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Atmospheric Measurement Techniques Discussions

Interactive comment on "Determination of water-insoluble light absorbing matter in rainwater using polycarbonate membrane filters and photometric detection" *by* J. E. Engström and C. Leck

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Dear Editor: We thank the reviewers for thoughtful concerns and suggestions for this manuscript and for their help in improving the English writing in the manuscript (which is always a hurdle for a non-native). All comments have been addressed in this submitted draft. We will address each reviewer comment in order.

Review 1

The method described in the manuscript is not particularly new though indeed there were only very few such applications in atmospheric science. It is relatively straight-

forward to concentrate insoluble particles on a substrate than measure absorption by photometry.

Which other methods does the reviewer have in mind? Prior to the method described in this manuscript, to our knowledge, there is only Ogren's (1983) method developed for rainwater determinations of light absorbing matter in precipitation. We agree that it is relatively straightforward to concentrate insoluble particles, being airborne, on a substrate than measure absorption by photometry. However, the challenge with rainwater determinations is possible losses of soot, given its chemical properties, during collection and filtration both necessary steps before the sample could be concentrated on the substrate. These challenges are also already identified by Rev. 1 (see below comment): "Soot analysis in precipitation is very difficult if not impossible due to the fact that soot particles likely deposit on any surface they are allowed to contact with for prolonged time - which is often the case in wet only samplers." Here the reviewer contradicts his/her own comments, which need clarification.

In terms of analytical methodology, the authors carefully evaluate the applicability of the method using both standard soot solutions and ambient samples. The basic question, however, is how effectively colloidal particles can be filtered out from a solution. Nucleation mode pure soot particles or those which had attached to water soluble particles (which dissolve in precipitation) are unlikely to be captured by the filter substrate or only with low efficiency. Soot attached to larger insoluble particles, on the other hand, more likely ends up on the filter.

Nucleation mode soot particles are not likely to found neither in the ambient nor in the synthetic samples. "Fresh" particles quickly aggregate together and form larger structures. By inspection in optical microscope we have verified that the soot particles (too small to be seen individually) are seen as an evenly distributed shading on the filter surface, with sporadic appearance of larger structures in the size range around 20 μm. See section 2.3.

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Thus the amount of soot detected depends on the state of mixing of soot particles in the precipitation which could be highly uncertain.

Here we are uncertain if the reviewer means the amount of soot captured on the substrate or the optical properties of soot at the absorption determination? In a rainwater sample, all inorganic material is dissolved. So what is captured on the substrate is beside soot possible non-water soluble organic material, externally or internally mixed. As usually organic matter do absorb in shorter wave lengths than soot, we regard the possibility for interferences to be minor.

Another issue that should be discussed how the authors managed to disperse the synthetic soot in MilliQ water: were there flocks on the surface, or deposition on the walls of the vial, etc.?

Up to a few days after dissolution (ultrasonic bath) of the synthetic soot in MilliQ water no flakes or big agglomerates were visible by the naked eye in the solution or on the walls of the container. See section 2.3.

How well synthetic soot represents absorption properties of the atmospherically aged and possibly more hydrophilic soot particles in rainwater?

We agree that this comment is crucial to the applicability of the present method to ambient atmospheric conditions. This was why we went through the same testing procedures using both standard soot solutions and ambient rainwater samples. The statistical significance of the result will be clarified and discussed further in the revised manuscript. See section 5.

Soot analysis in precipitation is very difficult if not impossible due to the fact that soot particles likely deposit on any surface they are allowed to contact with for prolonged time - which is often the case in wet only samplers.

As already pointed out above we are aware of that soot particles easily adsorb to surfaces which is exactly why we have statistically quantified the losses for each part

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of set up including both the bottle and the funnel in the wet only sampler. These test concluded the necessity to brush the funnel and bottle after collection for further soot determine.

If we combine all uncertainties that the authors considered, that is multiply sample collection and storage efficiency (cca. 0.7) with filtration efficiency (0.85), we end up with an overall efficiency around 50 % only.

Here the reviewer has unfortunately used incorrect numbers. The gain of soot during storage and filtration is 0.78 and the filtration efficiency 0.85, which together give the efficiency of 65%. The total precision of the method is estimated to 10%.

If we add that soot concentrations are expressed in mass of synthetic soot (whose absorption efficiency was likely different from that of aged soot in precipitation), the results of soot analysis will be highly uncertain.

As stated/established above.

Furthermore, the suggestion by the authors that one should brush the funnel and measure sample loss for each sample is highly impractical for any routine application.

Yes, we agree that this makes the presented method extra labor intense, but it is needed so quantitative results could be gained. The brushing protocol has already been tested at the Maldives Climate Observatory Hanimaadhoo during a 3 month period and found running smoothly.

Of course, it is likely that the signal will be somehow proportional to the degree of "pollution" in rainwater, but would add little if any to our understanding of wet scavenging processes of atmospheric soot.

This none profound statement needs further clarification.

Review 2

Summary. This paper describes a method for determining the amount of absorbing

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material in rainwater. The procedure described is careful and biases are quantified. Authors claim that this method has higher efficiency than that of previous work (Ogren).

The filtration efficiency can objectively be measured as we have presented for the Nuclepore filters to be 82% +- 11% or 88% +- 0.5% depending on concentration. Whether the method as whole is more efficient is more subjective, but yes, we regard this method to be both time and labor saving compared to Ogren's method.

I have some suggestions for clarifying the paper and further exploring uncertainties. I also have some small corrections. COMMENTS: General: The procedure assumes that soot mass is proportional to absorption.

Yes!

That is, the soot in rainwater must have the same absorption as the Printex soot. How reasonable is that assumption? This is critical and should be discussed.

We agree (see similar comment by Rev. 1): "that this comment is crucial to the applicability of the present method to ambient atmospheric conditions". This was why we went through the same testing procedures using both standard soot solutions and ambient rainwater samples. The statistical significance of the result will be clarified and discussed further in the revised manuscript. See section 5.

Synthetic samples were used for most of the characterization. Later in the paper, authors discuss that the synthetic samples could have been more hydrophobic than the rainwater samples. Authors should comment on the validity of applying the findings to atmospheric samples.

A comment for clarification of the result have been added in the revised manuscript. See section 2.3 and 2.4.

Equation 2: There is an offset in optical depth: OD=0.0228 will read as zero. Why is that? This suggests that detection limit is about 2 ug/cm2 (based on a rough estimate of absorption cross-section). Other factors affecting the detection limit should be

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discussed.

We don't understand the reviewer's calculation, but according to our own calculations a detection limit of 0.025 OD gives a concentration on the filter of 0.1 μg/cm2. Possible factors affecting the detection limit could be the sensitivity of the soot photometer, losses at collection and filtration as being discussed in the manuscript.

General: Some literature shows that optical depth is not exactly linear in loading. (e.g. Weingartner, 2003 although this study examined a different kind of filter.) Could this be a problem here and if not, why not?

The main reason why the OD is not linear is that at high concentrations multiple scattering and shadowing occur on the substrate surface. However, as shown for the range of concentrations tested in the present study, the determination of OD is linear. To be close to linear in loading is important for the quality of the soot measurements and could be gained by adjusting the total volume of sample for filtration.

Section 2.3: The loading on the filter, not the rain concentration is important for this calibration. This should be clarified.

In this case we discussed a representative range of concentration for ambient samples, given in units of mass per volume concentration. If we on the other hand are discussing a suitable amount of soot loading in the filter, we agree that OD or soot mass per filter-spot area is a better measure.

Page 251: Loss in ambient samples is lower than loss in laboratory samples. Is this statistically significant? I miss the statistical test results.

If we as an example study the combined loss of soot to the funnel and bottle: synthetic soot loss is 35% -+8%, ambient soot loss at MCOH is 16% +- 2% and ambient soot loss at NCO is 21% +-3%. So the difference is statistically significant.

Figure 1 is not very useful. It needs labels. Figs 2 and 3 are not very instructive either. I do not feel that they contribute much to the paper discussion.

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We would like to keep these figures in the manuscript to make it possible for others to copy the construction. The missing labels of Figure 1 will be added.

WRITING: Page 238 Line 10 "have" should be "has" Page 238 Line 20 Place "the" before "primary" Page 239 Line 1 "act as a cloud condensation nucleus" should be "act as cloud condensation nuclei"

Page 240 Line 10 add "the" before "tunnel" Page 240 Line 11 "weighting" should be "weighing" Page 242 Line 9 I think NOC should be NCO, correct? Page 242 Line 18 "passing" should be "passed" Page 245 Line 18 "were" should be "was" Page 245 Line 20 "were" should be "was" Page 246 Line 5 "mentions" should be "mentioned" Page 245 Line 7 "where" should be "were" Page 248 Line 21 "ranch" should be "range" Page 250 Line 23 "aimes" should be "aims" Page 251 Line 2 "necessary" misspelled Page 251 Line 6 "funnel" misspelled Page 251 Line 12 "have" should be "has" REFERENCES Weingartner, E., H. Saathof, M. Schnaiter, N. Streit, B. Bitnar, and U. Baltensperger (2003), Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers, J. Aerosol Sci, 34, 1445-1463.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 237, 2009.

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