

Organic carbon detection in crude-oil plant emissions in South Italy

M. Calvello¹, F. Esposito², G.Pavese¹, M.Lovallo³, L. Mangiamele³

¹IMAA-CNR Tito Scalo (Pz)

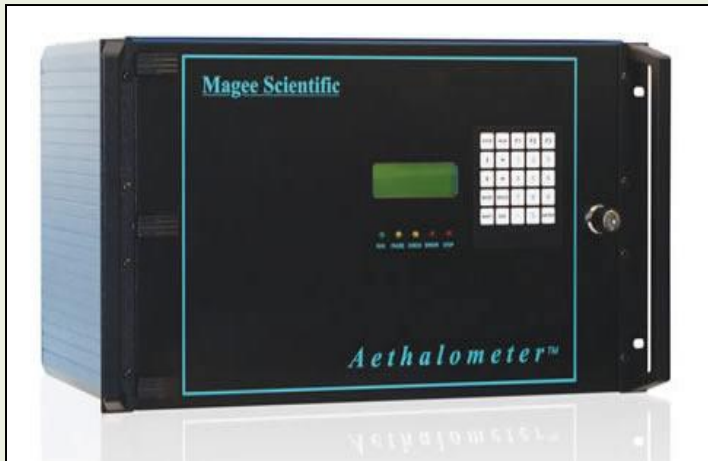
²DIFA-Università della Basilicata, Potenza (PZ)

³ ARPAB, Via della Fisica C/D, 85100 Potenza (PZ)

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Magee Aethalometer AE31

7 wavelengths Aethalometer : 370, 470, 520, 590, 660, 880 and 950 nm



- ❖ Flow rate: 3.8 lpm
- ❖ Size selective inlet: 2.5 μm
- ❖ Inlet height: 2 m above ground
- ❖ Filter: quartz fiber tape
- ❖ Temporal resolution: 5 min

Optical attenuation method

$$ATN(\lambda) = -\ln \frac{I_S(\lambda)}{I_R(\lambda)}$$

Irradiance through the reference filter

Irradiance through the loaded filter

$$ATN(\lambda) = \frac{S(\lambda) \cdot C \cdot V}{A}$$



$S(\lambda)$ = Mass Absorption Cross section

C = aerosol mass concentration

V = Sampled volume

A = Spot area

Shadowing effect: instrument is set in such a way that the particle accumulation area changes every hour

Black Carbon (BC) content estimation

Standard Algorithm

1) Hypothesis of a mass absorption cross section inversely proportional to the wavelength:

$$S(\lambda) = K / \lambda$$

Calibration constant $K = 14.625 \mu\text{m m}^2 \text{g}^{-1}$

2) Estimation of the spectral absorption coefficient $\sigma_{ab}(\lambda, t)$ and of the BC content (at the standard wavelength $0.88 \mu\text{m}$) after an interval Δt :

$$\sigma_{ab}(0.88, t) = \frac{A}{\langle F(t) \rangle} \frac{ATN(t + \Delta t) - ATN(t)}{\Delta t} = S \cdot \langle BC(t) \rangle$$

Organic Carbon (OC) detection

Standard Algorithm

Some **Organic** compounds in carbonaceous aerosol strongly absorb at UV wavelengths



In the Magee algorithm, the **difference between BC computed at 370 nm and BC computed at 880nm** is used to qualitatively detect the presence of organic compounds introducing the **UVPM** (UV-absorbing Particulate Matter).



UVPM: amount of BC that absorbs UV photons with the same efficiency of organic compounds

Brown Carbon

Standard Algorithm ?

Brown Carbon (BrC) → carbonaceous aerosol whose absorption coefficient has a spectral dependence higher than 1, resulting in a coloured appearance



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



Wrong information on OC detection if the standard procedure is used

Spectral dependence of σ_{ab}

Multiwavelength aethalometer measurements allow to verify the **spectral behaviour** of carbonaceous aerosol absorption coefficient.



Angström empirical formula for $\sigma_{ab}(\lambda)$:

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

- α and β are the Angström parameters
- $\langle C \rangle$ is the aerosol concentration

And for the mass absorption cross section **$S(\lambda)$** :

$$S(\lambda) = K_{GEN} \left(\frac{\lambda}{\lambda_0} \right)^{-\alpha}$$

K_{GEN} (m^2g^{-1}) is the mass absorption coefficient at $\lambda_0 = 1\mu\text{m}$

Best-fit technique

$$\sigma_{ab}(\lambda) = \beta(\lambda / \lambda_0)^{-\alpha}$$

To obtain α and β parameters, a **fit procedure** is applied to the measured $\sigma_{ab}(\lambda)$ in the 470-950 *nm* spectral range excluding the UV channel

If α is > 1 **BrC presence** is assumed

β parameter is used to estimate BC or BrC content indicated with $\langle C \rangle$ in the formula

$$\langle C \rangle = \frac{\beta}{K_{GEN}}$$

New OC detection I

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} :

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

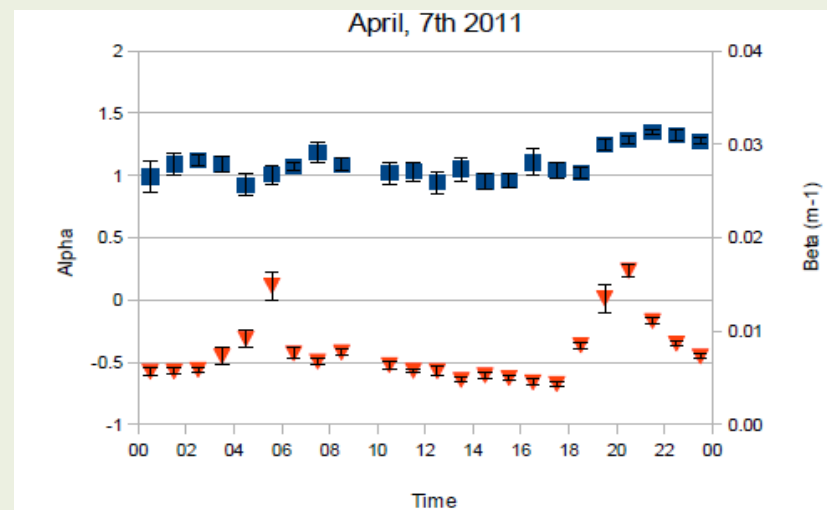
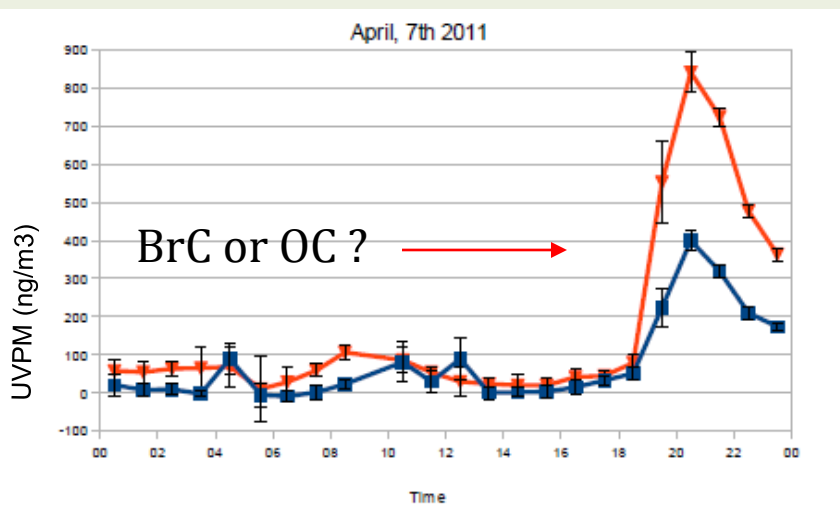
σ_{UV} measured at 370 nm

α and β calculated by the fit procedure

New OC detection II

Starting from the calculation of $\sigma_{OC}(\lambda)$, the **UVPM_{New}** can be calculated by the new technique to be compared with **UVPM_{Mag}** calculated with the Magee procedure:

$$UVPM_{New} = \frac{\sigma_{OC}}{S} = \frac{\sigma_{OC}}{K_{GEN}} \left(\frac{\lambda}{\lambda_0} \right)^{-\alpha}$$



▼ UVPM_{Mag}

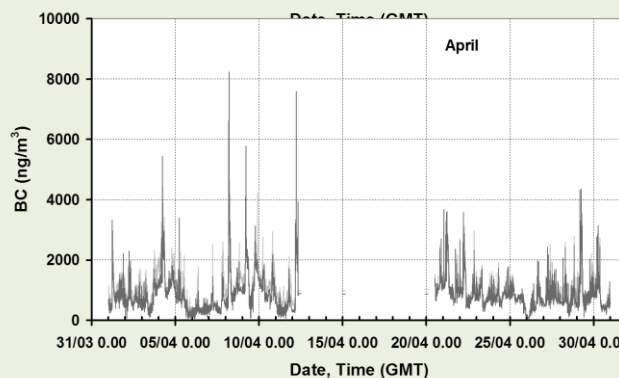
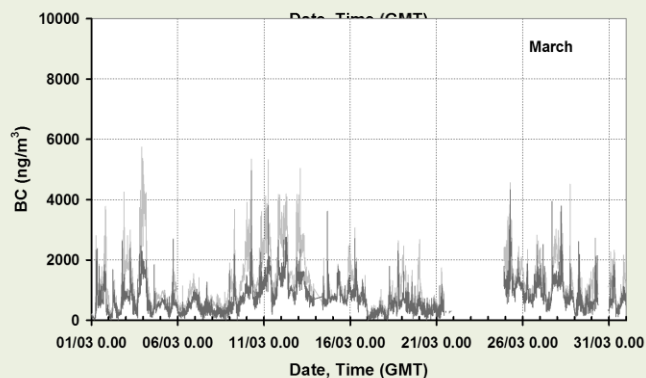
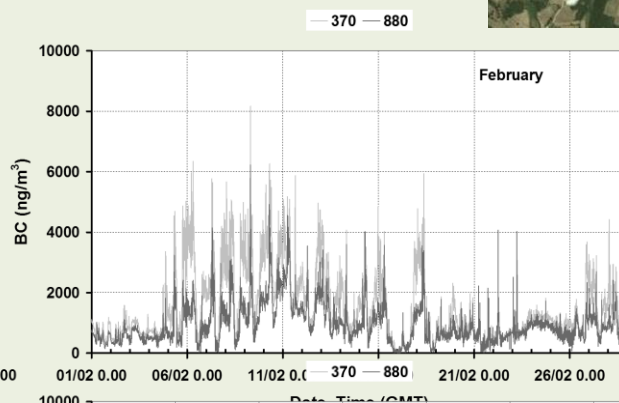
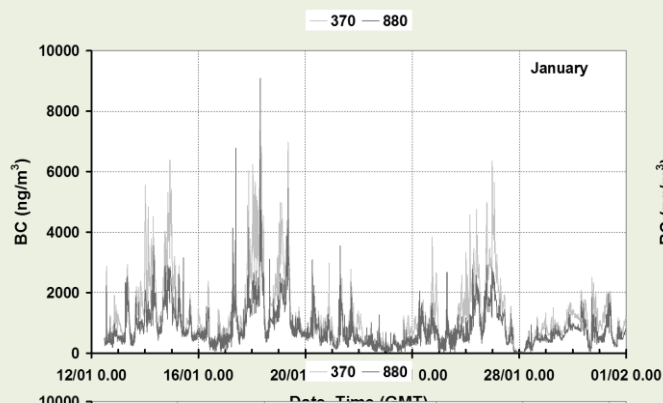
■ UVPM_{New}

α e β temporal trend

Agri Valley database I

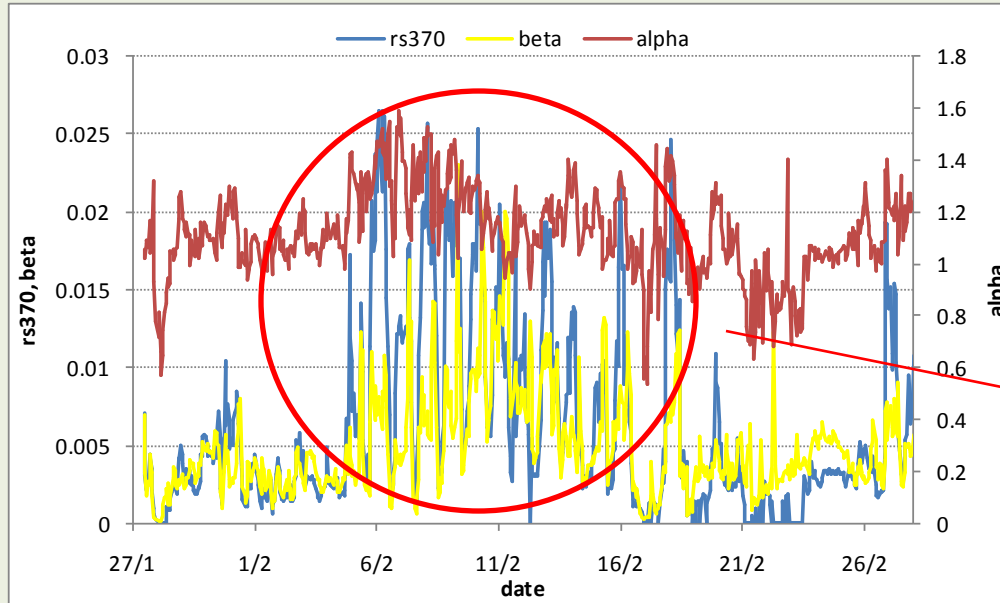
ENI Oil Center, Viggiano (40.33°N, 15.92°E, 582 m *a.s.l*)

Rural site with intensive extraction activities of crude oil. Continuous and controlled smoke emissions from the crude oil pre-treatment plant.



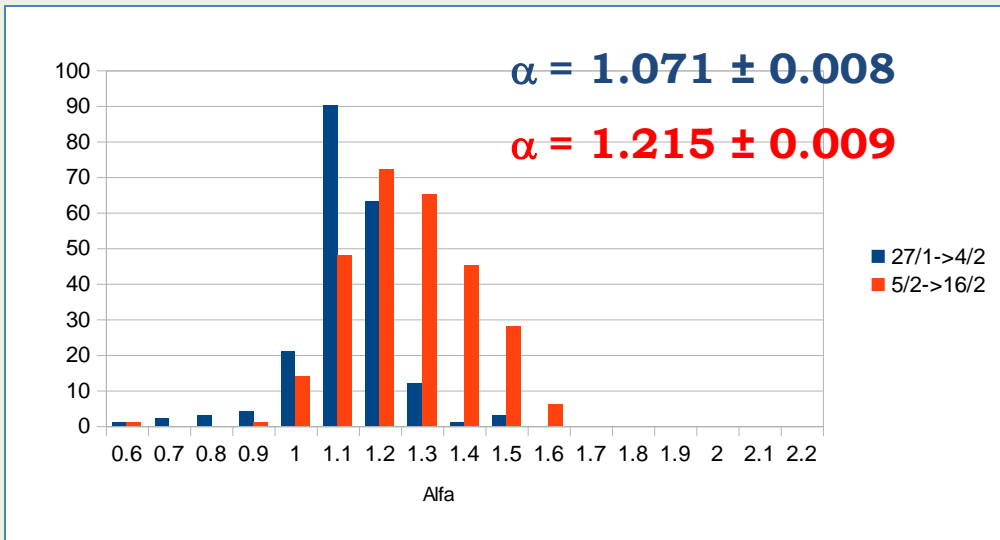
BC values at 370 nm always greater than BC values at 880 nm

Agri Valley database II



Temporal trend (jan., 27- feb., 28) for α and β parameters and for **residuals** at 370 nm

Intense emission episode

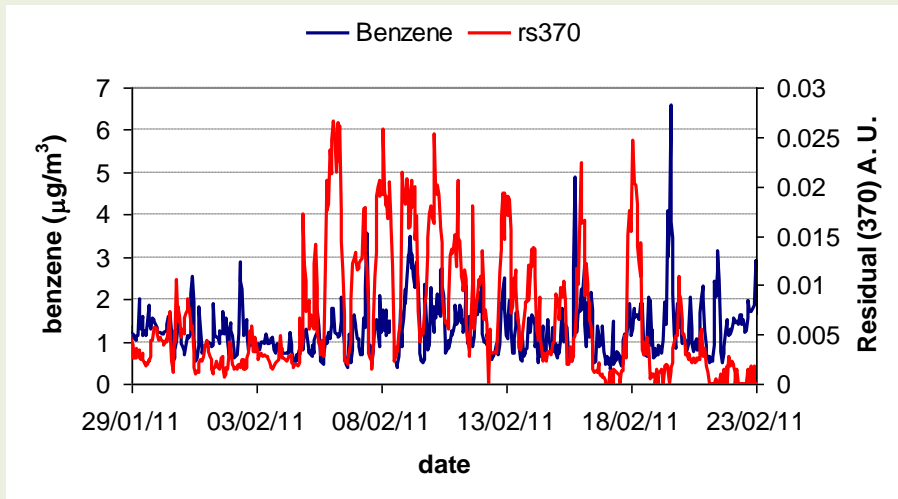
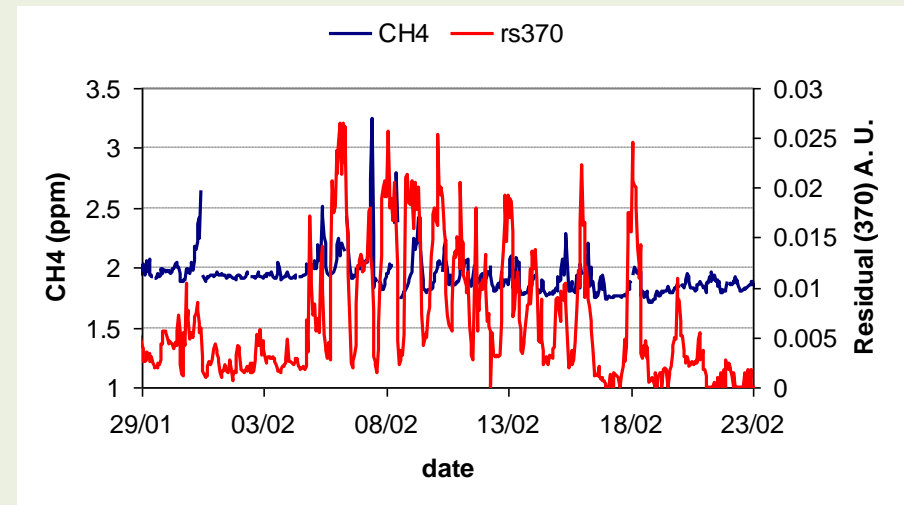


α parameter histograms:

- **In blue** for the period january, 27- february,4 (low emission)
- **In red** for the period february 5-16 (high emission)

Comparison with some Organic compounds concentrations measured at the site I

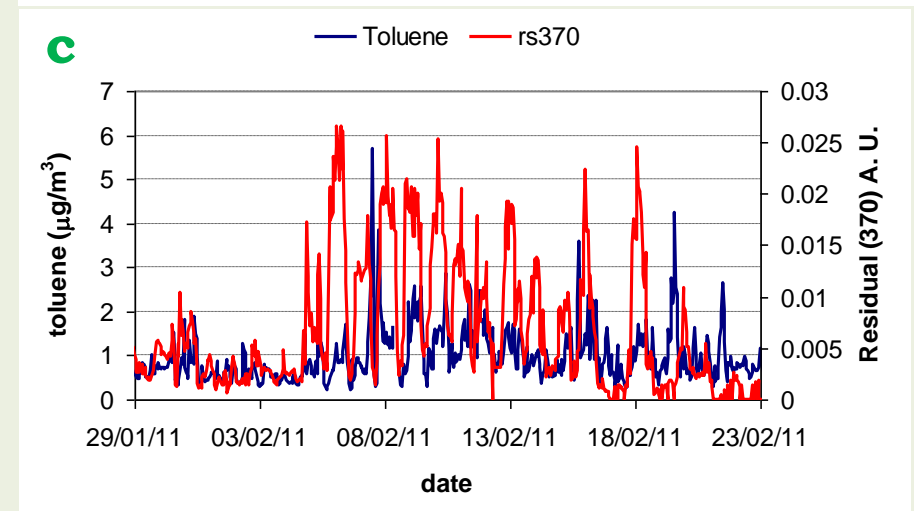
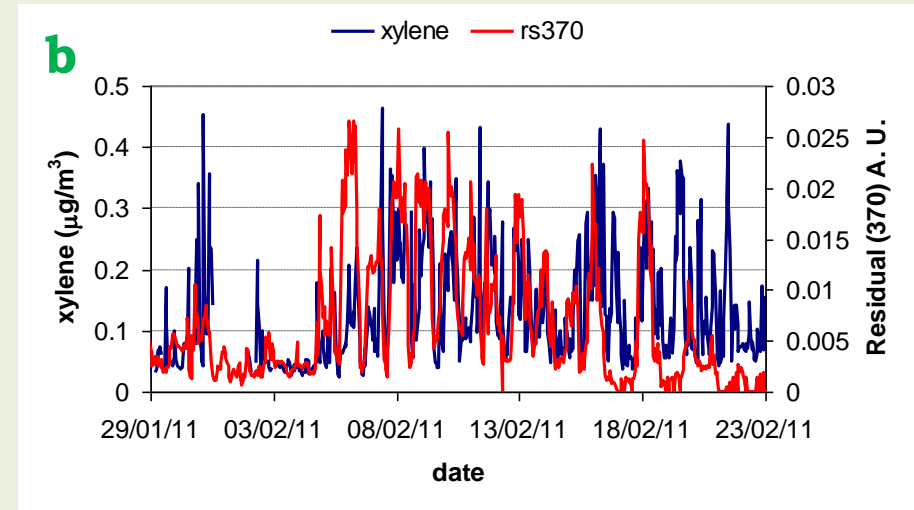
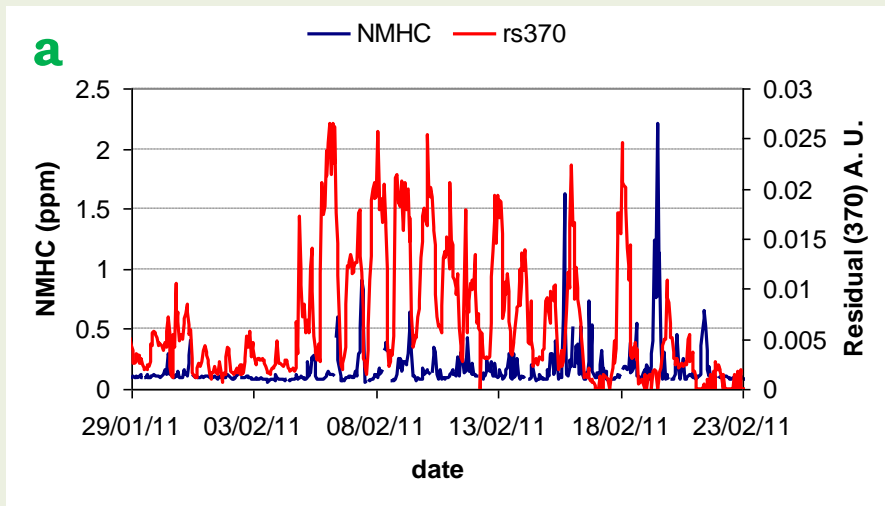
Temporal trend (january, 27-february, 28) for 370 residual and **Methane** (CH₄) concentrations measured at the site



Temporal trend (january, 27-february, 28) for 370 residual and **Benzene** concentrations measured at the site

Comparison with some Organic compounds concentrations measured at the site II

Temporal trend (january, 27-february, 28) for 370 residual and **NMHC** (a), **xylene** (b) and **Toluene** (c) concentrations measured at the site



Tito long-term database I

Tito, IMAA-CNR (40.35°N, 15.41°E, 750 m *a.s.l*)

Small industrial zone in a wide rural area. No particular BC emission sources are present apart from vehicular traffic. Main road passing at about 1 Km.

Most data collected during spring-summer seasons of years 2008, 2009, 2010.



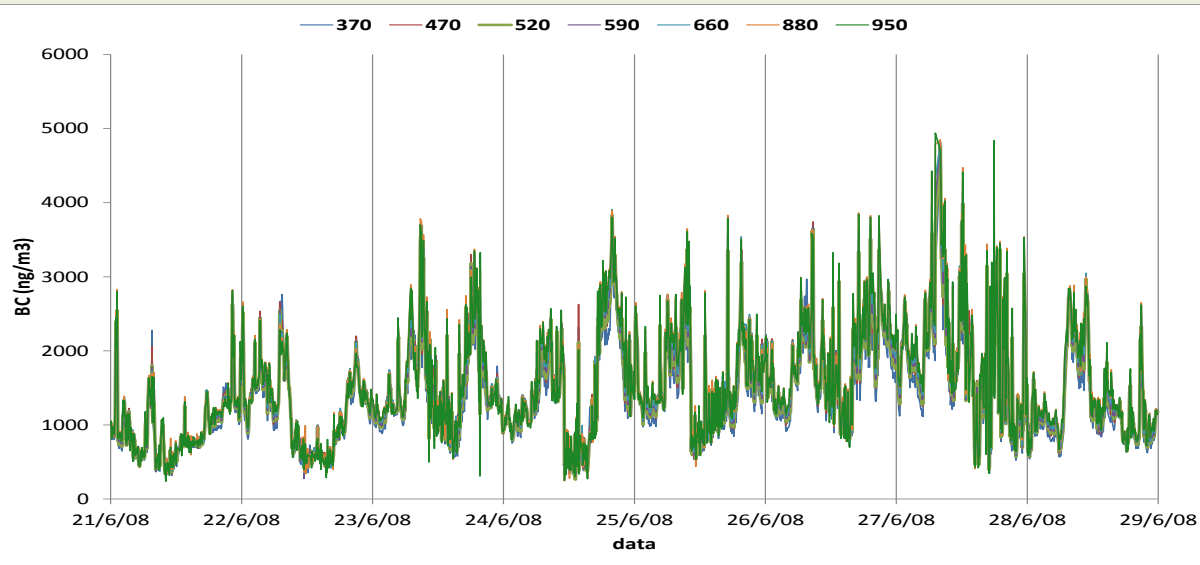
Year	<BC> (ng/m ³)	St. dev
2008	1539.4	727.4
2009	1305.7	1021.7
2010	1084.3	559.8

Annual mean BC value for a rural (semi-arid) region in India:

$$\langle \text{BC} \rangle = \mathbf{1970.0} \pm 120.0$$

Raghavendra Kumar, K. et al., Atmos. Res, 2011

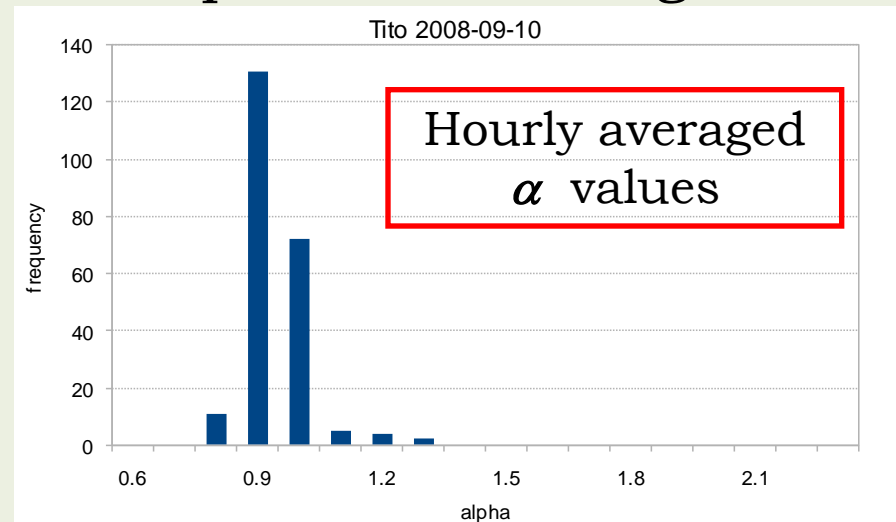
Tito long-term database II



Weekly trend, June 2008.
BC components at different wavelengths overlap

$\langle \alpha \rangle \pm \text{err}_\alpha = 0.9 \pm 0.1$
typical of vehicular traffic

α parameter histogram



Conclusions

- ❖ Carbonaceous aerosol spectral absorption behaviour has been verified by a Multiwavelength aethalometer
- ❖ A best-fit technique has been used for Angstrom α parameter calculation to distinguish between BC and BrC
- ❖ The best-fit parameters have been used to estimate the absorption coefficient in the UV channel as an indicator of OC presence
- ❖ Aethalometer data have been analysed for a site (Agri Valley database) with crude oil extraction and pre-treatment activities
- ❖ A correlation study has been carried out between Aethalometer data and Organic Compounds concentration data in Agri Valley
- ❖ A comparison has been made between the Agri Valley short-term database and the Tito Scalo long-term database showing two different prevailing sources of carbonaceous aerosol

Thank you for your attention!!!

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