Organic compounds and PM at a background site in the Karst of Trieste: biogenic VOCs, secondary aerosol and oxidation processes

Presenter: Dott. **Arianna TOLLOI**

Primary Authors:

Dott. TOLLOI, Arianna (Università degli Studi di Trieste - DSCF) <arianna.tolloi@phd.units.it>

Dr. ROMEO, Michele (Università degli Studi di Trieste - DSCF) <michele.romeo.mr@gmail.com>

Dr. PIAZZALUNGA, Andrea (DEPARTMENT OF EARTH AND ENVIRONMENTAL SCIENCES - University of Milano Bicocca) <andrea.piazzalunga@unimib.it>

Dr. BARBIERI, Pierluigi (Università degli Studi di Trieste - Dipartimento di Scienze Chimiche e Farmaceutiche) barbierp@units.it

Co-authors:

Dr. LICEN, Sabina (Università degli Studi di Trieste - DSCF) <slicen@units.it>

Prof. ADAMI, Gianpiero (Università degli Studi di Trieste) <gadami@units.it>

Activities of the Research Group:

2006 PRIN SITECOS: PM_{10} and $PM_{2,5}$ Via Svevo (urban) + Porto San Rocco (periurban coastal)

2007 Procura della Repubblica: PM_{10} and $PM_{2,5}$ Via San Lorenzo in Selva RFI (**industrial**) Via Fleming (periurban)

2009 Procura della Repubblica: PM_{10} Via Pitacco e via Giardini (Urban/**industrial**)

2011 Università di Trieste: PM_{10}HV Via Giardini and via Ponticello (Urban/**industrial**)

2012 Università di Trieste: PM_{10}HV Borgo Grotta Gigante (*rural*, ongoing) + via Ponticello (Urban/**industrial**, until 09/2013)

2013 Procura della Repubblica: PM_{10} Via San Lorenzo in Selva (**industrial**)

2013 iniziato le attività del dottorato in Biologia Ambientale Arianna Tolloi “Emissioni e assorbimento di composti organici in matrici vegetali”,

Thesis:

***Berro Andrea**, “Caratterizzazione di composti secondari, inorganici e organici di origine biogenica nel particolato atmosferico campionato in un sito di background della provincia di Trieste“ triennale in Chimica, AA 2012-13*

Caratterizzazione giorno/notte ioni e nitro-solfo BSOA (Aahrus)

***Chenet Tatiana,** “Alcani alifatici ed idrocarburi policiclici aromatici nel particolato atmosferico in un sito di background della provincia di Trieste” Chimica, AA 2012-13*

Cere ed ipa nell’aerosol

***Ghirardello Giulia,** “Composti volatili e composizione del particolato atmosferico in un sito del Carso Triestino” magistrale in Biologia Ambientale, AA 2012-13.*

Relazioni tra emissioni piante e composizione gas e aerosol

Calesso Gianluca “Studi sui composti organici semi-volatili nell’aerosol in un sito del Carso Triestino” *triennale in Chimica, AA 2012-13*

metodo derivatizzazione ed esperimenti per valutare ossidazione

In corso tesi su:

O_3 e emivita BVOCs/ biomass burning /modelli computazionali “MEGAN”

Aim of the study

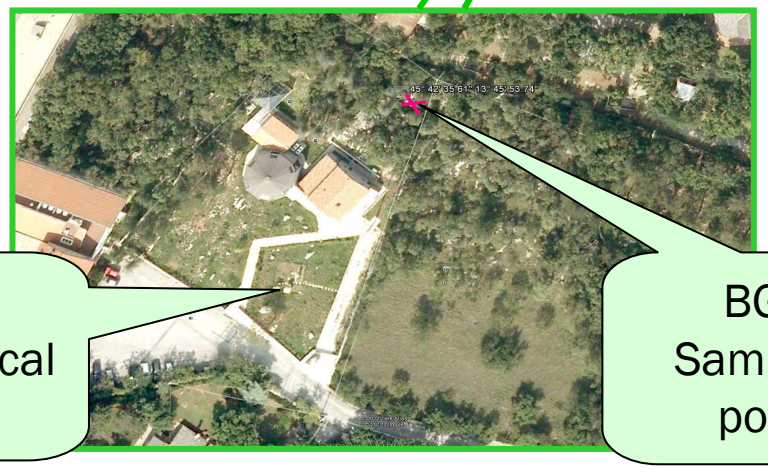
- Individuation and characterization of a **rural site** in the **province of Trieste** for air quality monitoring
- Air pollutants in **hot spots** are often monitored in order to protect **public health**
- Remote sites (e.g. Antarctica) are interesting to study the long-range transport of POPs
- But so we don't consider **dynamics of chemicals in atmosphere in terms of regional scale:**
  - Natural background on the urban\industrial atmospheric characteristics
  - Urban\industrial influence on the surrounding natural environment

The selected rural site:

Borgo Grotta Gigante (BGG)

Selected for:

- its relative distance from important urban centers
  - Trieste:
    - 200 000 inhabitants
    - 35 millions tons/year crude oil
    - 500 000 tons/year cast iron
  - and Monfalcone:
    - 30 000 inhabitants
    - Thermoelectric plant 976 MW coal and fuel oil
- and for its logistic.



Monitoring and analysis

- Since summer 2012
- Weekly
- Kind of samples:

❑ VOCs

- BTEX
- BVOCs

TD-GC-MS

❑ PM_{10}

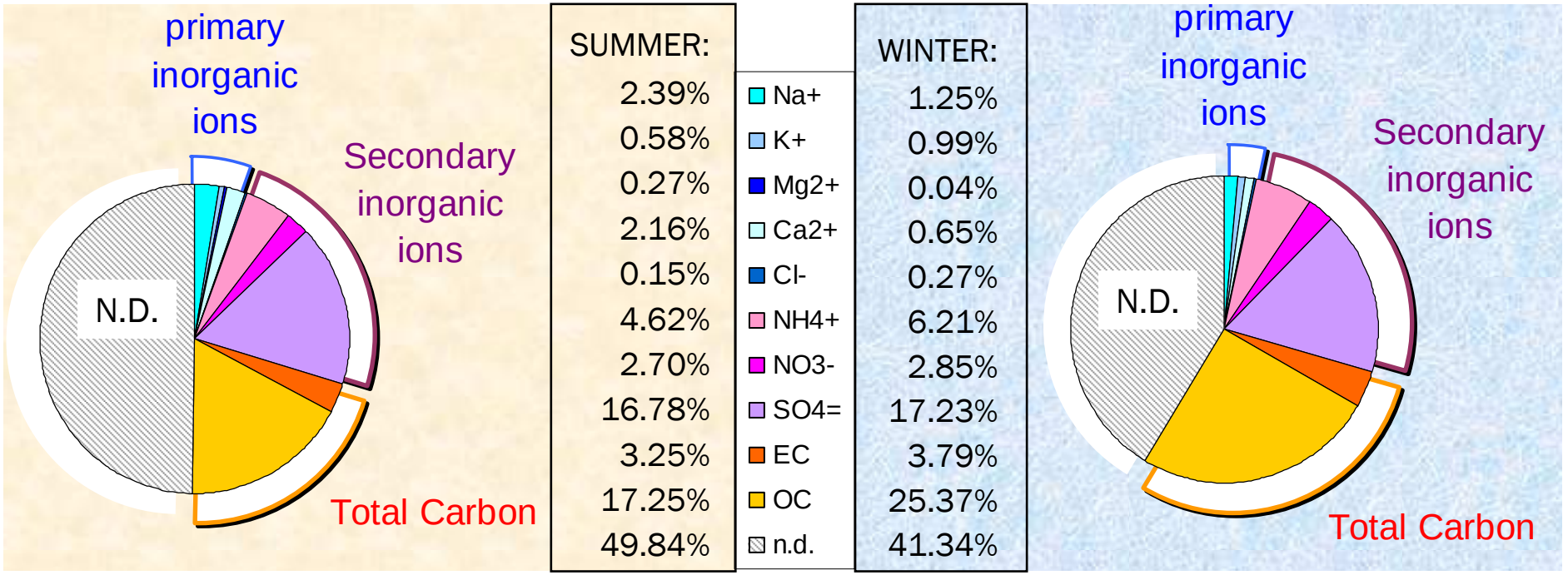
- Water soluble ions (IC)
- EC/OC (TOT)
- PAHs (GC-MS)
- n-alkanes (GC-MS)
- LG (GC-MS)
- BSOAs (GC-MS and HPLC-qTOF MS)
- Metals (ICP-AES)

Ultrasonic bath

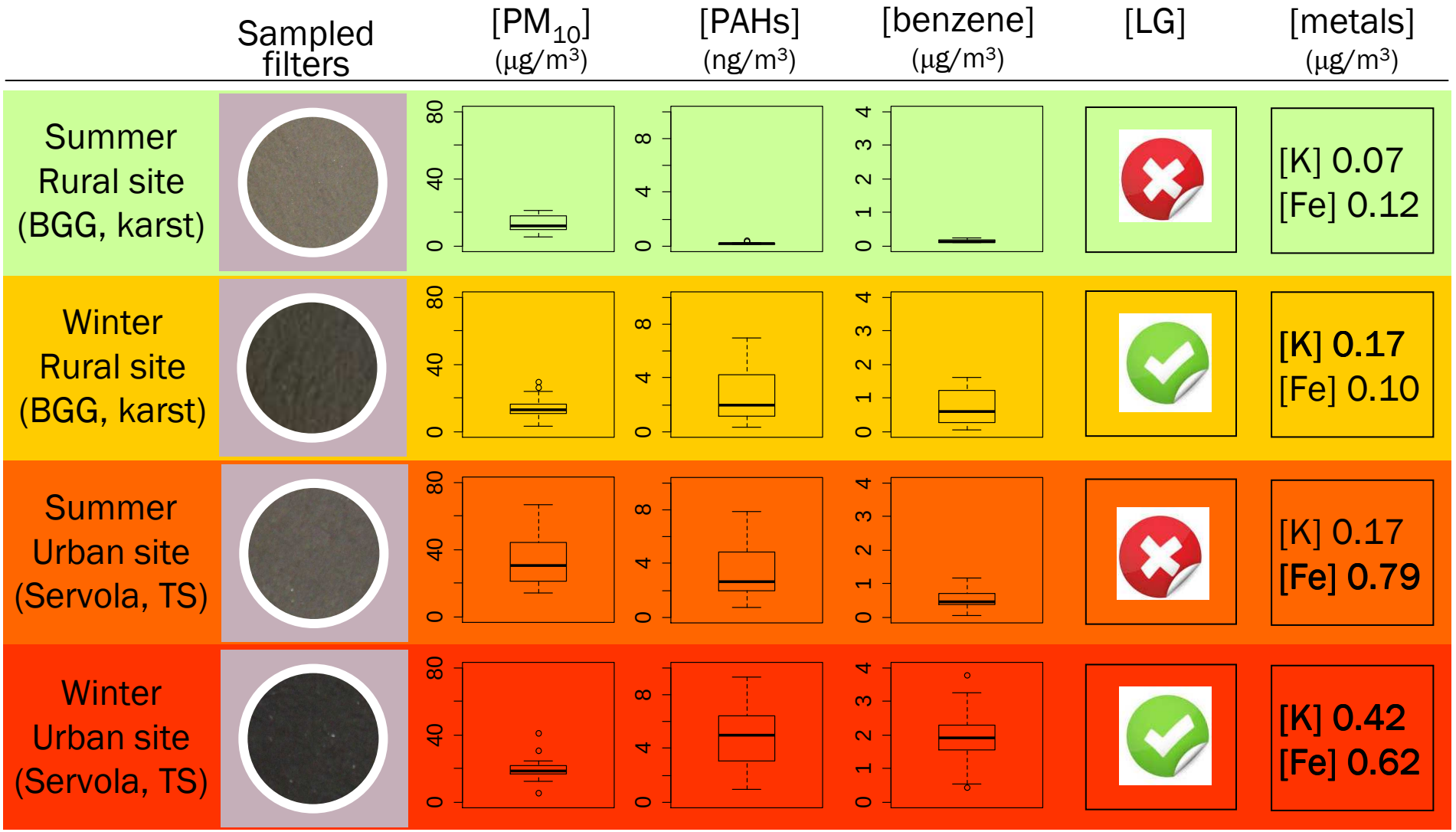
What about macro-constituents of PM_{10} at BGG

Analysis of water-soluble ions → MilliQ extraction → IC
Analysis of EC/OC → TOT

µg/m^3	PM_{10}	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NH_4^+	NO_3^-	$SO_4^=$	EC	OC
SUMMER	14.5	0.35	0.08	0.04	0.31	0.02	0.67	0.39	2.43	0.47	2.50
WINTER	14.5	0.18	0.14	0.01	0.09	0.04	0.90	0.41	2.50	0.55	3.68

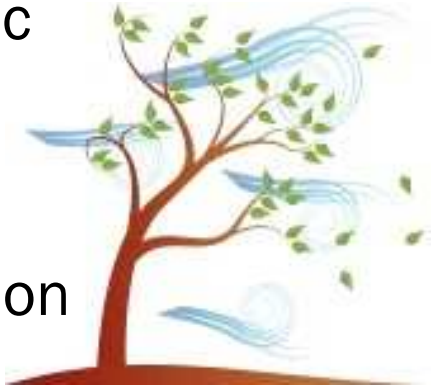


What about the influence of human activities at BGG: a comparison with a urban-industrial site



What about the influence of biogenic activity at BGG

In PM_{10} we found primary biogenic organic compounds derived from cuticular abrasion

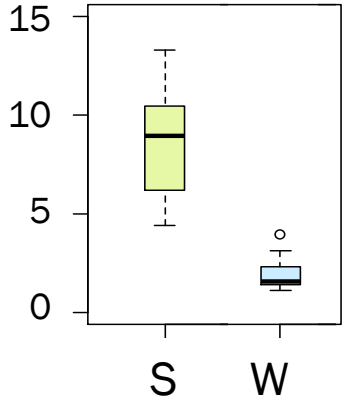


CPI at BGG during Summer and Winter:

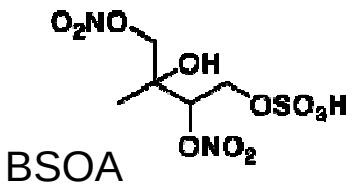
$$CPI = \frac{\Sigma \text{ odd n - alkanes}}{\Sigma \text{ even n - alkanes}}$$

→ ≥ 6 foliar abrasion

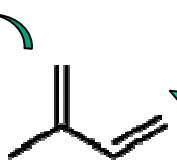
→ ≈ 1 not biogenic



A lot of biogenic organic aerosols (BSOAs) derive from the evolution in atmosphere of biogenic volatile organic compounds (BVOCs) [NB: estimated 600 Tg/y of isoprene from nature]



BSOA
(nitroxyorganosulfate)



BVOC
(isoprene)

BVOCs emission

Quercus pubescens isoprene emitter

Sesleria autumn. terpene emitter

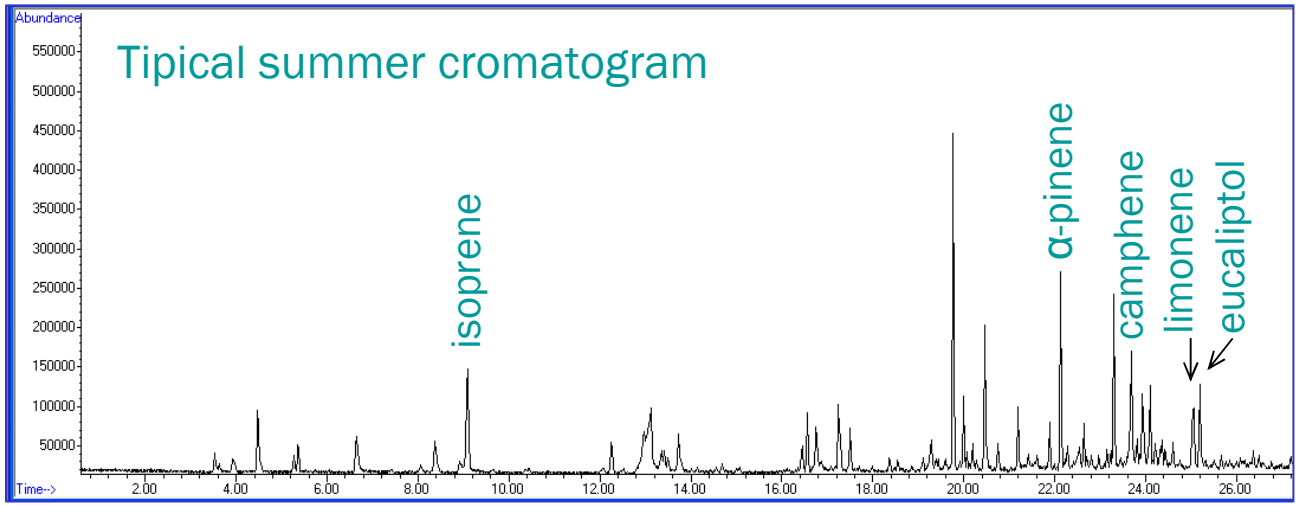
Cotinus coggygria terpene emitter

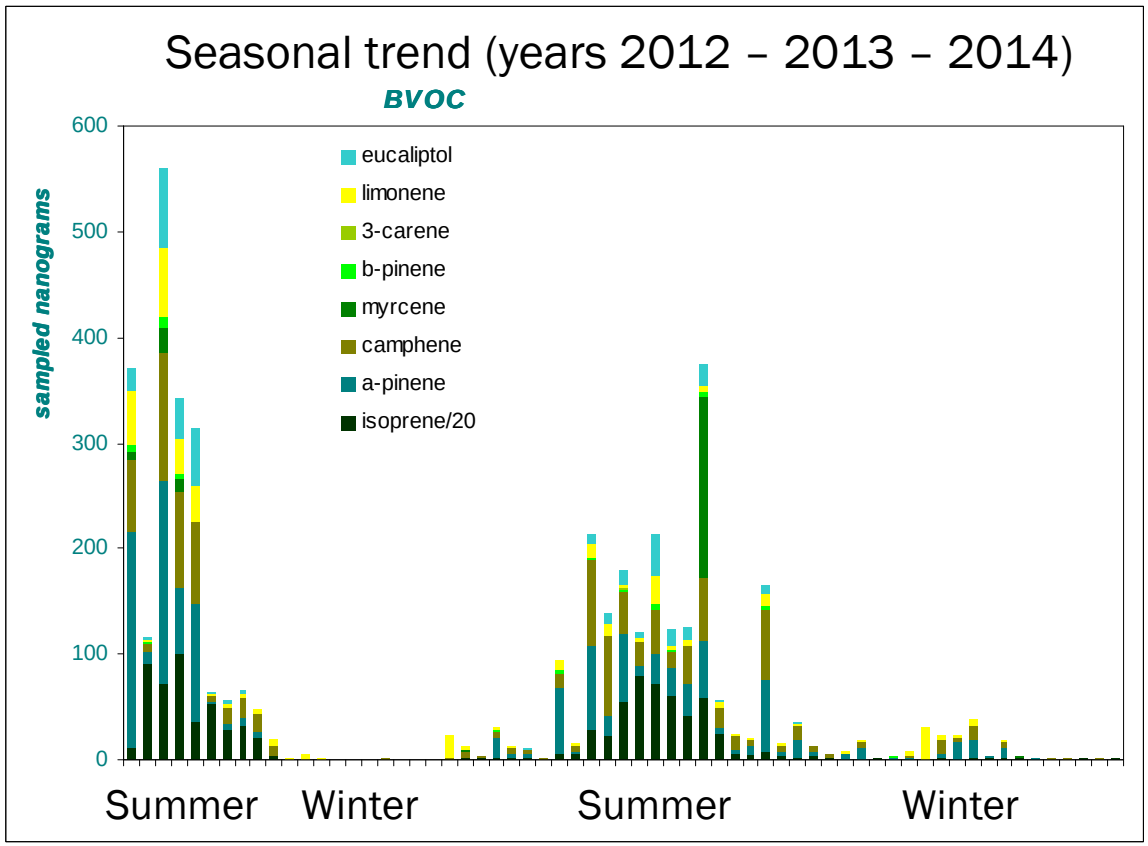
Juniperus communis miscellaneous emitter

Fraxinus ornus miscellaneous emitter

- Phytosociological recognition (ass. *Ostryo-Quercetum pubescentis*)
- individuation of the major BVOC-emitters of the list (cf. emission factors and land coverage)

BVOCs emission





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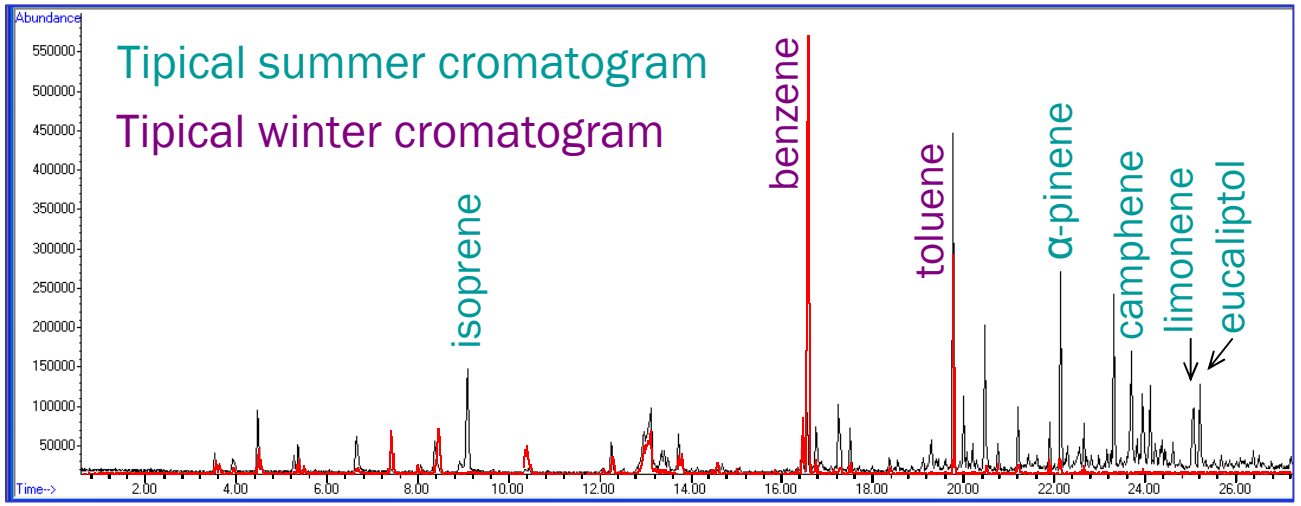
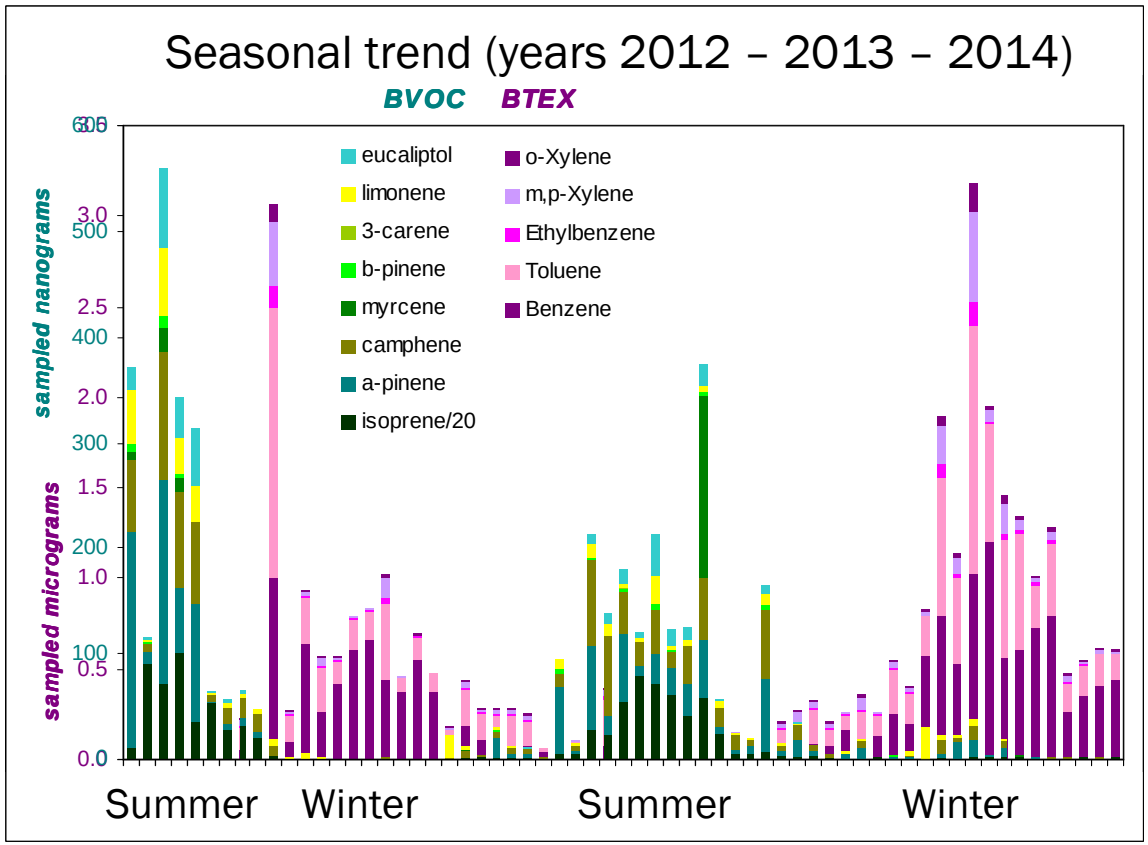
- Quantification of the most abundant BVOCs emitted in the area (cf. emission factors vs coverage)

BVOCs emission





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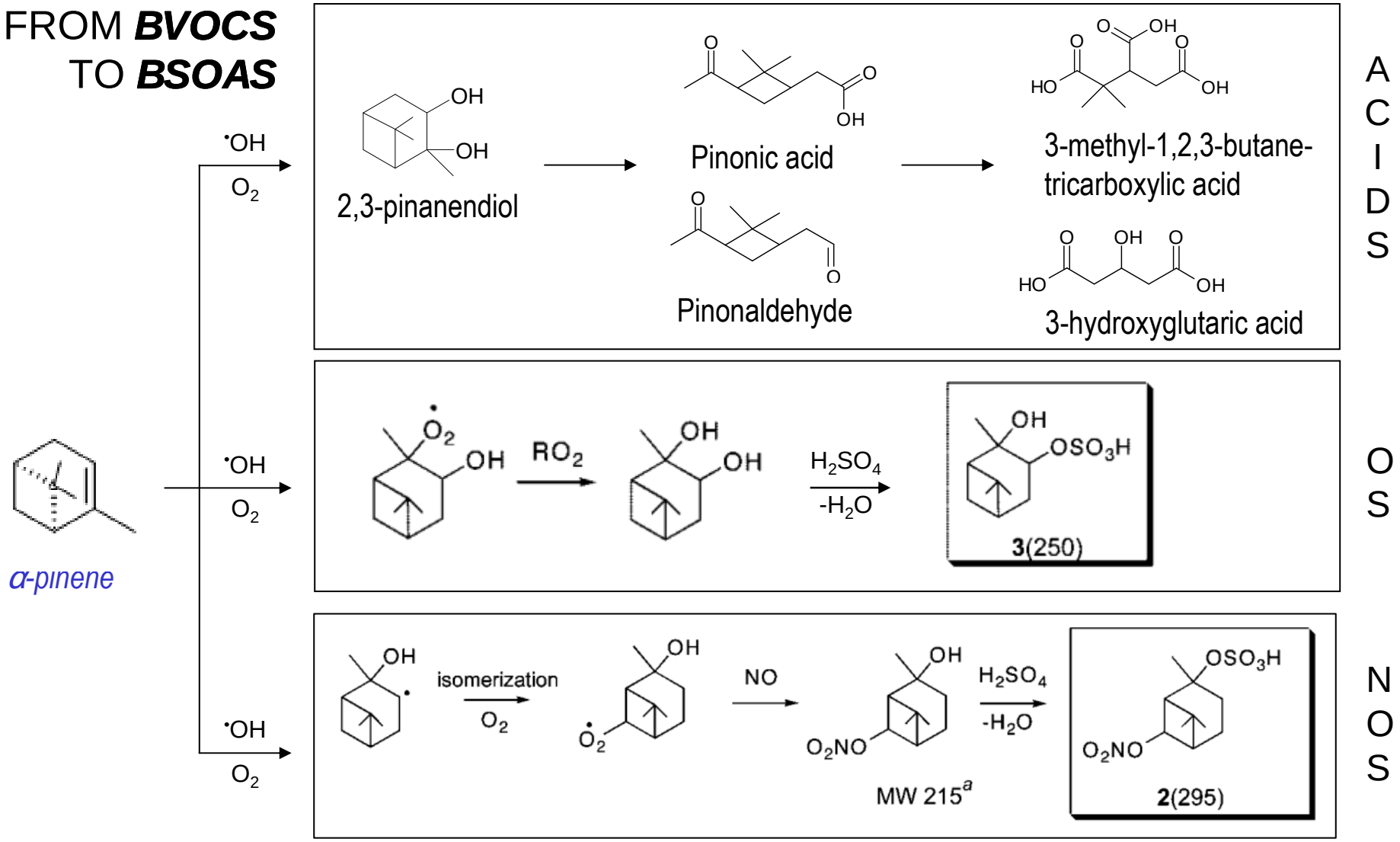
- Seasonal cf.

FROM ***BVOCS***
TO ***BSOAS***



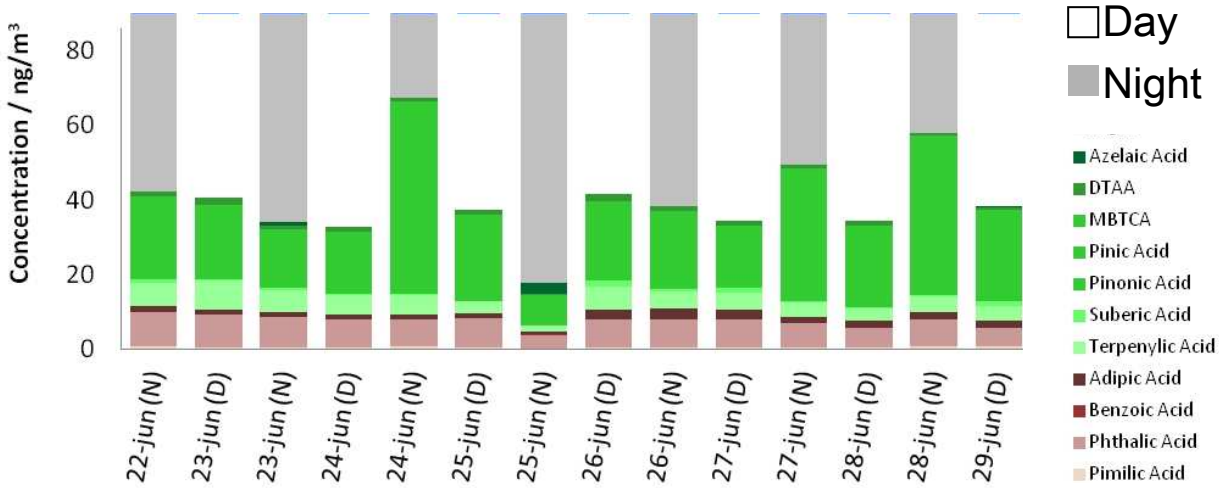
VAPOUR PHASE ***PARTICLE PHASE***

Case of study: day-night variations of some BSOAs (HPLC-qTOF-MS analysis):

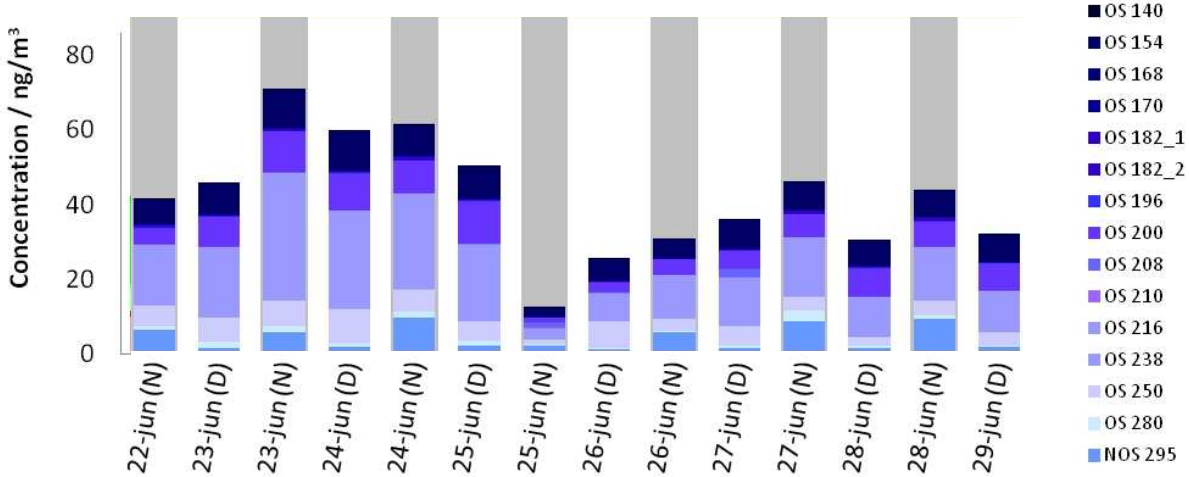
AARHUS UNIVERSITET

In day/night sampled PM_{10} (summer 2012) were found organic acids, **organosulphates** (OS) and **nitrooxyorganosulphates** (NOS) mainly derived from α-pinene and isoprene.

Carboxylic acids

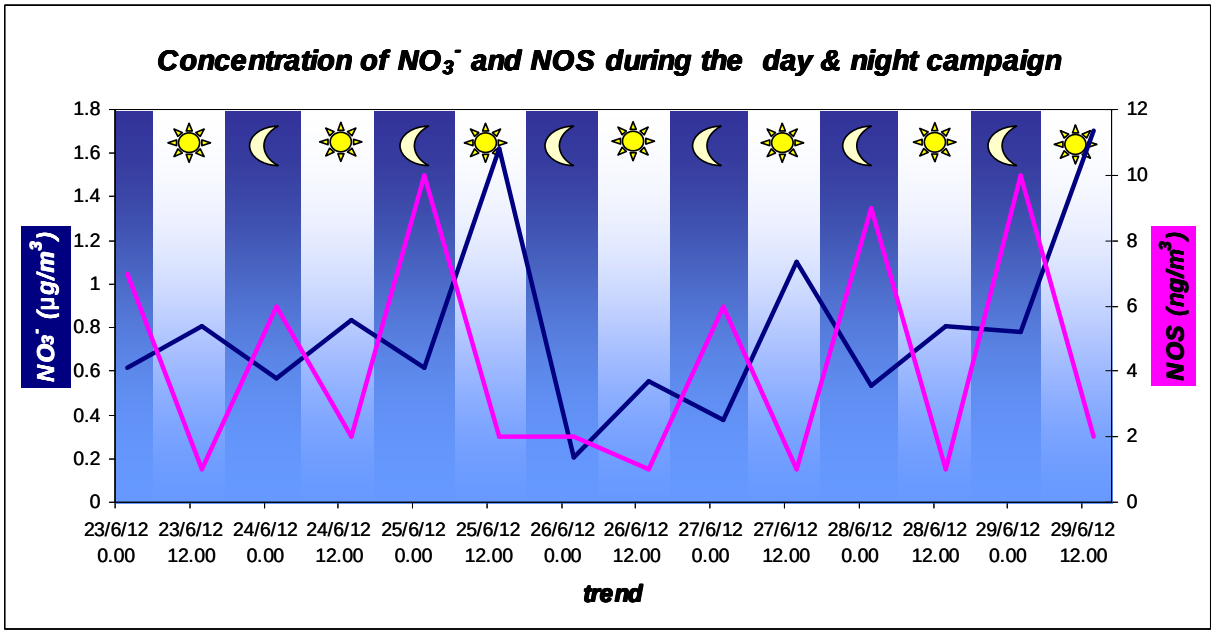


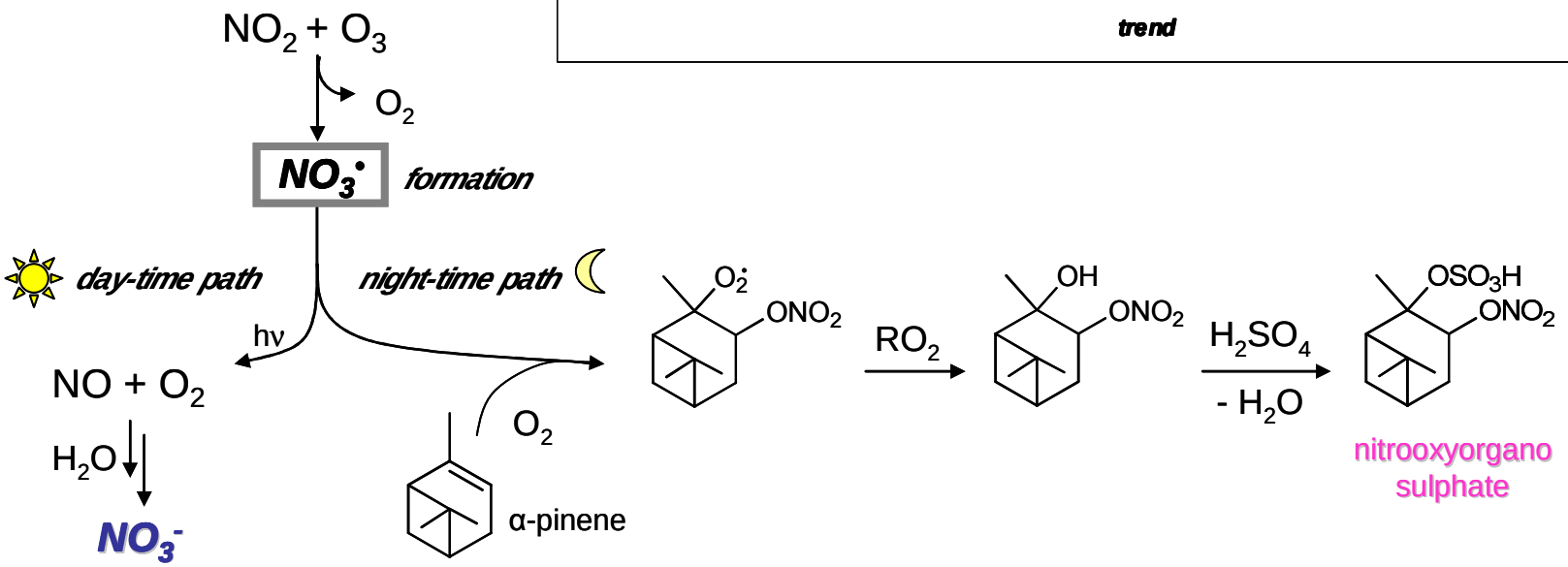
Organosulphates and nitro-oxy-organosulphates



Influence of photochemistry: some evidences

Day/night opposite trend for nitrate ions (NO_3^-) and nitrooxyorganosulphates (NOS). They are almost two orders of magnitude different.





Work in progress

- Quantification of other BSOAs (e.g. dicarboxylic acids)
- Studies on [O_3] and its role on half-life of emitted BVOCs
- Insights on the study of biomass burning
- Modeling of BVOCs emissions (MEGAN → other models (e.g. NEMO)

Thank you for your attention.

arianna.tolloi@phd.units.it