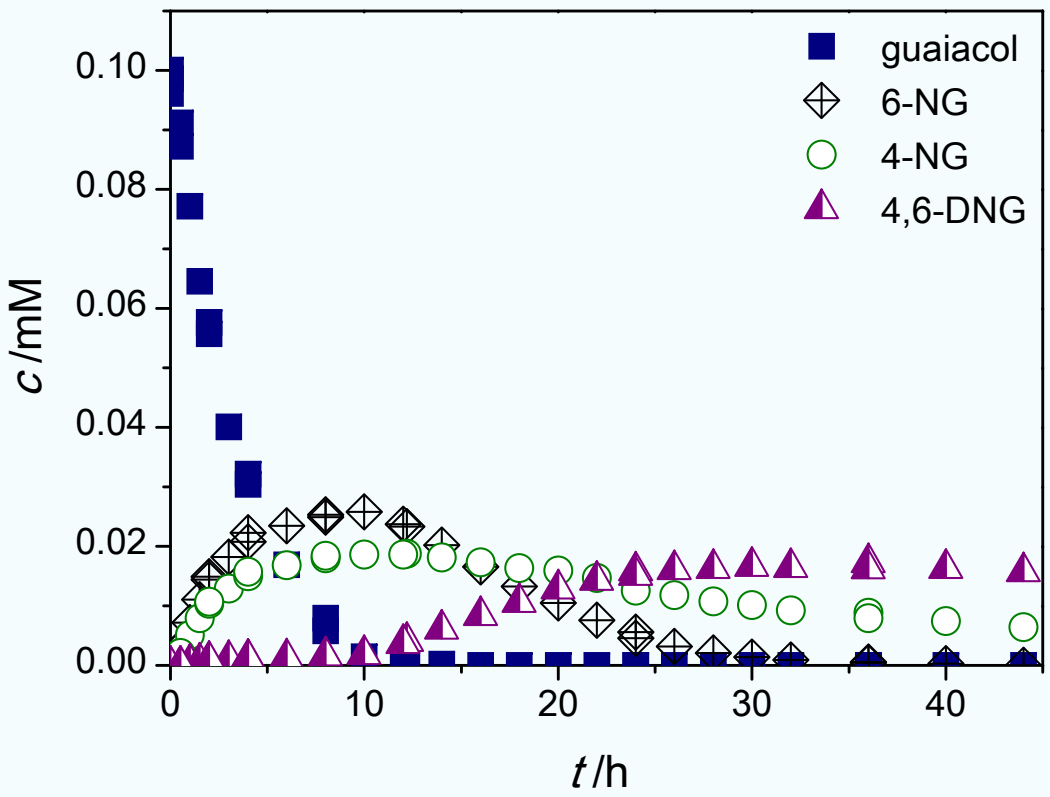
- Column: Atlantis T3 (150 x 2.1 mm I'd., 3 µm)
- Mobile phase: ACN/THF/aqueous amm. formate pH 3 = 30/4/66 (v/v/v), 5 mM buffer conc.
- Flow rate: 0.2 mL min^{-1}; Injection volume: 10 µL
- Column temperature: 30 °C

HPLC-(–)ESI/SRM-MS chromatograms of PM10 winter sample from Ljubljana (SRM transitions for 4,6DNG and NGs, only)

4,6DNG and 4NG detected, 6NG – not detected!

Z. Kitanovski, A.Čusak, I. Grgić, M.Claeys: Atmos. Meas. Tech. Discuss. 7, 3993–4032, 2014, doi:10.5194/amtd-7-3993-2014

Aqueous phase photonitration of guaiacol on longer scale



Poster Z140 (AS3.3)
by A. Kroflič & I. Grgić

Exper. conditions: 0.1 mM guaiacol, 1.0 mM H_2O_2 and 1.0 mM $NaNO_2$ under UV/Vis irradiation, T = 25°C, pH = 4.5.

SECONDARY ORGANIC AEROSOL (TRANS)FORMATION THROUGH AQUEOUS PHASE GUAIACOL PHOTONITRATION: A KINETIC STUDY

Ana Kroflič & Irena Grgić - Analytical Chemistry Laboratory

Kemijski inštitut Ljubljana Slovenija | National Institute of Chemistry Slovenia

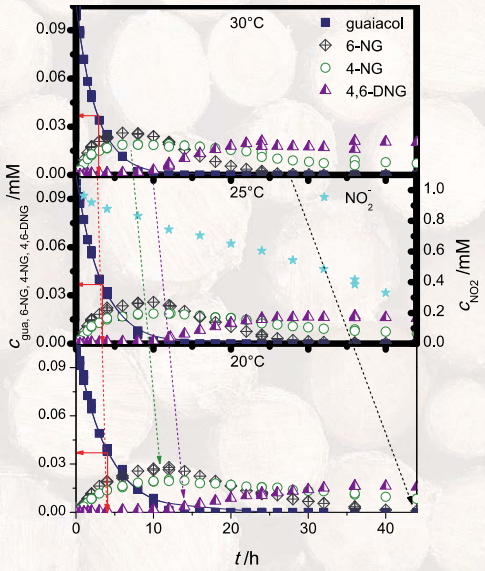
BACKGROUND

Atmospheric aerosols play a crucial role in the Earth's climate and public health. Notwithstanding all the studies of secondary organic aerosol budget, composition, and its formation mechanisms, a gap still insists between field observations and atmospheric model predictions (Hallquist et al. 2009, Lim et al. 2010). An interest in atmospheric aqueous phase chemistry has thus increased lately. It calls for more complex and time consuming studies at the environmentally relevant conditions allowing confident extrapolation to the desired ambient conditions.

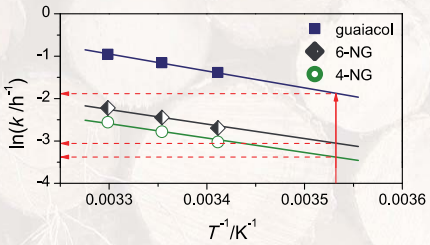
Toxic nitro-aromatic and other organic compounds, which often cause adverse health effects, have already been found in real aerosol samples. Recently, two nitro derivatives of a biomass burning tracer guaiacol have been detected in winter PM_{10} samples from the city of Ljubljana, Slovenia (Kitanovski et al. 2012). Moreover, aqueous photonitration reaction was proposed as their possible production pathway.

RESULTS

The kinetics of guaiacol (100 μM) photonitration in aqueous solution (pH = 4.5) was investigated in the presence of H_2O_2 (1 mM) and NO_2^- (1 mM) upon simulated solar irradiation (Xenon lamp, 300 W). During the experiment the DURAN® flask with the reaction mixture was held in the thermostated bath and thoroughly mixed. Guaiacol and its main nitro-products (4-nitroguaiacol, 4-NG; 6-nitroguaiacol, 6-NG; and 4,6-dinitroguaiacol, 4,6-DNG) were quantified in every aliquot, taken from the reaction mixture, by use of HPLC. In addition, the concentration of NO_2^- was monitored spectrophotometrically.



Graph 1: Guaiacol (100 μM) photonitration in aqueous solution (pH = 4.5) in the presence of H_2O_2 (1 mM) and NO_2^- (1 mM) upon simulated solar irradiation (Xenon lamp, 300 W).



Graph 2: Temperature dependence of the determined pseudo-first order rate constants of guaiacol degradation and initial 6-NG and 4-NG formation upon the conditions in the reaction mixture.

The reaction of guaiacol photonitration follows the pseudo-first order kinetics:

$$\frac{dG}{dt} = -k'[G][NO_2^\bullet] \qquad k = k'[NO_2^\bullet]$$

Guaiacol lifetime* was calculated as $t = {}^{1}/_{k}$ for each of the investigated temperatures. Moreover, a prediction of guaiacol lifetime at low temperature was also made.

T/K	t/h
298.15	3.2
273.15	10.9

* time required to decrease the initial guaiacol concentration for an exponential factor of e^{-1}

CONCLUSIONS

The long-term reaction monitoring explained the **absence of 6-NG in real aerosol samples** analyzed by Kitanovski et al. (2012).

The kinetics of **guaiacol photonitration** in aqueous solution was described by the **pseudo-first order reaction rate.**

The **nitrite kinetics** in the reaction mixture is **zero-order.**

The **guaiacol lifetime at low temperature** was predicted.

Literature:

- Hallquist, M. et al. (2009) Atmos. Chem. Phys. 9, 5155–5236.
- Lim, Y.B. et al. (2010) Atmos. Chem. Phys. 10, 10521–10539.
- Kitanovski, Z. et al. (2012) J. Chromatogr. A 1268, 35–43.

Contact us:

National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia
Email: ana.kroflic@ki.si
Phone: +386 (1) 4760 361
@ Kroflič

Conclusions

- The aqueous-phase photonitration of guaiacol as a source of SOA in the atmosphere was studied.
- Off-line semi-prep. RP-HPLC-DAD-SPE-NMR-MS was successfully used for SOA product purification, isolation and structure elucidation.
- The main low-volatility SOA products of photonitration of guaiacol in aqueous phase were: *6NG, 4NG and 4,6DNG*.
- 4,6DNG and 4NG were identified in winter PM10 using HPLC/(–)ESI-MS/MS.
- The *absence of 6NG* in PM10 was explained with the help of long-term reaction monitoring.
- More info: poster Z140 (EGU2014-11201) by Ana Kroflič & I.Grgić.

Acknowledgements

- Prof.Dr. Magda Claeys,University of Antwerp, Belgium
- Slovenian Research Agency (Contract no. P1-0034-0104)
- Slovenian Environment Agency

Thank you for your attention!