

Le carbone-suie dans l'atmosphère Européenne: identification, transfert, dépôts et impacts

Second year report

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General motivation

Black carbon (BC) is particular matter emitted by incomplete combustion of fossil fuels and biomass. It is considered the second contributor, after CO₂, to climate warming. This is due to his absorbing properties of light; in fact is the strongest atmospheric light absorber in the visible spectrum. Despite the total impact on the planetary radiative budget is significant a substantial uncertainty is still present on particular mechanism in which BC is involved: seasonal variability of effective atmospheric forcing, how BC acts as cloud condensation nuclei and BC radiation impact on criosphere. Our work was born with the idea to minimize the uncertainties related to some important step of the BC cycle as transformation in the atmosphere, cloud interactions and transport to remote polar areas.

Technical principles

For our project we adopted a freshly developed instrument for selective measurement of refractory BC (rBC): the single particle soot photometer (SP2) which exploits a laser induced techniques. Under an extreme source of energy, rBC is brought to his incandescence temperature with consequent light emission, which is proportional to the rBC mass. This approach is extremely sensitive and is not influenced by presence of others chemical species. Beside the sensitivity and selectivity, the instrument allows extracting the size distribution of rBC and non-rBC particles, and investigating the mixing state of rBC.

Black carbon transformation in the atmosphere

We investigated optical properties of BC over Europe, focusing on spatial and seasonal variability. Absorption coefficient (b_{abs}) and BC mass concentrations data were collected from 9 EUSAAR supersites, spacing from the Mediterranean region, to the Scandinavia, including the central Europe. All the selected sites are part of the ACTRIS network and representative of rural background, excluding the French station of PDD, influenced by the planetary boundary layer dynamic. The work was focused on a specific optical property called mass absorption cross section (MAC), which is defined as the light absorption for unit of BC mass. MAC is calculated as following:

$$MAC^{\lambda} [m^2/g] = \frac{b_{abs}^{\lambda} [Mm^{-1}]}{BC [\mu g/m^3]}$$

The MAC is of crucial importance since is used in modeling to estimate radiative forcing from modelled BC burdens. A second application is related to filter based instruments that measure absorption coefficient from which the equivalent BC (eBC) concentration is calculated using the MAC (Figure 1). For such applications MAC had been always considered as constant, without accounting seasonal and spatial variability.

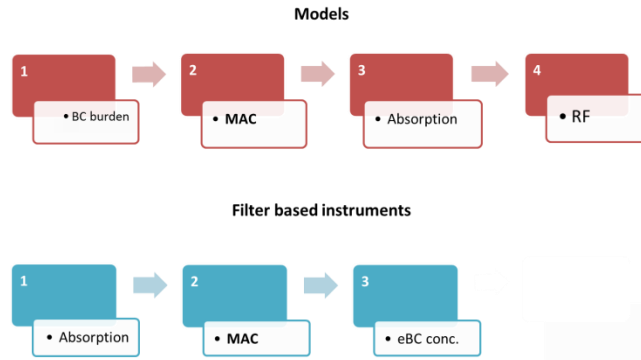


Figure 1. Application of mass absorption coefficient for simulation studies and for field measurements.

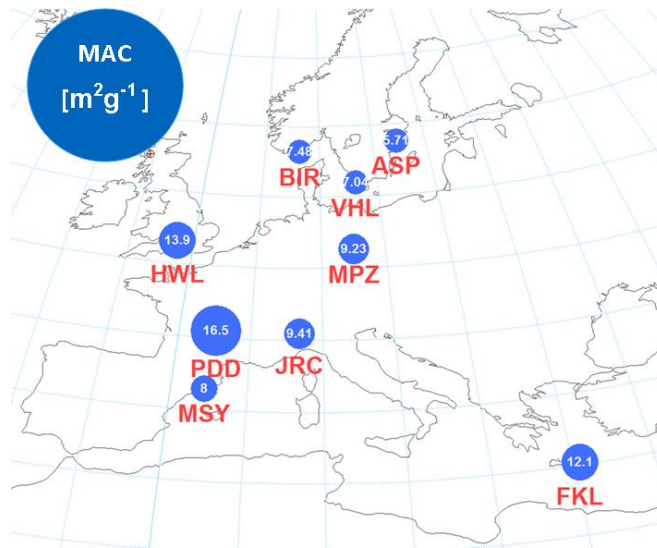


Figure 2 Spatial variability of MAC over Europe. Values given as geometric mean.

BC concentration was measured using a thermo optical technique, (the correct nomenclature would impose to call it elemental carbon). Absorption coefficient was measured with filter based instruments (MAAP, Aethalometer and PSAP). Correction and harmonization procedures were applied to compensate instrumental artifacts. Observed MAC values ranged between 5.7 to 16.5 m²g⁻¹ (Figure 2). Excluding the high altitude PDD site, not representative of rural background, the range became thinner 5.7-13.9 m²g⁻¹. We identified a MAC for Central Europe (10.8 m²g⁻¹), Mediterranean (10.8 m²g⁻¹) and Scandinavia (6.7

m^2g^{-1}). The MAC spatial homogeneity suggested that European BC undergoes similar aging process, which may involve seasonal cycles. All Mediterranean and central European sites experienced a common MAC seasonal cycle, peaking in summer (Figure 3a). On the other side the Scandinavian sites were characterized by constant MAC, without any particular periodicity (Figure 3b). This different seasonality is probably the key to understand the difference in the absolute MAC values between northern and southern Europe.

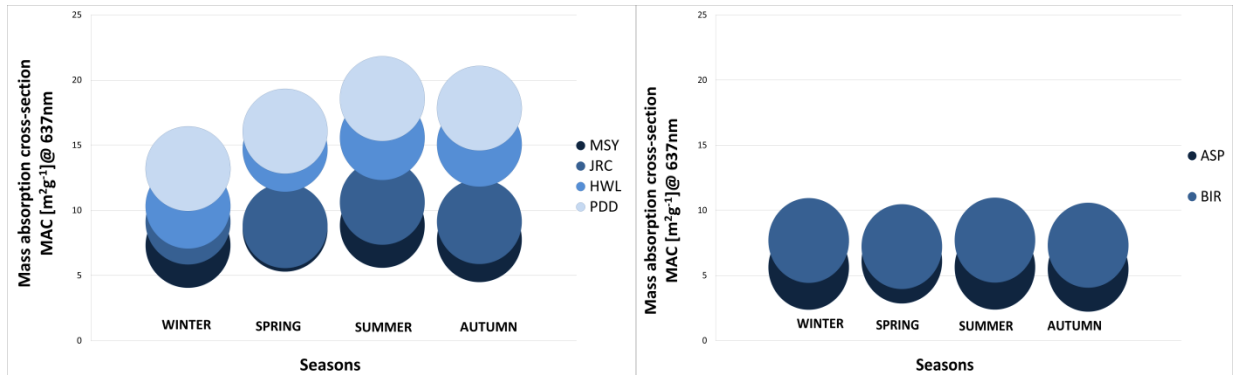


Figure 3. Seasonal variability of the mass absorption cross-section in Europe and Mediterranean (a) and in Scandinavia (b). Vavihill was not included due to data lack.

For five over the nine sites was possible to examine the aerosol composition, accounting especially for non-absorbing aerosols such as sulfate, organic matter and nitrate (SON). Within some days, these species coagulate over BC cores to form a non-absorbing layer that enhances absorption. A discussion about this process is still going on and good understanding is still missing. We investigate how the MAC may change in function of SON relative concentration respect to BC. Figure 4 shows the relationship between MAC and aerosol composition. Excluding Birkenes, a positive proportionality between MAC and mixing was found. The MAC increased with the SON:EC mass ratio, underling that BC absorption is dependent also by non-absorbing material. The slope of the curves go from 0.4 to 0.52, it means that increasing the SON:EC ratio by 10 times, MAC experiences an increase of $4.8 \text{ m}^2\text{g}^{-1}$. This result confirms that a mixing with non-absorbing aerosol induces a growth of BC absorption.

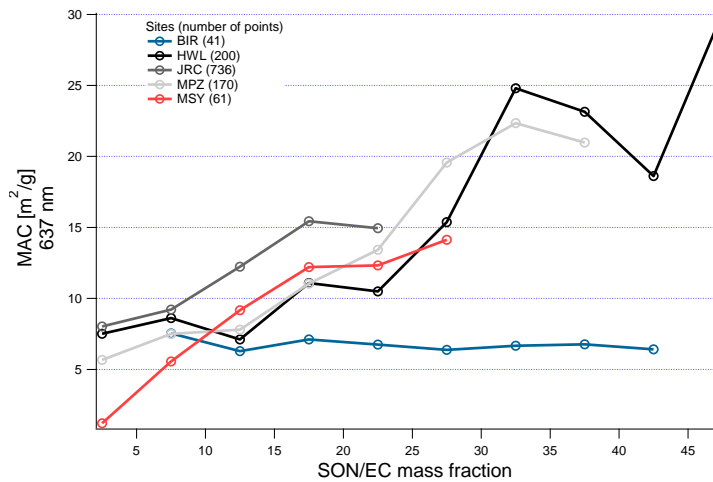


Figure 4. MAC and aerosol composition. Sulfate, organic matter and nitrate defined as SON.

Chasing the black carbon in the arctic

The campaign took place at Ny-Alesund, Spitzbergen, Svalbard Norway and was part of the CLIMSLIP project, which aimed to investigate the role of short live pollutants in the arctic. The campaign lasted from March to April 2012. In this period high aerosol concentration, due to long range transport and biomass burning events in ester Europe, are usually observed (Figure 5). Atmospheric measurements were deployed at the Zeppelin station (514m asl) and Corbel station (5m asl). At Zeppelin a SP2 was installed, permanent instrumentations were composed by a 7-wavelengths Aethalometer (Athens University), a 3-wavelengths nephelometer (Stockholm University) and a continuous soot monitoring system (COSMOS) (Tokyo University). A second 7-wavelengths Aethalometer (LGGE) was settled at the seaside Corbel station. Optical study of arctic aerosol was conducted.

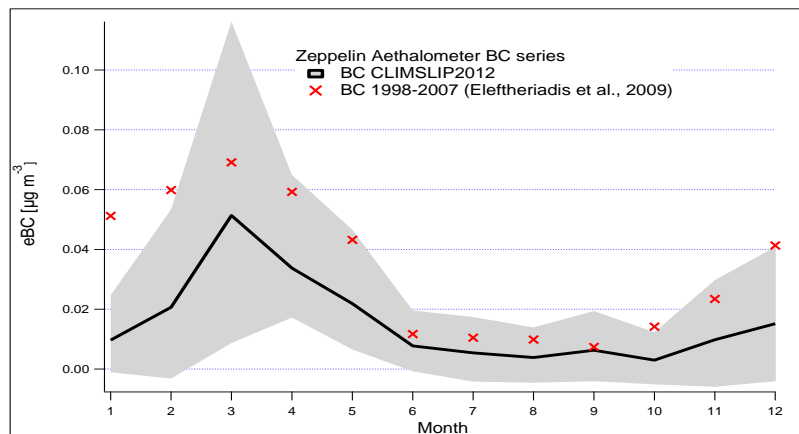


Figure 5. Equivalent BC mass concentration seasonality for 2012. Data from DEMOCRITOS Aethalometer installed permanently at Zeppelin station. Collaud-Coen correction and MAC of 6.7 m²g⁻¹. were used.

The mass absorption cross section (MAC) was determined using absorption coefficient from Aethalometer and rBC concentration from SP2. Observed MAC was $6.7 \text{ m}^2\text{g}^{-1}$ and $10 \text{ m}^2\text{g}^{-1}$ at 880 and 550nm respectively. Elefteriadis et al. (2009) used a MAC of $16 \text{ m}^2\text{g}^{-1}$. An overestimated MAC will result in an underestimation of eBC calculation from filter based instruments and to an overestimation of RF in model simulations. High single scattering albedo, (>0.8), indicated that non-absorbing aerosols were predominant. Zeppelin station is considered to be representative of free troposphere, without any influences from ground local emission, including sea spray. Due to its large size, sea salt has a low Angstrom exponent (α). At Corbel site α of 0.84 ± 0.29 was observed, while at Zeppelin higher value (1.23 ± 0.48) was found. Thus, no sea salt interfered with measurements, suggesting that for the considered period, the air masses are mainly coming from long range transport with negligible local origin. A comparison of BC measuring techniques was performed at Zeppelin and included an Aethalometer, a COSMOS and a SP2. eBC concentrations from COSMOS and corrected Aethalometer were agreeing well with the SP2 (correlation coefficient >0.81). An overestimation of about 10% for both filter based instruments was found compared to SP2. Our results confirmed the reliability of filter based technique, and related correction procedure at remote site with low black carbon concentration. Averaged rBC was found to be 33 ng/m^3 , with a mean diameter of 122 nm. rBC represented only the 6% of all detected particles, of this 6%, the 97% was coated. With a qualitative approach was found that the 60% of coated particles had a thick coating ($>20\text{nm}$) (Figure 6). rBC Population was dominated by cores with a diameter between 100 and 150nm, with a coating thickness between 20 and 200nm. Considering a 150nm core with its maximum coating (200nm) the absorption enhancement is in the 1.5-1.85 range (Bond et al., 2006). That would induce an underestimation of radiative forcing with models that do not include mixing state effects of non-absorbing material over rBC.

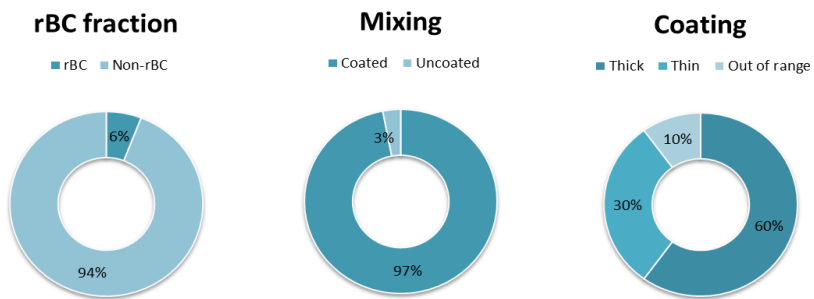


Figure 6. rBC population study conducted with the SP2. internal mixing is assumed to take the core shell geometry.

Snow samples were collected on two different glaciers (KongSvagen and Austrelovenbreen) at different altitude and at Corbel station. Sea salt was the mayor component in mass (56-86%), while rBC represented less than 1% of the deposited mass. Lack of rBC-ions correlations indicated the absence of specific local rBC sources. The rBC averaged mass concentration was $0.57 \mu\text{g/l}$ and $1.2 \mu\text{g/l}$ at Kongsvagen and Austrelovenbreen glaciers. Compared to literature these two values are 4 and 2 times smaller, this it may be due to year to year variability and to the different technique. Simulations are needed to infer if such concentrations would have any radiative impact.

BC and cloud interaction

This section is under development. Data are coming from two CLACE campaigns from 2013 and 2014 kept at the high elevation site of Junfaujoch (Switzerland). The station is representative of free troposphere. Our investigation is mainly based on two SP2 instruments linked to two different inlet systems: total inlet (TI) and ice selective inlet (ISI). The ISI is design to sample only the ice crystals, rBC found at the ISI is thus acting as ice nuclei (rBC_{IN}). The data presented here are preliminary and related to some cloud events of the CLACE camping of 2013.

Here are reported the results concerning a stable cloud (cloud 19) that last from 19th to the 20th of February 2013. The total rBC concentration was $7\text{ng}/\text{m}^3$, while rBC_{IN} levels were lower ($<1\text{ng}/\text{m}^3$ and $<1\text{\#}/\text{cm}^3$). The rBC at the total inlet is the minor component (27%), while non-refractory material accounted for 73%. The non-refractory particles were scavenged more efficiently, dominating the aerosol population accounting for the 98% (Figure 7). During this specific cloud event, rBC does not act as ice nuclei, but further analysis are needed to confirm the hypothesis of rBC as non IN. It seems that the cloud-rBC interaction is also size dependent, rBC appeared to be more easily activated at high diameter, during ISI sampling the amount of large particles ($>150\text{nm}$) increased from 19% to 43% (Figure 8).

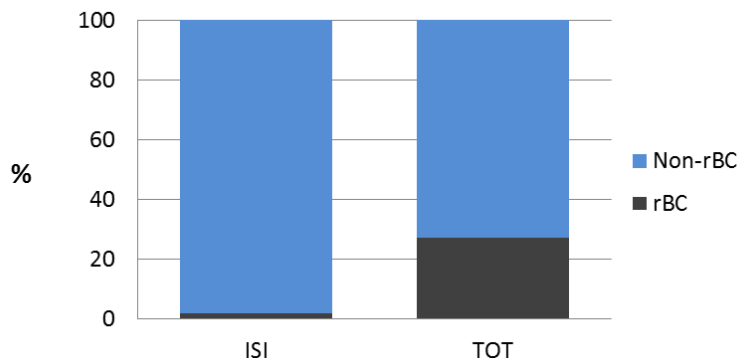


Figure 7 Fraction of rBC and non-rBC particles during the cloud event number 19.

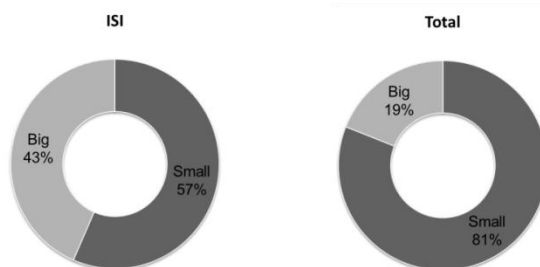


Figure 8 Size distribution for activated (ISI) and ,total (TOT) rBC. 150nm was chosen as threshold diameter.

Preliminary conclusion

rBC was found to undergo a deep modification of its optical properties during its lifetime in Europe. This is confirmed by strong seasonal variability of MAC. Despite seasonal cycle the absolute MAC values of each background station are similar, oscillating in a narrow range ($6\text{-}13\text{ m}^2\text{g}^{-1}$). This may suggest that in Europe and Mediterranean the aging processes are similar, other mechanisms may take place in Scandinavia where MAC was lower and no seasonal cycle was observed. A positive correlation between MAC and non-absorbing aerosol fraction was found, the reasons of this correlation were beyond the goals of this work. But this observation suggested that absorption enhancement due to mixing state is a probable event with strong repercussion on RF estimation.

MAC observed at Svalbard ($8\text{ m}^2\text{g}^{-1}$ at 637nm) was in the lower range of previous study. At Zeppelin the rBC was the minor component of aerosol (6%), this is confirmed by high single scattering albedo (>0.9). Despite low concentration around 30 ng/m^3 , the radiative atmospheric impact of rBC may have a strong role due to its thick coating ($20\text{-}150\text{nm}$) that may enhance the absorption by a factor of $1.5\text{-}1.85$ (Mie calculation). This effect is of great importance if it is considered that almost the totality of rBC was coated. The impact of rBC in snow needs more investigation and model simulations, any further hypothesis or conclusions will be weak.

From preliminary analysis it seems that rBC does not act as ice nuclei. At the high altitude station of JFJ less than the 1% of rBC was found into the ice crystals. Large rBC particles are more easily activated. At the present state of art (two clouds over twenty were analyzed) we can state that rBC is not an IN.