LIGHT ABSORPTION AND RADIATIVE EFFECTS OF WATER-SOLUBLE AND METHANOL-SOLUBLE BROWN CARBON UNDER HIGH RESIDENTIAL WOOD BURNING EMISSIONS

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WATER, METHANOL SOLUBLE BROWN CARBON MEASUREMENTS IN IOANNINA

- Scope: Investigation of water, methanol soluble OC mass and related absorption characteristics. Estimates of radiative forcing of the WS_BrC, MeS_BrC relative to EC for the first time in Greece and southeastern Europe.
- Ioannina Campaigns: Summer 2019 (July-August), Winter 2019/20 (December-February)
- Chemical analysis of 24-hrs $PM_{2.5}$ samples (OC/EC analyzer, Ion chromatography)
- WSOC mass concentrations were measured using a Shimadzu TOC-VCSH total OC analyzer
- Monosaccharide anhydrides (including levoglucosan and mannosan) were analyzed using High-Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD)
- Aethalometer AE-33 [BC_{ff}, BC_{wb}, spectral absorption, AAE]
- Meteorological parameters (temperature, RH, rainfall, wind speed, direction)

PROTOCOL FOR ESTIMATES OF METHANOL-SOLUBLE OC MASS

- For the quantification of MeS OC a relatively novel, ***direct procedure*** was followed.

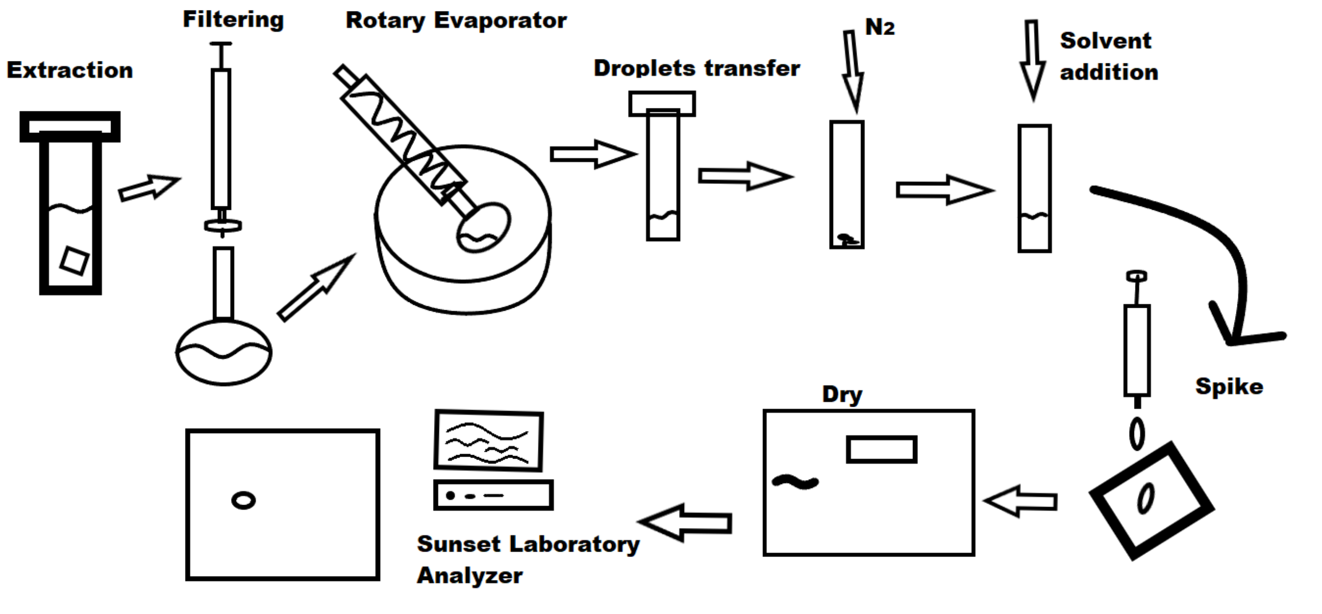
→ Punches from the $PM_{2.5}$ filters were extracted in methanol

→ Extracts were filtered and evaporated in a Rotary Evaporator to a few drops

→ The residue was washed with methanol and concentrated to dryness under a gentle nitrogen stream

→ The remaining compounds were dissolved with methanol and transferred on unexposed filter punches

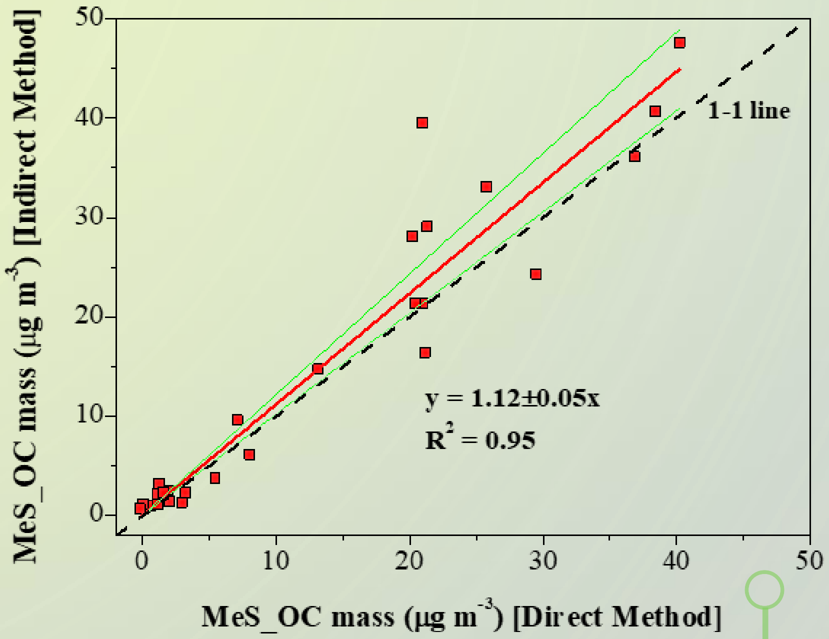
→ The filter punches were spiked with the methanol solutions, dried and then analyzed in the Sunset OC/EC Analyzer



COMPARISON BETWEEN DIRECT AND INDIRECT METHODS FOR MES_OC

- The methanol soluble mass of OC was also calculated, through the ***indirect procedure*** that is frequently used in reported MeS_BrC studies

  - Comparison was performed on a subset of 27 samples (summer and winter).
  - Overestimation of the calculated MeS_OC mass with the indirect method (MeS_OC / OC: 74 % vs. 65 %)



LIGHT ABSORPTION ANALYSES IN FILTER EXTRACTS

- Measurements of light-absorbing BrC in water- and methanol- extracts by UV–Vis spectrophotometry.
- A 1 cm^2 punch was placed in 15 mL of ultrapure water and another punch in 15 mL of methanol.
- The extracted solutions were filtered and then introduced into a 1m long Liquid Waveguide Capillary Cell (LWCC).
- The LWCC was coupled to a UV-Visible spectrophotometer
- Absorptions were measured at 365 nm relative to 700 nm forWS_BrC and MeS_BrC.
- $AbsWS/MeS\_BrC\_365\ (Mm^{-1}) = (A365 - A700) * Vextr. * fdil * \ln(10) / (Vair * l)$
- All acquired values were blank corrected

ESTIMATES OF BRC RADIATIVE FORCING

- The fractional radiative forcing of BrC (WS and MeS) relative to EC (RRF_{WS_BrC}, RRF_{MeS_BrC}), was estimated using the formulas (integrated in the wavelength band 300–2500 nm):

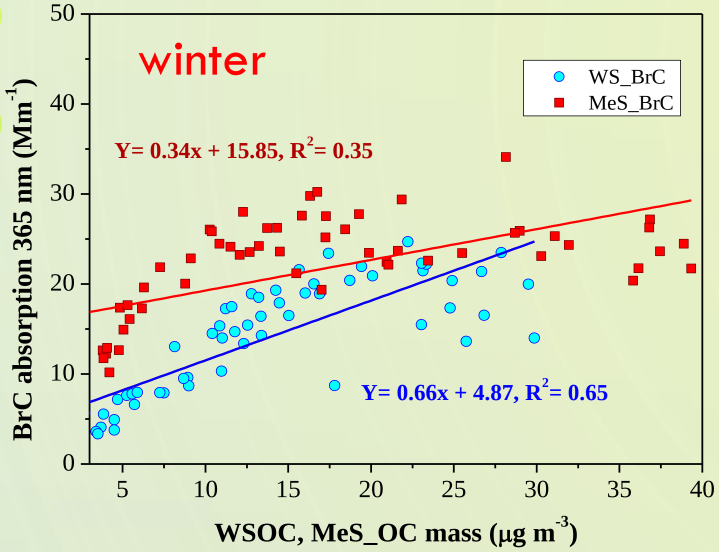
- $\frac{I_o - I}{I_o}(\lambda, BrC) = 1 - e^{-(MAE_{(WS/MeS)\_BrC} * \left[\frac{\lambda_o}{\lambda}\right]^{AAE_{(WS/MeS)\_BrC}} * C_{(WS/Mes)OC} * BLH)}$

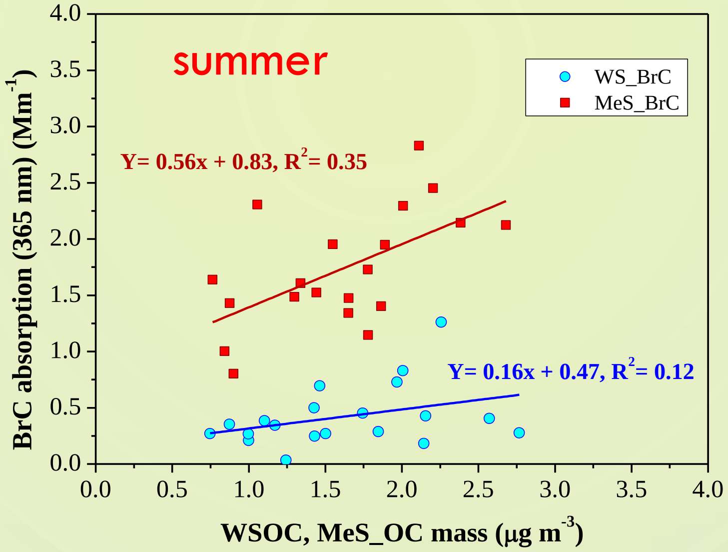
- $\frac{I_o - I}{I_o}(\lambda, EC) = 1 - e^{-(MAE_{EC} * \left[\frac{\lambda_o}{\lambda}\right]^{AAE_{EC}} C_{EC} * BLH)}$

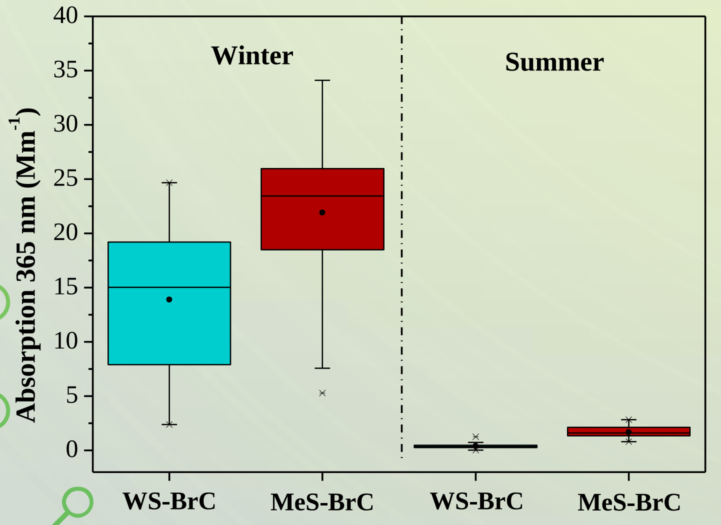
- $RRF_{BrC} = \frac{\int_{300}^{2500} I_{o(\lambda)} \left[\frac{Io - I}{Io}(\lambda, BrC)\right] d\lambda}{\int_{300}^{2500} I_{o(\lambda)} \left[\frac{Io - I}{Io}(\lambda, EC)\right] d\lambda}$

- $I_o(\lambda)$ is the solar emission flux (Wm^{-2} nm^{-1}) for clear-sky conditions, obtained from the Air Mass 1 Global Horizontal (AM1GH) solar irradiance model (Levinson et al., 2010). The reference wavelengths (λ_o) were 365 nm for BrC (WS/MeS) and 658 nm for EC. AAE(WS/MeS)_BrC corresponds to the calculated $AAE_{365\text{-}590}$ values and AAE_{EC} was set to 1. $C_{(WS/MeS)OC}$ and C_{EC} are the mass concentrations of extracted OC components and EC, respectively.

WS_OC, MES_OC MASS AND RELATED ABSORPTIONS



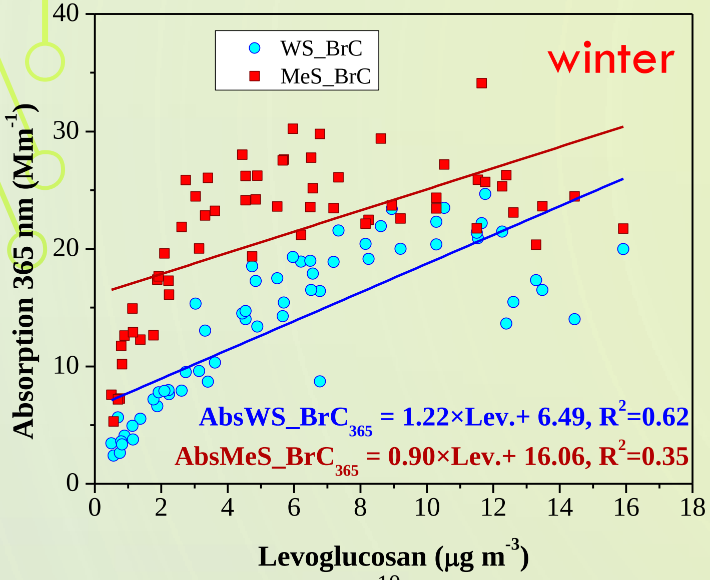


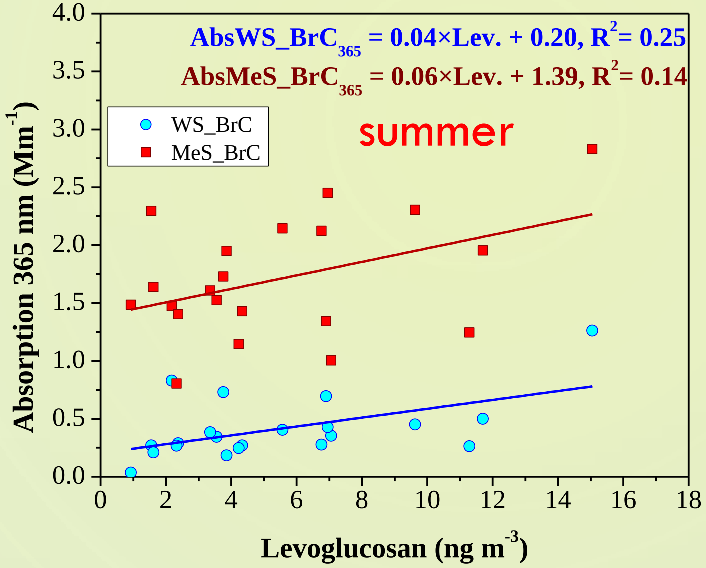


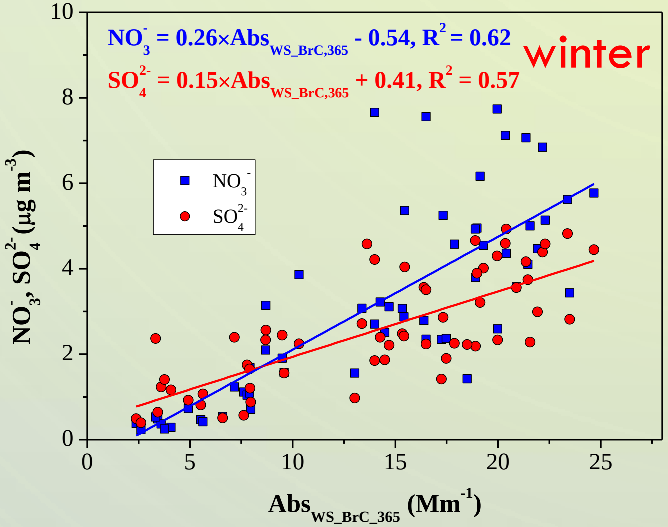
AbsWS_BrC: 13.9 ± 6.5 Mm^{-1} (winter)
AbsWS_BrC: 0.4 ± 0.3 Mm^{-1} (summer)
AbsMeS_BrC: 21.7 ± 9.1 Mm^{-1} (winter)
AbsMeS_BrC: 1.7 ± 0.5 Mm^{-1} (summer)

- The direct method resulted in a MeS_OC contribution of 68% and 71% to OC in winter and summer, respectively.
- WSOC/OC: 0.56 (winter), 0.64 (summer).
- The MeS_OC mean concentration was 17.6 μg m^{-3} in winter and 1.8 μg m^{-3} in summer.
- Significant correlations between WSOC, MeS_OC masses and absorptions.
- For intense BB conditions, the absorptions of water and methanol extracts remain mostly constant.
- Lower correlations in summer signaling photo-dissociation of BrC chromophores, no BB sources, possible biogenic emissions with low absorbance.

WS_OC, MES_OC MASS AND RELATED ABSORPTIONS



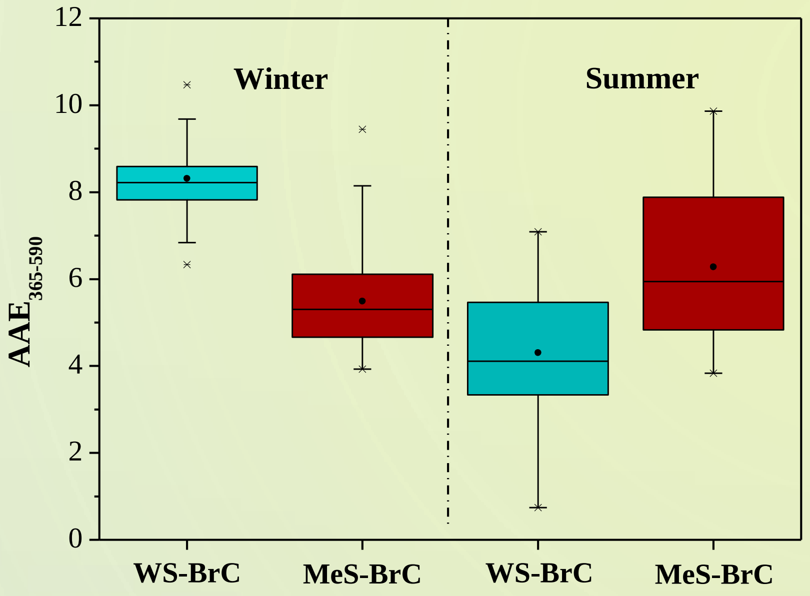


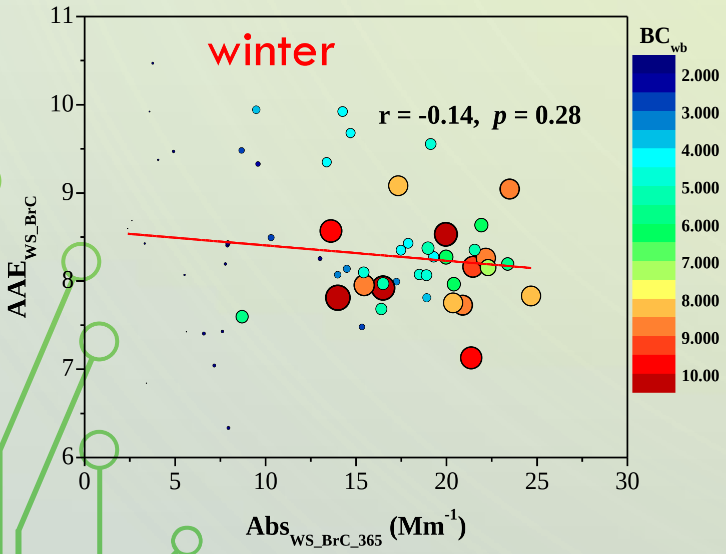


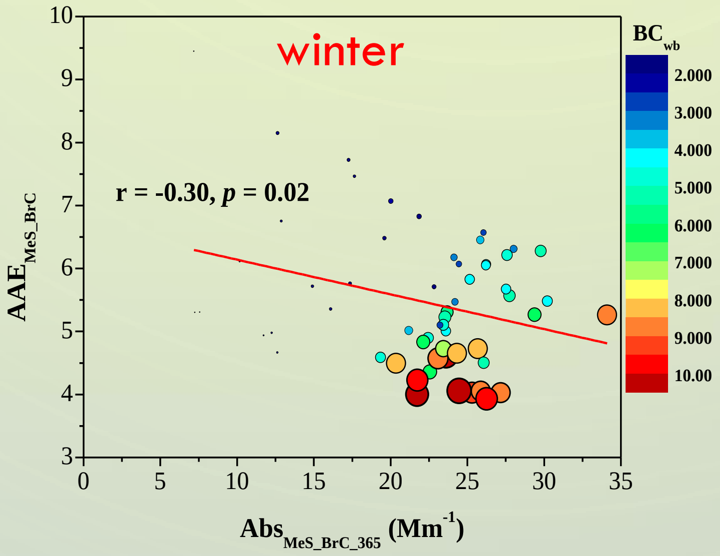
Significant correlations of WS_BrC absorption with NO_3^- ($R^2 = 0.62$) and SO_4^{2-} ($R^2 = 0.57$) in winter imply secondary formation of water-soluble light-absorbing compounds.

- Strong correlation between water and methanol BrC absorptions in winter ($R^2 = 0.60$).
- In winter, $Abs_{WS\_BrC\_365}$ was strongly associated with levoglucosan ($R^2 = 0.62$), revealing RWB origin.
- MeS_BrC absorption exhibited a moderate association ($R^2 = 0.35$) with levoglucosan, which decreased considerably for levoglucosan concentrations above 6 µg m^{-3}.
- For Lev.< 6 µg m^{-3}, the correlations improved to $R^2 = 0.89$ for WS_BrC and $R^2 = 0.80$ for MeS_BrC.
- In summer substantial heterogeneity between the origin and fate of chromophores ($R^2 = 0.14$).

AAE FOR WATER AND METHANOL SOLUBLE EXTRACTS

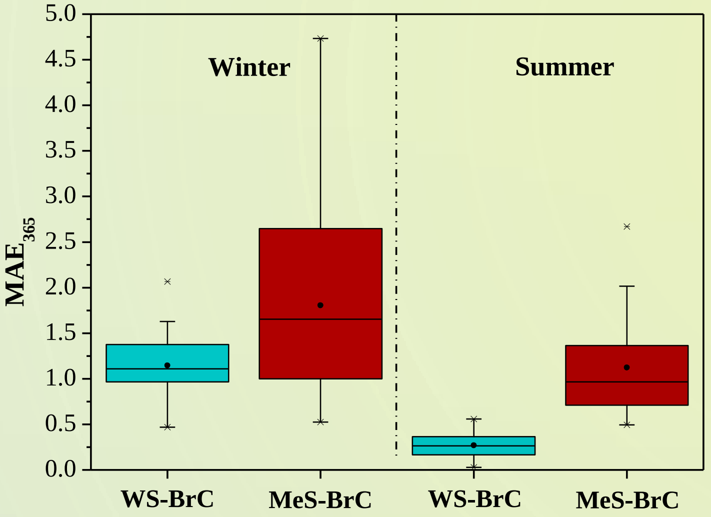




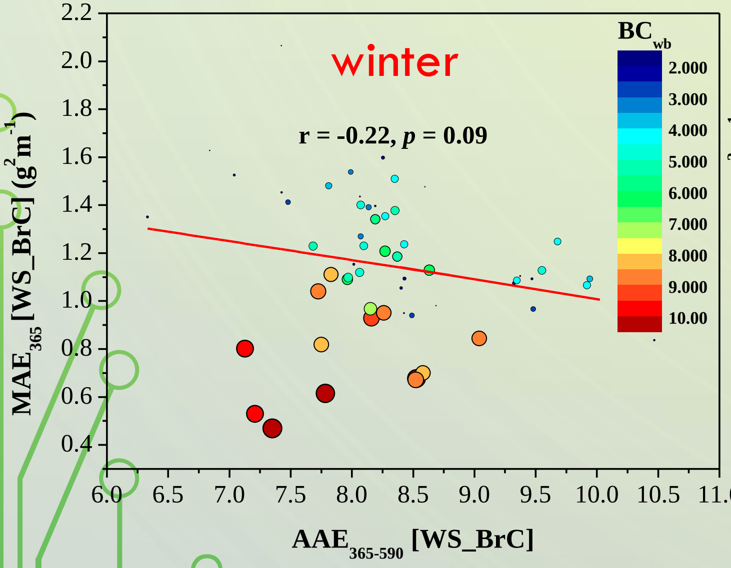


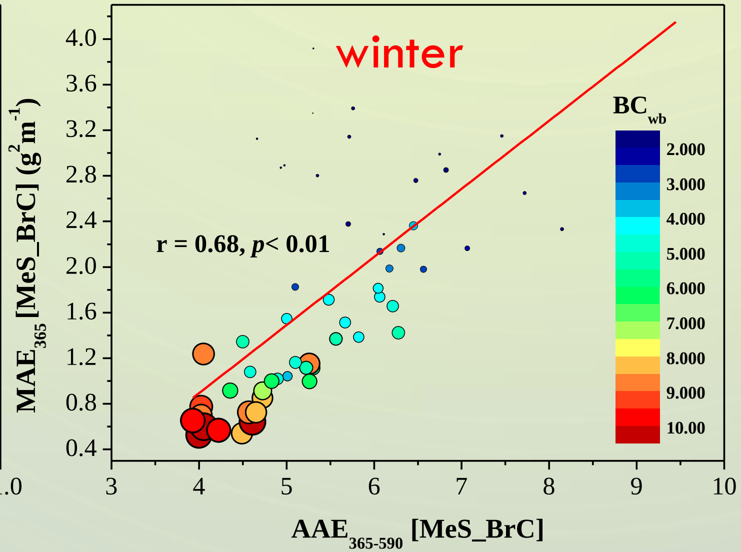
- Winter AAE_{WS_BrC} : (6.3 to 10.5; mean of 8.3±0.8). Characteristic of BB conditions.
- Summer mean AAE_{WS_BrC}: 4.3±1.9. No BB-sources and probably photo-bleaching of secondary WSOC.
- Winter AAE_{MeS_BrC} : 5.5±1.1. Lower compared to AAE_{WS_BrC},. It indicates larger absorbance by high-molecular weight chromophores from BB that absorb in the visible. These can be extracted more efficiently by methanol.
- Summer AAE_{MeS_BrC}: 6.3 ± 1.9. Slightly higher than that in winter. Larger variation shows more heterogeneity in sources.
- AAE_{MeS_BrC} were negatively related with MeS_BrC absorption, while lowest AAE are for highest BC_{wb}. This indicates that under high BB conditions, methanol extracts efficiently BrC chromophores at mid-visible spectrum.

MASS ABSORPTION EFFICIENCY (MAE)

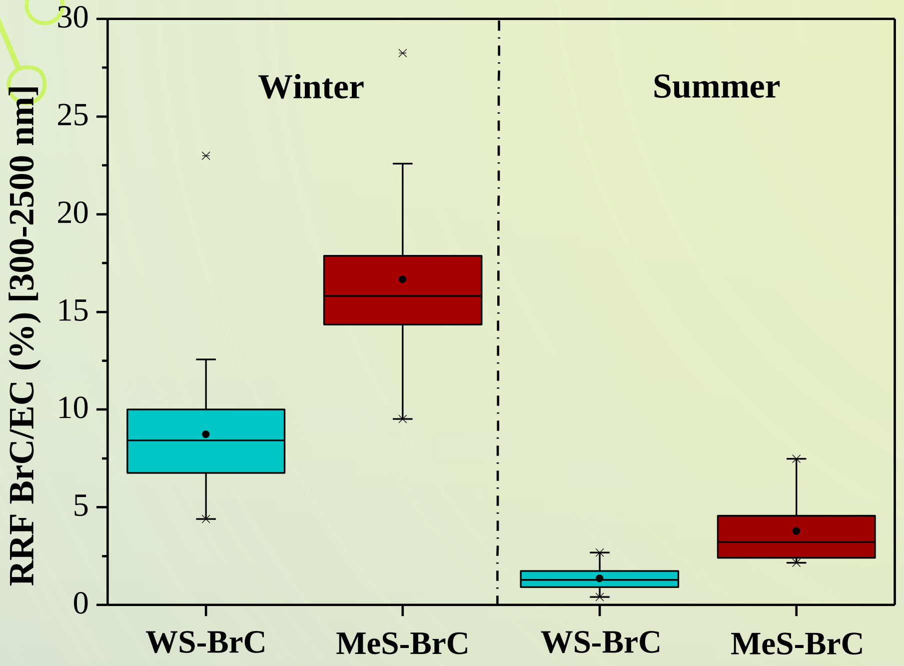


- Winter MAE_{WS_BrC} : 1.15 ± 0.30 $m^2\ g^{-1}$. In summer: 0.27 ± 0.14 $m^2\ g^{-1}$ due to the photo-oxidation of BrC.
- Significantly higher mean MAE_{MeS_BrC} values in winter (1.81 ± 0.98 $m^2\ g^{-1}$) and summer (1.12 ± 0.57 $m^2\ g^{-1}$), for MeS_BrC. It indicates pronounced differences in the absorptivity between WSOC and WIOC, possibly driven by the inclusion of high-MW aromatics, found in both BB and fossil fuel combustion.
- MAE_{WS_BrC} vs AAE_{WS_BrC} (r = -0.22). This suggests that samples with higher absorbing efficiency at 365 nm generally exhibit a smoother decrease of absorption with wavelength.
- For methanol extracts, a positive correlation (R^2 = 0.46) was observed in winter. For peak BB conditions (BC_{wb} > 8 µg m^{-3}), lowest AAE_{MeS_BrC} and MAE_{MeS_BrC} values were observed.



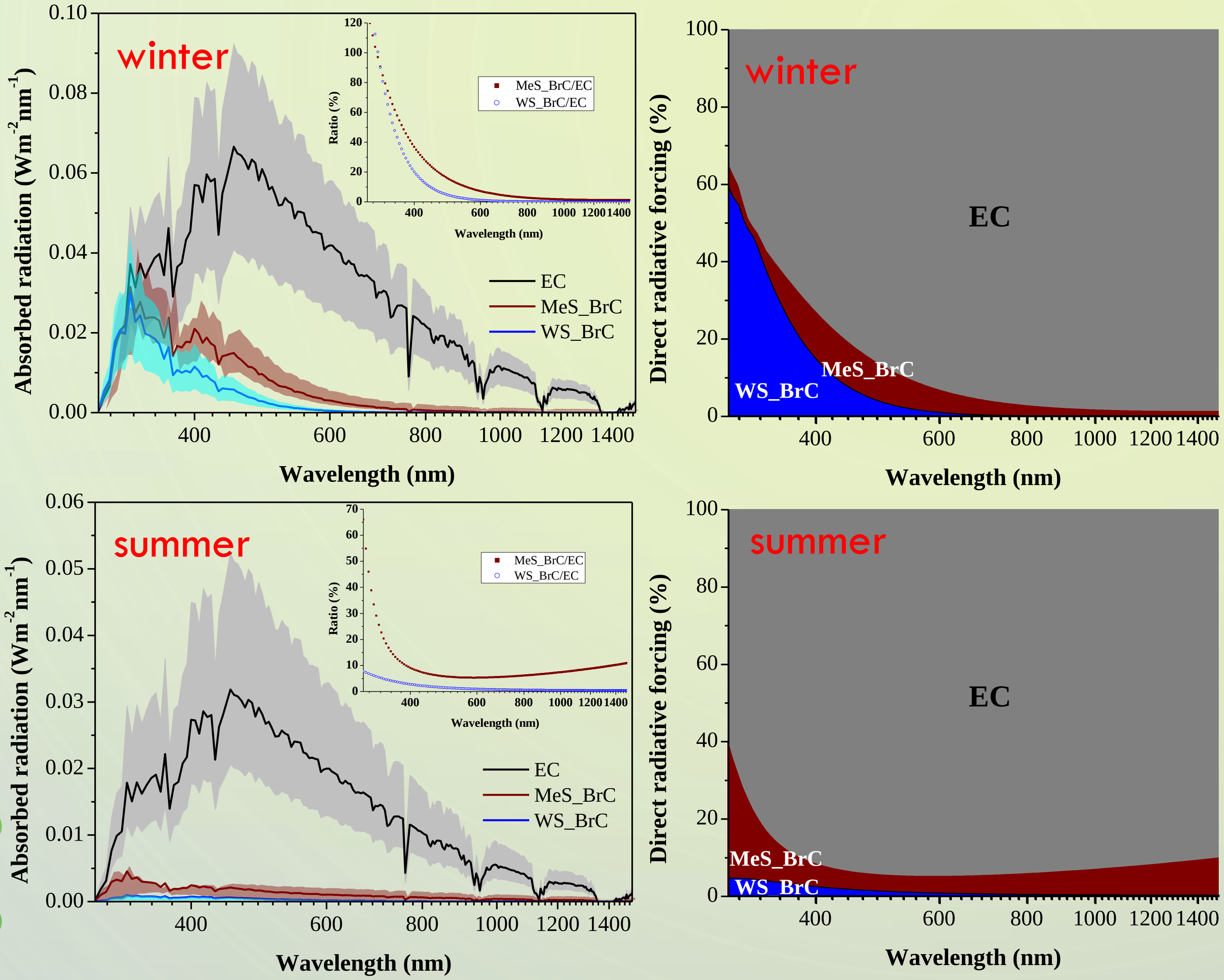


RADIATIVE FORCING OF WATER- AND METHANOL-SOLUBLE BRC



- RRF_{WS_BrC} of 8.7 ± 3.0% (range: 4.4%-14.9%) in winter (300–2500 nm). Higher RRF for the MeS_BrC (16.7 ± 3.7%).
- In summer, the photo-dissociation and volatilization of BrC chromophores drastically reduced the mean RRF_{WS_BrC} (1.4%) and RRF_{MeS_BrC} (3.8%) in 300–2500 nm.
- The winter/summer integrated ratios of absorbed solar radiation (300–2500 nm) were 2.1, 4.3 and 12.8 for EC, MeS_BrC and WS_BrC, respectively, highlighting the large impact of WS_BrC absorption under RWB conditions, especially in the UV.

RADIATIVE FORCING OF WATER- AND METHANOL-SOLUBLE BRC



- The solar radiation absorbed by EC, WS_BrC and MeS_BrC shows a large increase in RRF_{WS_BrC} and RRF_{MeS_BrC} at UV and near-visible wavelengths.
- At 365 nm, RRF_{WS_BrC} was estimated 39.2%, and 54.6% for RRF_{MeS_BrC}.
- The mean winter RRF_{WS_BrC} at short wavelengths (300–400 nm) was 48.5%, rising to 60.2% for RRF_{MeS_BrC}.
- In summer, mean RRF_{WS_BrC} (4.1%) and RRF_{MeS_BrC} (16.6%) in 300–400 nm.

The large BrC contributions in the UV, apart from the RF effect, may even modulate photochemistry.

THANK YOU

Ioannina, Greece