

Long-term observations of carbonaceous aerosols and related gaseous emissions near a crude-oil plant in South Italy

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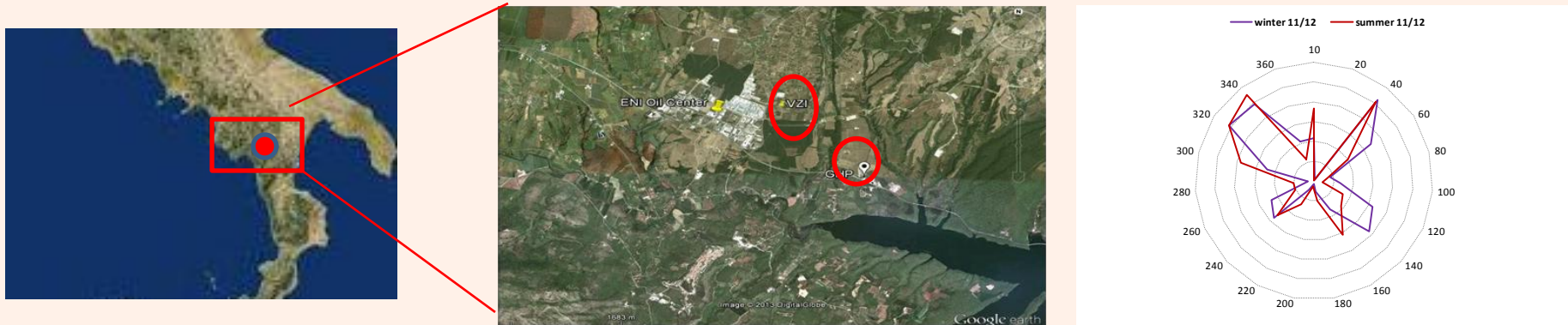
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Agri Valley site



Rural site with a **big onshore oil field** and a **pre-treatment plant (COVA)** with continuous combustion processes : an **unicum** in such an urbanized and agriculture-dedicated area

Two different measurement points both downwind respect to the COVA:

roof of Grumentum Park Hotel (**GPH**, 12 m a.g.l) about 2 km far from COVA in the South East direction

“Viggiano Zona Industriale” (**VZI**) ARPAB (Basilicata Region Environmental Protection Agency) monitoring station located at less than 1 Km East from COVA

One **two-year database for 2011-2012**

Sampling and methods



VZI site : ARPAB monitoring station (40.18 N, 15.54 E, 565 m a.s.l)

Gaseous organic compounds concentrations :
benzene, **toluene**, Non-methane-Hydrocarbons (**NMHC**)



meteorological data:
wind speed and **direction**,
T, **RH(%)**, **solar radiation**

7 wavelengths Aethalometer : (370-950 nm)

- **Size selective inlet**: 2.5 μm
- **Filter**: quartz fiber tape
- **Temporal resolution**: 5 min

Attenuation measurements



Absorption coefficients σ_{aer} at the 7 wavelengths



Black Carbon (BC) concentrations obtained assuming a mass extinction coefficient S_{aer} inversely proportional to the wavelength

Aethalometer data processing

1) Shadowing effect  tape advancing time has been set to the value of 1 hour

2) OC detection  enhanced absorption of organic fraction at the shorter λ

UVPM
(UV-absorbing
Particulate Matter)



BC computed at 370 nm



BC computed at 880nm

For carbonaceous aerosol whose absorption coefficient has a spectral dependence higher than 1



Hypothesis of a mass absorption coefficient inversely proportional to the wavelength no longer valid

suitably implemented algorithm



Fitting procedure applied to absorption coefficients σ_{aer}



Fitting procedure for the OC detection

Total measured UV absorption coefficient σ_{UV} is expressed as:

$$\sigma_{UV} = \sigma_{aer} + \sigma_{OC} = S \cdot \langle C \rangle + \sigma_{OC}$$

aerosol contribution to the absorption

absorption due to a mix of organic compounds

The fit applied to the spectral range 470-950 nm is used to extrapolate the aerosol contribution σ_{aer} :

$$\sigma_{OC} = \sigma_{UV} - (S \cdot \langle C \rangle) = \sigma_{UV} - \beta \left(\frac{\lambda}{\lambda_0} \right)^{-\alpha}$$

σ_{UV} measured at 370 nm

α and β Ångström parameters calculated by the fit procedure

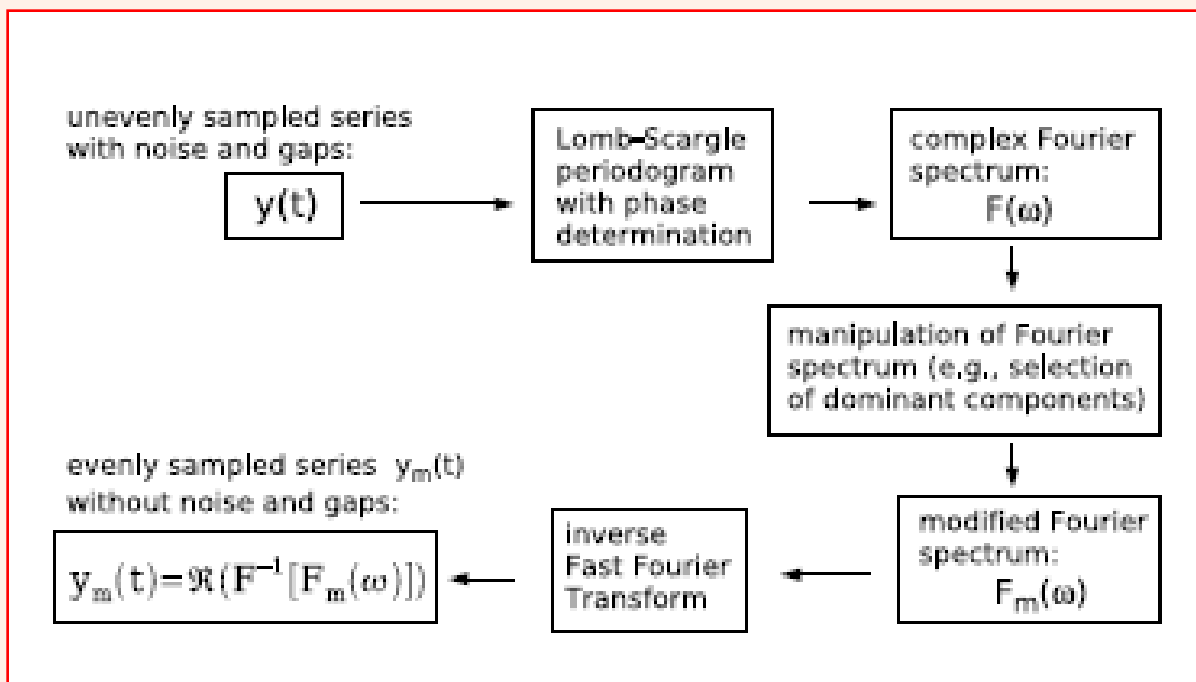
Lomb-Scargle technique

Statistical Lomb-Scargle periodogram technique applied for:

frequency analysis of
not equally-spaced
data



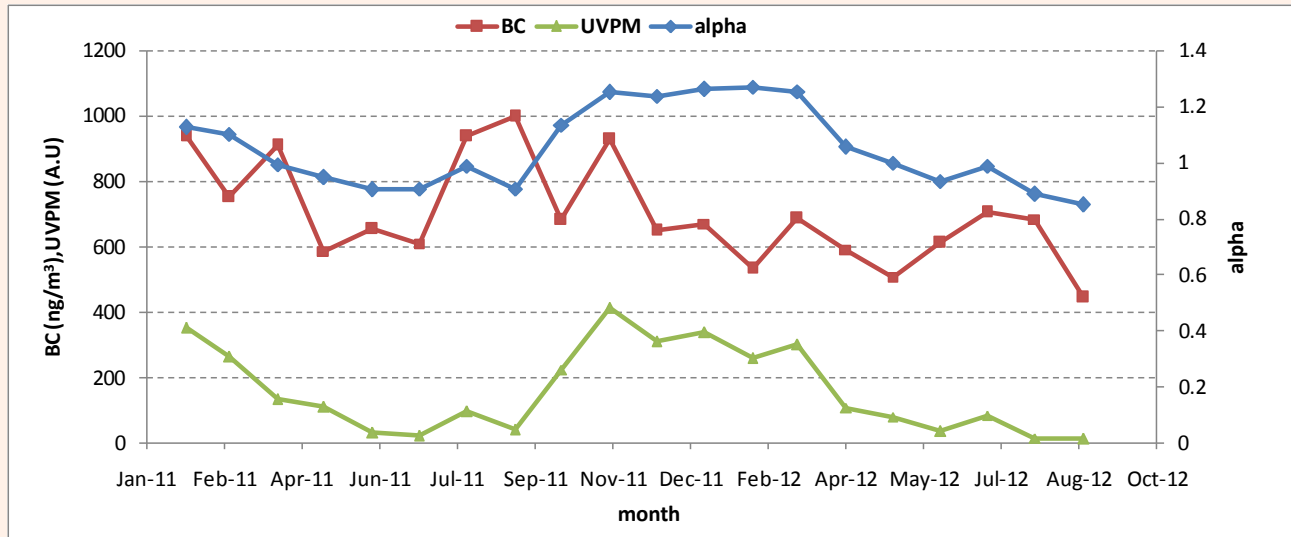
reconstructed spectra on both seasonal and
annual basis for the two-year database



From: Hocke, K., and
Kämpfer, N. (2009)
Atmos. Chem. Phys.,
9, 4197-4206

For present analysis reconstructed spectra are representative of *background emissions* to be compared with much *intense emissions* taking place in shorter periods during the year

Two - year aethalometer database I



Monthly mean values

BC err (ng/m³) = **777.6** 373.9
for the **two-year**
database '11-'12

BC err (ng/m³) = **705.1** 180.7 for the **summer** database '11-'12

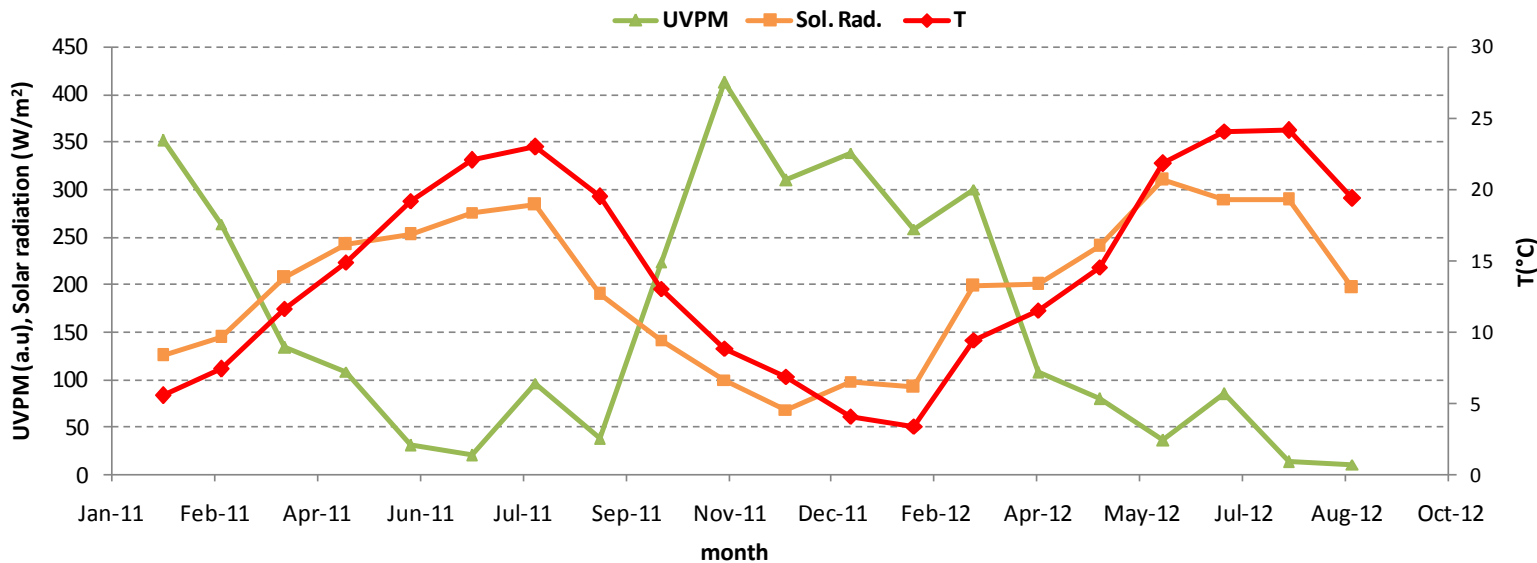
BC err (ng/m³) = **926.7** 602.1 for the **winter** database '11-'12

- BC** concentrations higher in winter
- Seasonal trends more evident for **UVPM** and α parameter with higher values in winter



Focus on winter for further analysis

UVPM and meteorological parameters

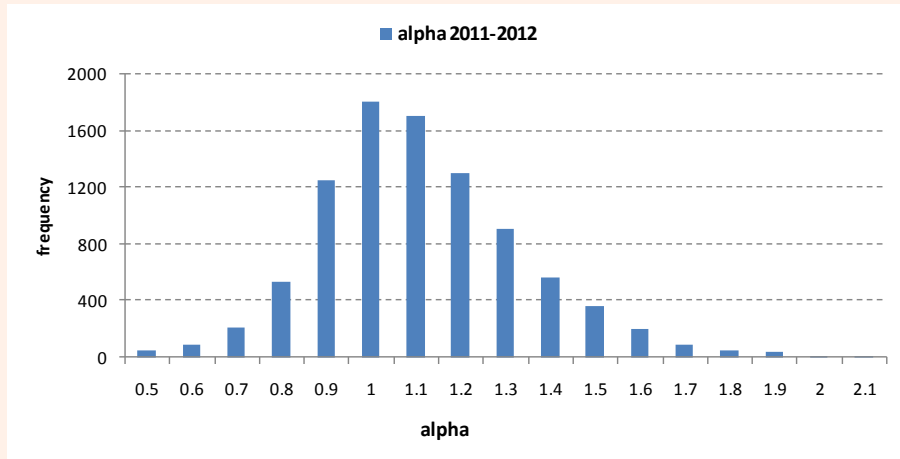


UVPM reduction with increased **solar radiation** and **temperature** values



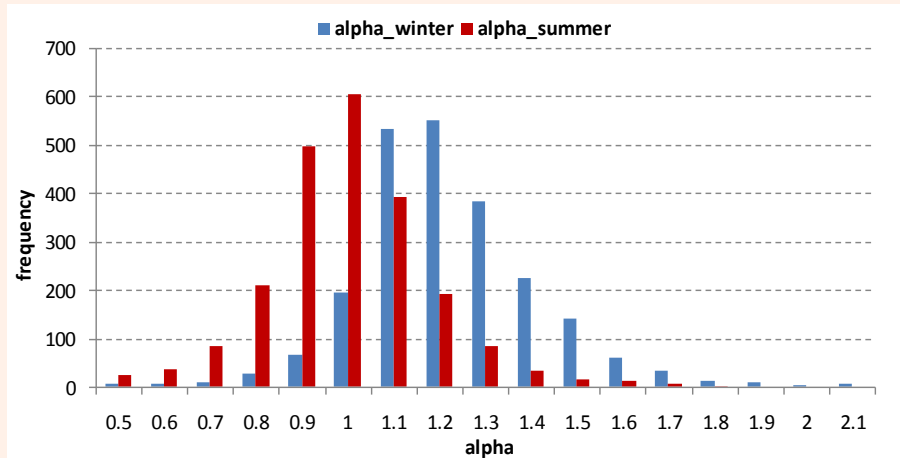
photochemical processes and *volatilization* reduce the probability of organic molecules adsorption on BC particles

Two - year aethalometer database II



Alpha hourly mean values

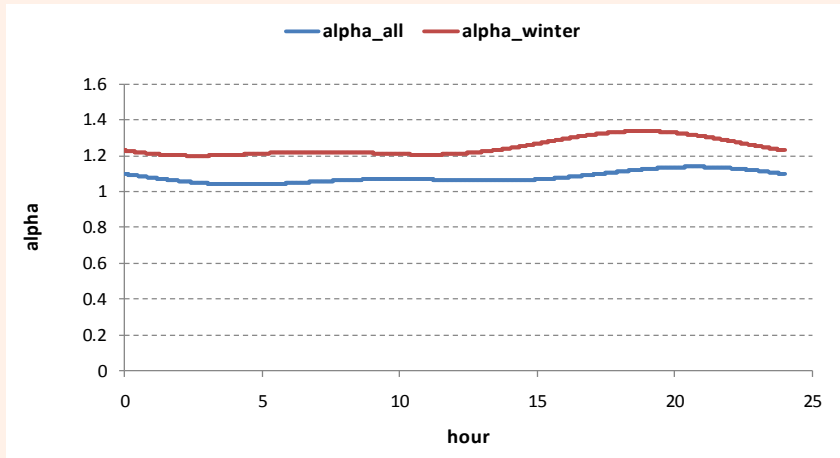
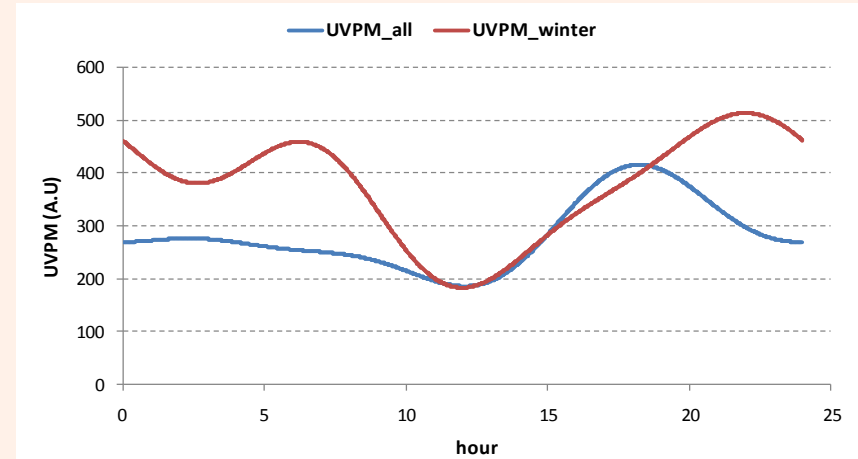
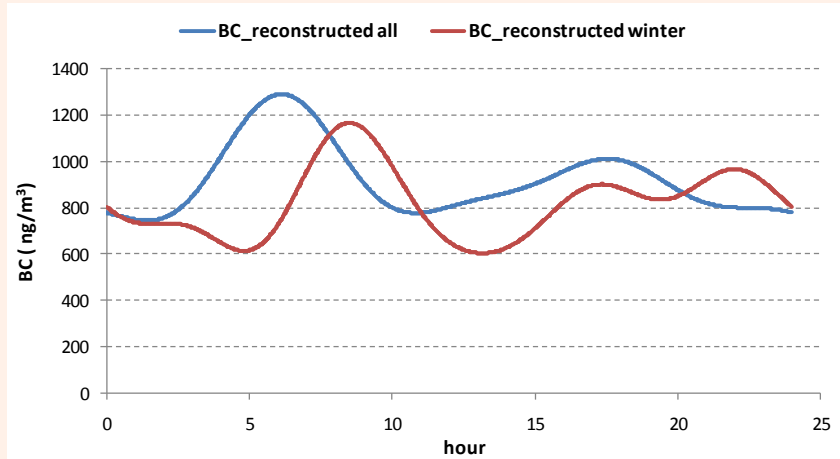
$\langle \alpha \rangle$ err $\alpha = 1.0 \pm 0.1$
for the two-year database
2011-2012



$\langle \alpha \rangle$ err $\alpha = 1.19 \pm 0.08$
for the winter database
2011-2012

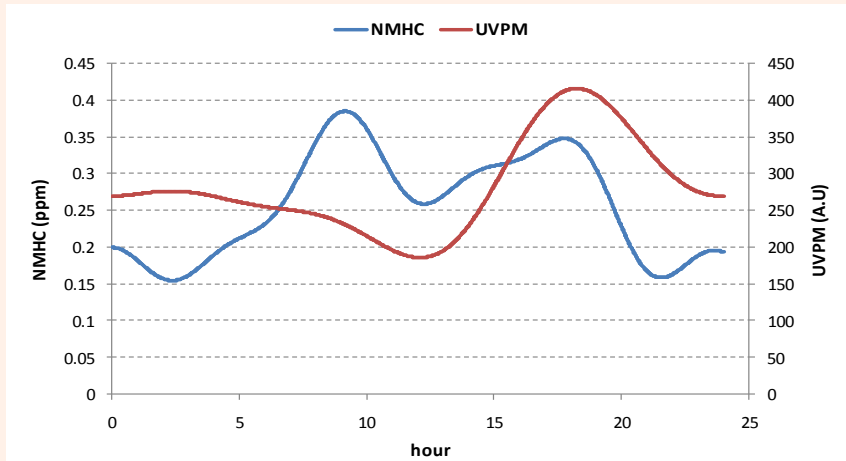
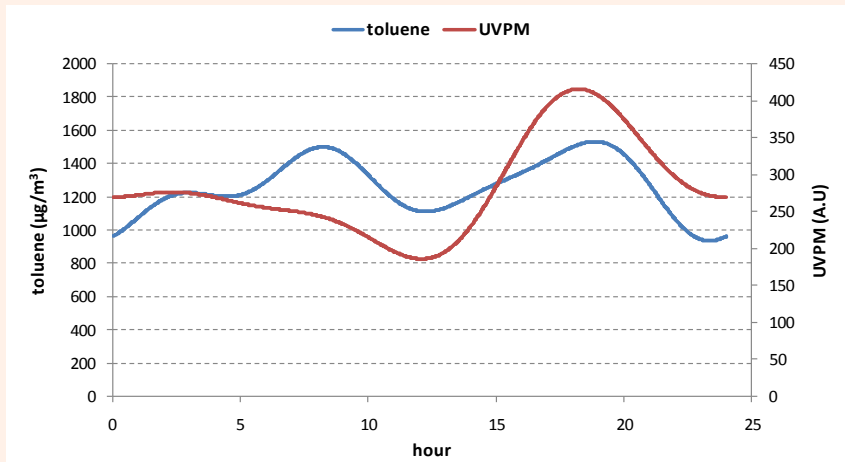
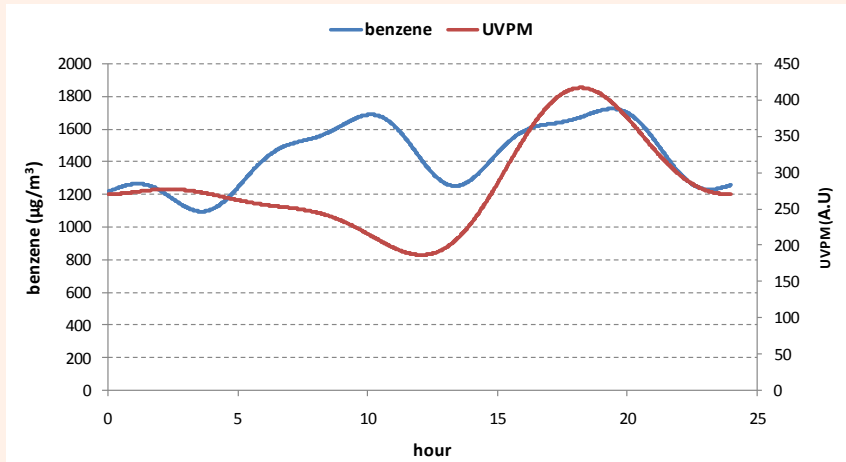
$\langle \alpha \rangle$ err $\alpha = 0.92 \pm 0.05$
for the summer database
2011-2012

Lomb-Scargle periodograms



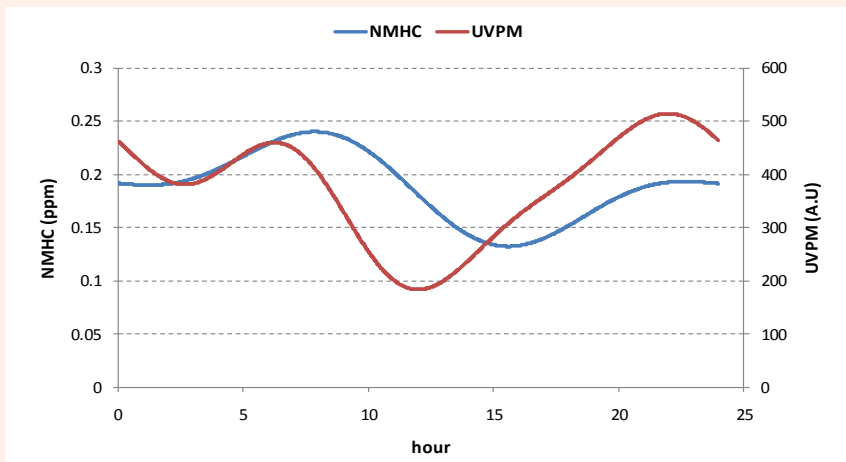
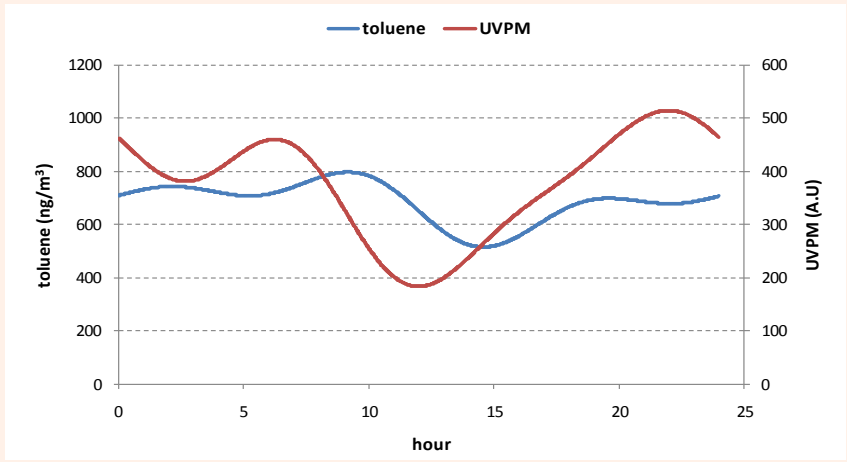
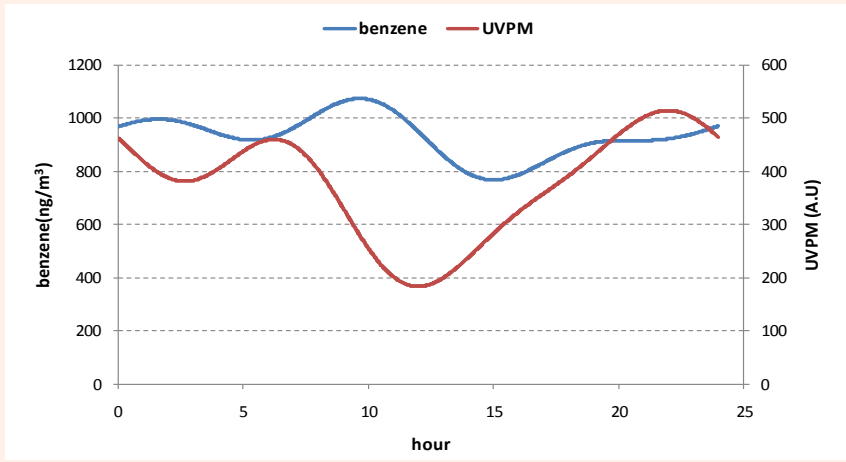
Reconstructed spectra of BC, UVPM and α "typical day" as obtained by Lomb-Scargle periodogram for the entire database (blue curve) and for the winter database (red curve)

Comparing UVPM to gaseous emissions on a long-term scale I



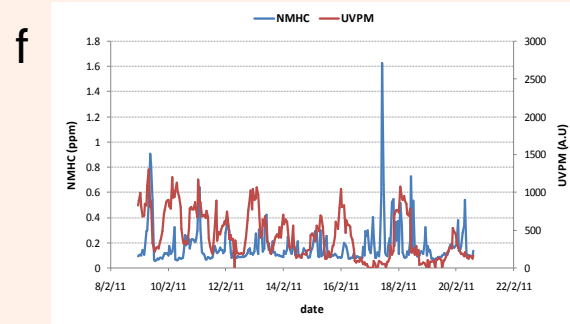
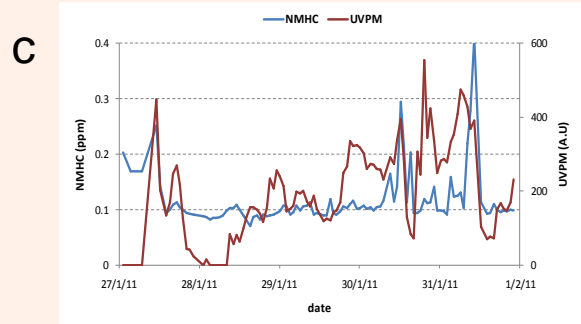
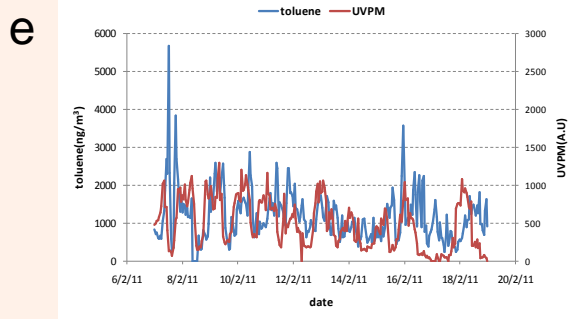
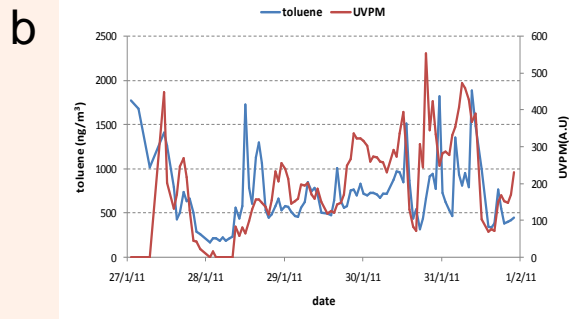
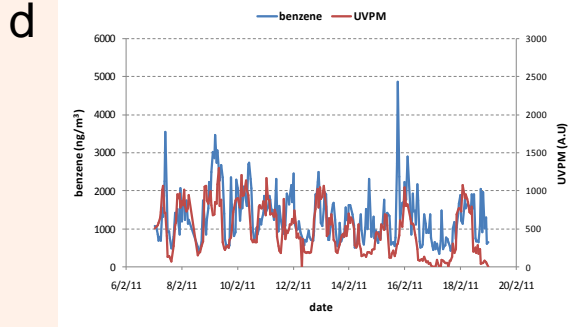
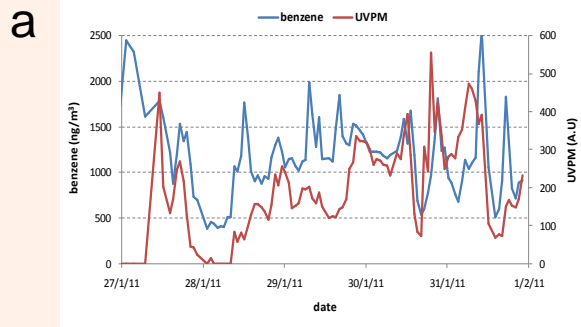
Reconstructed spectra of benzene, toluene, NMHC and UVPM "typical day" as obtained by Lomb-Scargle periodogram for the two-year database

Comparing UVPM to gaseous emissions on a long-term scale II



Reconstructed **winter** spectra of benzene, toluene, NMHC and UVPM “typical day” as obtained by Lomb-Scargle periodogram for the two-year database

Comparing UVPM to gaseous emissions on short-term scales



Temporal variation of toluene, benzene, NMHC concentrations and UVPM hourly mean values for the periods January 27-31, 2011 (graphs a,b,c) and February 7-20, 2011 (graphs d,e,f)

Summary and conclusions

- Aethalometer data were obtained at a site (Agri Valley) with crude oil extraction and pre-treatment activities. Analysis of BC concentrations were carried out on a two-year basis. OC component was detected through UVPM quantity
- Aethalometer data have been studied in relation to gaseous organic compounds concentration data (benzene, toluene, NMHC) measured at the same site by applying the statistical Lomb-Scargle technique
- UVPM shows a stronger seasonality with an enhancement during winter: hypothesis of reduction in summer for increased solar radiation and temperature (photochemical reactions and volatilization processes)
- Winter “ typical day” reconstructed spectra can be considered as representative of background emissions. In this case similar trends were found for UVPM and gaseous organic compounds suggesting similar dynamics in aerosol formation and/or adsorption processes onto atmospheric particles on a long-term basis. Looking at periods with much intense emissions even better agreement was found
- Necessity to enlarge the database to improve statistics and to study emissions for this peculiar site on different time-scales

Thank you for your attention!!!

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