

Interactive comment on “Sources and light absorption of water-soluble brown carbon aerosols in the outflow from northern China” by E. N. Kirillova et al.

Anonymous Referee #3

Received and published: 18 September 2013

The manuscript present a novel and interesting assessment of water-soluble brown carbon sources and absorption using a combination of isotopic techniques that have never been used for this purpose. The significance of this work, the better understanding of light-absorption of brown carbon and its contribution to aerosol light absorption is beyond any doubt. However, there is a fundamental aspect that needs to be thoroughly discussed before releasing this publication.

My major concern is related to the off-line spectrophotometric measurements of water-soluble brown carbon absorption. While the technique is a standard method admittedly for dilute solutions (and this was checked by the authors in a series of dilu-

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tion experiments), its application becomes severely limited or even impossible towards very concentrated solutions. I wonder what the authors have in their mind about how water-soluble brown carbon absorbs light in ambient aerosol particles, haze particles or cloud droplets. Can these compounds be solubilized all under ambient conditions in an aerosol or haze particle? The compounds likely responsible for light-absorption are not simple organic molecules but complex macromolecular similar to humic substances. Humic substances are well known to change conformation and consequently all of their properties when the conditions in a solution changes: their colour, solubility, molecular weight, etc. may all change. They are even affected by the presence of other electrolytes (e.g. salting out). It may mean that when we measure optical absorption in dilute solutions, and use the very same results for the calculation of their atmospheric absorption with respect to BC absorption, we make a large error that would render all of our efforts meaningless. Lambert-Beer's law explicitly sets the conditions of dilute solution even for the simplest inorganic dyes. In concentrated solutions there are effects such as self-absorption, shadowing or scattering that causes that the equation can no longer be used. (To say nothing of the effects detailed above for complex macromolecules that are also concentration dependent.)

In contrast, atmospheric BC absorption is a well-established phenomenon that is supported by numerous field, laboratory and theoretical studies, yet loaded with substantial uncertainties especially in global radiative transfer modeling. As regards atmospheric absorption of water-soluble brown carbon, dry aerosol particles contain about 50 (m/m) % water, haze particles about 90 %, and dilute solutions similar to those in the laboratory experiments only exist in cloud droplets. Thus, how can we extrapolate the atmospheric light-absorption of water-soluble brown carbon under so much different conditions? How can we draw the definitive conclusion that BrC contributes by 13-49 % of BC absorption? In my opinion the overly simplistic approach taken by the authors is not scientifically sound.

Following the logic above it is also possible that the harsh treatment (acid fumigation)

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of the filter before the isotope analysis changes the physical and chemical state of the complex molecules, including their solubilities. These issues must be resolved before publication of the manuscript in ACP.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 19625, 2013.

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