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**Determination of
water-insoluble light
absorbing matter**

J. E. Engström and
C. Leck

Determination of water-insoluble light absorbing matter in rainwater using polycarbonate membrane filters and photometric detection

J. E. Engström and C. Leck

Department of Meteorology, Arrhenius Laboratory, Stockholm Univ., 10691 Stockholm, Sweden

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Correspondence to: J. E. Engström (erik.engstrom@misu.su.se)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

A method for determination of water-insoluble light absorbing matter in rainwater has been developed. After collection the rainwater samples were filtered using polycarbonate membrane filter in the laboratory. After drying the filter in filtered air, the amount of water-insoluble light absorbing matter (soot) on the filters was determined with photometry at a wavelength of 555 nm. The precision for the method was better than 10% calculated as relative standard deviation. The overall loss of soot due to adsorption during collection and filtration was $22\pm 2\%$. The detection limit was estimated to 0.025 in optical density, or 2 ng/ml expressed as a concentration assuming a filtration volume of 30 ml. Analysis of environmental samples have been successfully performed with the described method at the Maldives Climate Observatory Hanimaadhoo and Nepal Climate Observatory. At Maldives the average soot concentration in rain was $0.048 \mu\text{g/ml}$ and at the Nepal observatory $0.086 \mu\text{g/ml}$.

1 Introduction

During the last century the increasing emissions of gases and aerosol particles, due to human activities, have changed the composition of the atmosphere (IPCC, 2007). The increase of aerosol particle concentration is visible to the human eye as haze layers (atmospheric brown clouds) that can be seen even from space over populated areas around the world. This haze with sometimes a brownish appearance consists mainly of inorganic salts, organic compounds, soot and crustal material. Primary effect of the aerosols is impact on the atmospheric radiation balance (Ramanathan et al., 2001, 2005). Secondary effects are increased health problems and effects on the hydrological cycle that can influence the availability and quality of fresh water (Ramanathan et al., 2001, 2005; WHO, 2006). In order to predict the effects of these brown clouds knowledge is needed about their sources and sinks. One important aspect is to understand the wet scavenging process of soot.

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

The ability of soot particles to act as a cloud condensation nucleus (CCN) depends on the size and the chemical nature of the surface of the particle. The hydrophobic property of freshly emitted soot suggests that it is not likely to act as a CCN. During its residence time in the atmosphere soot can undergo coagulation and condensation (mass transfer of a gas phase compounds to the aerosol particle), and thereby alter the chemical nature of the surface of soot from hydrophobic to more hydrophilic. Given a more hydrophilic nature soot can be activated to form cloud droplets. Repeated cycling in and out of cloud droplets can promote a build up of water-soluble material on the soot particles, through liquid phase reactions (Ogren and Charlson, 1983).

Measurement of soot in air has been performed for some decades and a handful of methods are available as described by Bond et al. (1999) and more recent papers (Kopp et al., 1999; Petzold et al., 2005). However measurements of soot in rainwater are rare. Ogren et al. (1983) demonstrated a method that has been used in a few studies (Ogren et al., 1984; Ogren and Charlson, 1984). Ogren et al. used quartz fiber filters (2500 QAST, Pallflex Corp., Putnam, MA) for filtration of the rain samples. The organic carbon components of the collected particles on the filter were then oxidized with hydrogen peroxide in a basic solution, followed by combustion. Ogren determined the collection efficiency of the quartz fiber filters to 50 to 80% for rain samples.

In an attempt to exclude time consuming chemical treatments and the risk for sample losses during repeated treatments a new method for collection and determination of water-insoluble light absorbing matter has been developed. It uses the well established light absorption measurements on particulate samples accumulated on Nuclepore polycarbonate membrane (PCMB) filters (Heintzenberg, 1988) which allow subsequent chemical analyses, instead of using quartz fiber filters as in Ogrens method.

The new method was carried out in three steps. After collection of rainwater with wet-only collectors, the samples were filtered in the laboratory with a filtration unit consisting of a cylinder and a filter holder. After drying the filter in a box with filtered air, the soot amount (water-insoluble light absorbing matter at a wavelength of 555 nm) on the PCMB filters was determined with photometry.

This study was performed as a contribution to the Atmospheric Brown Cloud (ABC) project, which aims at increasing the knowledge of the effects of aerosols on climate, environment, health and economy.

2 Experimental section

2.1 Collection of rainwater

To minimize contamination from dry deposition, wet-only collectors were used (designed and built at Dept. of Meteorology, Stockholm University). The lid was controlled with a rain sensor and opened only during rain events. Inside the wet-only collector a borosilicate glass funnel was placed. The funnel was connected to a borosilicate glass bottle with no possibility for rain to enter from the side of funnel. The total amount of rain sample collected was determined by weighting the bottle prior and after exposure. To avoid biological growth in the rain samples, filtration was performed within 24 hours after onset of each rain event.

2.2 Filtration procedure

Figure 1 shows a schematic drawing of the filtration unit. After collection the rain sample was poured into the stainless steel cylinder through the top valve. Thereafter the sample passed through the filters in the filter holder. After filtration the filter was transferred from the filter holder to a Petri-slide[®] with the lid half open to dry in a box with filtered air (free from particles, SO₂ and ammonia).

Jacko connectors (made of polypropylene plastic) and stainless steel tubing fixed the steel tube to the filter holder (made of polyethen plastic) (Figs. 2 and 3). To remove large objects such as insects and plant debris a pre-filter (Nuclepore[®] PCMB filter, 25 mm diameter, 8.0 μm pore size) was at position A in the filter holder (Fig. 1). The pre-filter rested on a polypropylene plastic mesh. The main filter (Nuclepore[®] PCMB

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

filter, 37 mm diameter, 0.4 μm pore size) was at position B in the filter holder (Fig. 1). To concentrate the soot collected at the filter and thereby achieve a higher signal to noise ratio in the determination of soot by photometry (see Sect. 2.5), the filter had a 8 mm in diameter silicon rubber gasket above the filter as introduced by Heintzenberg (1988).

This confined the filtration area on the main filter to 0.5 cm^2 (radius 0.4 cm) and allowed for optical reference measurements on the individual sample filters beside the soot spot. To support the center of the main analytical filter, a disc made of polypropylene porous plastic, (8 mm diameter) was placed underneath.

The filtration unit was designed to operate with both vacuum and pressurized air. However, trial vacuum filtration of high concentrated ambient rain samples showed blocking of the filter pores, with reduced filtration efficiency as a consequence. To overcome these shortcomings using vacuum filtration, the filtration unit was set to operate under pressure (5 bar, 1×10^5 Pa). In characterization tests of each part of the filtration unit separately vacuum filtration was however still used.

2.3 Synthetic samples

Based on trial ambient samples from ABC-field stations representative soot concentrations (between 0 and 0.153 $\mu\text{g}/\text{ml}$ with a average value of 0.065) of synthetic samples were selected. The synthetic soot samples were made with Printex 75 (primarily particle diameter 17 nm) (Degussa, Brenntag-Nordic AB). The Printex 75 samples were weighed and then mixed with Milli-Q water ($18 \text{ M}\Omega^{-1} \text{ cm}^{-1}$) and a dissolved inorganic ion matrix to a known concentration (For ion composition, see Table 1). The ion-matrix was composed to mimic an average composition in rain at the field station at Hani-maadho, Maldives (see Sect. 2.4).

2.4 Field samples

The performance of the method described in this study was tested on samples collected at the Maldives Climate Observatory Hanimaadho (MCOH) and at Nepal Cli-

mate Observatory (NCO). MCOH is located at Hanimaadhoo, an island in the northern part of the Maldives (longitude 73.183° E, latitude 6.776° N, at sea level). The site has no significant local soot emissions upwind from the station, therefore the composition of the air and rain is rather dominated by the main wind directions and regional sources.

5 During the winter monsoon (November–March), the main wind is northeasterly with air influenced by anthropogenic activities such as combustion, from the Indian sub-continent. During the summer monsoon (June–September), the main wind direction is southwesterly with marine air from the Indian Ocean.

10 NOC is located at Godavari (longitude 85.38° E, latitude 27.59° N, altitude 1590 m), at the mountain side of the Katmandu valley south east of the city. The site is in a clearing surrounded by a mixed of thick deciduous and evergreen broadleaved forest. The air composition is largely affected by emissions from Katmandu, but no strong anthropogenic emission point sources are present in the immediate surroundings of the observatory.

15 2.5 Determination of soot

Photometry was used to determine soot on the filters according to the setup by Heintzenberg (1988). The light source was a Xenon lamp from Osram. The light was focused with a lens onto the 8 mm sample spot, then passing through the soot filter, and finally through an optical fiber connected to the photo multiplier detector.

20 An interference filter before the detector selected a wavelength of 555 nm±23 nm. The photometer measured the light intensity after the soot spot on the filter (*s*), the same after the blank filter at the side of the spot (*f*) and the background signal when no light reached the detector (*bg*). The optical density (OD) was calculated with the formula:

$$OD = \ln \frac{f - bg}{s - bg} \quad (1)$$

25 A new feature of the Heintzenberg set up was the rotation of the filters to increase the area integrated at determinations of the blank filters. The random measurement

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



error of the instrument was less than 1%, above an OD of 0.1. A calibration curve was acquired with a set of filters with a known amount of synthetic soot loaded on the filters (see Sect. 2.3). The calibration curve enabled the determination of the amount of mass of soot on the filter:

$$5 \quad m_{\text{soot}} = \frac{\text{OD} - 0.0228}{0.0244}. \quad (2)$$

Here m_{soot} is the concentration of soot on the filter as $\mu\text{g}/\text{cm}^2$. Knowing the volume of the samples that was filtered the concentration of soot in the sample could be calculated as below,

$$C_{\text{soot}} = \frac{m_{\text{soot}} \times A}{V}, \quad (3)$$

10 where A is the area of the soot spot on the filter (0.5 cm^2) and V is the volume of the rain sample that was filtered.

3 Results

3.1 Characterization tests

15 Ambient rainwater samples were used to test the materials of choice for construction of the various parts used in the method. These test filtrations were performed under pressure.

The performance of the bottle, funnel and filtration unit were each exposed to synthetic samples. After exposure the samples were filtered and subsequently the amount of soot was determined with photometry. In testing the bottle, funnel and filtration unit
20 a reference filtration was performed with synthetic samples taken from the same batch. Vacuum was used to drive both the test and reference filtration.

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.2 Choice of materials for construction of funnel, bottle and filtration unit

Four different materials were tested; borosilicate glass, stainless steel, Teflon[®] and polyethen. These materials were exposed to wet deposition of ambient rain during 24 h. Prior to exposure the surface areas were cleaned three times with detergent (composed of water and ethanol only) using a plastic brush followed by rinsing with Milli-Q water. The detergent was added to improve the solubility of the particulate matter by changing the surface tension of the water medium, but not having any chemical effect.

After exposure to ambient rainwater the surfaces were washed again with detergent and plastic brush. The wash water was collected and filtered under pressure. The volume filtered was 10 ml due to the highly concentrated samples. After drying the filters, the amount of soot adsorbed on the various surfaces exposed was determined. Five tests were performed.

To determine which of the tested materials adsorbed least soot, statistical Anova calculations were performed with the results from the filtrations. According to the Anova calculations glass adsorbed least, followed by polyethen, steel and Teflon[®] (Table 2). However the uncertainty in the results was high. Guided by the results and by practicalities borosilicate glass was used for funnels and bottles. Stainless steel was used for the cylinder in the filtration unit for safety reasons in the case of filtration under pressure. To simplify the construction work polyethen was used for the filter holder, with a minimum contact area.

3.3 Soot losses by adsorption during sample storage

To test the soot adsorption in the borosilicate glass bottle during sample storage, the bottle was exposed to synthetic samples for 1 min, 5 min and 24 h respectively (sample volume 30 ml, sample concentration 0.1 $\mu\text{g/ml}$). After exposure the sample volume in the glass bottle was poured into the steel cylinder. Then followed subsequent filtration

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and the optical density of the soot on the filter were determined. For each selected time of exposure between 3 and 6 filtrations were performed. The difference in adsorption to a glass surface is marginal between 1 (9%) and 5 (10%) minutes time of exposure, with an adsorption up to 30% after 24 h.

5 3.4 Soot losses by adsorption during sample collection

To test for soot losses to the borosilicate glass surface of the funnel, two test matrices were designed. Test matrix 1 was designed to test the influence of time of exposure on adsorption as a function of concentration. Sample volume was set to be constant at 30 ml. Time of exposure varied between 5 and 30 min and soot concentration in sample
10 between 0.2 and 1.8 $\mu\text{g/ml}$. Test matrix 2 was designed to test the influence of sample volume on adsorption as a function of concentration. Time of exposure was set to be constant at 5 min. Sample volume varied between 30 and 90 ml and soot concentration in sample between 0.2 and 1.8 $\mu\text{g/ml}$. For each combination of parameters in the two test matrices between 3 and 6 filtrations were performed.

15 When the glass funnel was tested according to matrix 1 the result showed that the soot adsorption was dependent on the sample concentration. In Fig. 4 the OD of reference samples are plotted with the OD of the samples exposed to the funnel. The relative soot adsorption were estimated to $7\% \pm 5\%$ (95% confidence interval) obtained with linear regression with a forced zero intercept. No significant effect of the time of
20 exposure were found.

When the funnel was tested according to matrix 2 the results showed no significant effect of the filtration volume.

3.5 Soot losses by adsorption during sample filtration

25 When the filtration unit was characterized according to matrix 1, the results showed that, similar to the funnel, the soot adsorption were dependent on the sample concentration (Fig. 5). The relative soot adsorption was $5\% \pm 4\%$ (95% confidence interval).

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

The time of exposure or the filtration volume (as tested in matrix 2) showed no obvious influence on the adsorption.

3.6 Precision of the filtration procedure

As mentions previously, the filtration unit was set to operate under pressure (5 bar) due to potential blocking of the filter pores (see Sect. 2.2). To test for differences between pressure and vacuum filtrations, six filtrations operated under pressure were compared with six filtrations operated with vacuum. All filtrations where performed with synthetic samples from the same batch. Sample volume was 30 ml, sample concentration 0.5 $\mu\text{g/ml}$ and exposure time 10 minutes. The determined average OD of the filters from the pressure filtration was 1.154 and 1.145 for the vacuum filtration. In this case when the actual filtration is tested OD is a more direct parameter to use, compared to sample concentration. The difference between the average OD measured using vacuum and pressure filtration were within the range of the standard deviation (5%). To extend the concentration range more tests with synthetic samples with six filtrations each under pressure were performed. Soot loadings varied between 0.3 and 2.5 OD (soot concentration between 0.2 and 1.7 $\mu\text{g/ml}$), all with a sample volume of 30 ml. For filtrations with a loading of 0.3 OD the precision was 9% and for loading between 1.0 and 2.5 OD 5%.

To further investigate the low concentration range, tests with ambient samples collected at the Stockholm University campus with soot loadings between 0.1 and 0.3 OD (sample concentration between 0.02 and 0.1 $\mu\text{g/ml}$) were performed. For the ambient samples no delay of the filtration was allowed, therefore time of exposure was less then 5 min. For ambient samples with soot loadings of 0.08, 0.15 and 0.3 OD the precision was 21, 13 and 5%, respectively.

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.7 Filter collection efficiency

The collection efficiency of the Nuclepore[®] PCMB filters with 25 mm diameter and 8.0 μm pore size (pre-filter) was tested. Synthetic samples were filtered under pressure through the pre-filter and the main filter (Filter A and B, Fig. 1). To study the amount of soot that passes through the pre-filter, an equal number of filtrations were performed without the pre-filter. The synthetic soot particles used in the test of the pre-filter were in the same size range as ambient soot particles. A filter loading was set to 0.3 and 2.5 OD respectively (sample volume 30 ml and concentration 0.2–1.7 $\mu\text{g}/\text{ml}$). No delay of the filtration was allowed. For a filter loading of 0.3 and 2.5 OD the collection efficiency was 0 and $2\pm 4\%$, respectively.

The collection efficiency of the Nuclepore[®] PCMB filters with 37 mm diameter and 0.4 μm pore size was tested. Both ambient and synthetic samples were filtered under pressure through the pre-filter and the main filter. To study the amount of soot that passes through the main filter, the filtrate was collected and filtered once again through a Nuclepore[®] PCMB filter with 37 mm diameter and pore size 0.2 μm . A smaller pore size (0.2 μm) was used for the second filter to collect particles that passed through the first filter (pore size 0.4 μm). Three test series of three to six filtrations each were performed. Soot loadings ranged between 0.08 and 2.5 OD (sample concentration 0.04–1.7 $\mu\text{g}/\text{ml}$) and sample volume between 5 and 50 ml. No delay of the filtration was allowed with time of exposure less than 5 min. For soot loadings below 1.0 OD the average filtration efficiency was $82\pm 11\%$. For a loading between 1.0 and 2.5 the average filtration efficiency was $88\pm 0.5\%$. The results showed no dependence on sample volume.

3.8 Detection limit for determination of soot

To estimate the detection limit for the determination of soot, Milli-Q water was filtered through 10 PCMB filters (according to the procedure in Sect. 2.2). The optical density

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

of the PCMB filters were then determined and the standard deviation of the signal was multiplied by three to obtain a value of the detection limit (transmitted light signal to instrument noise ratio of 3). The detection limit for determination of soot was with this procedure estimated to 0.025 OD. Assuming a filtration volume of 30 ml gives a
5 detection limit of 2 ng/ml expressed as a concentration.

3.9 Field tests with ambient samples

With the purpose to test the performance of the new method in conditions mainly affected by pristine marine areas, 48 ambient samples were collected and evaluated during the summer monsoon at MCOH between 3 June and 21 September 2005. The
10 volume of the collected rain samples ranged from 1810 to 32 ml and the average soot concentration was 0.048 $\mu\text{g/ml}$ (Table 3). Filtration volume varied between 10 and 100 ml with a median volume of 50 ml. Exposure time during filtration was less than 5 min.

To also test the method at conditions affected by strongly polluted urban areas, 18
15 ambient samples were collected and evaluated at NOC during the period of 21 October 2005 to 24 May 2006. The volume of the collected rain samples varied between 1154 and 44 ml and the average concentration of soot was 0.081 $\mu\text{g/ml}$ (Table 4). Filtration volume varied between 12 and 56 ml with a median volume of 50 ml. Exposure time during filtration was less than 5 min.

The detected concentrations of soot in the collected rain samples at MCOH and
20 NOC shows that the range of concentrations tested in laboratory well cover the ambient variation.

After collection of the ambient rain sample the soot adsorption of the funnel and bottle was characterized. After filtration, the funnel and bottle were cleaned with detergent
25 using a plastic brush followed by rinsing with Milli-Q water three times. The wash water was filtered according to the procedure described earlier (Sect. 2.2) for subsequent soot determination (Sect. 2.5). For each rain event the amount of measured soot in the rain sample, funnel and bottle was combined to get the amount of soot (100%) in

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the rain water before exposure. The results from the filtrations were scaled to amount of collected rain and amount of wash water. Then the fraction of soot could be calculated for the rain sample, funnel and bottle (Tables 3 and 4 and Figs. 6 and 7).

5 The field tests at MCOH showed a loss of soot during collection of ambient samples of 31% (bottle and funnel combined). The tests at NOC showed a soot loss of 27%.

4 Total loss of soot in method

To estimate the total soot loss in the method, the measured soot adsorption in the bottle, funnel and filtration were combined according as below:

$$\text{SootAds}_{\text{tot}} = 1 - ((1 - \text{ads}_1) \times (1 - \text{ads}_2) \times (1 - \text{ads}_3)) = 0.227. \quad (4)$$

10 Here ads_1 is the soot adsorption in the bottle (12.5%) for field samples (average of MCOH and NOC samples), ads_2 is the soot adsorption in the funnel (6.7%) for synthetic samples and ads_3 is the soot adsorption in the filtration unit (5.3%) for synthetic samples. The resulting total soot loss is $23\% \pm 2\%$.

5 Discussion

15 The characterization tests of soot adsorption in the borosilicate glass bottle during storage shows a continuing adsorption during 24 hours. The rate of adsorption should be dependent on the number of active sites available at the glass surface with functional groups where soot particles could be adsorbed. At start of exposure, the rate of adsorption is expected to be high due to a greater number of active sites. However, this
20 rate decreases strongly with time of exposure as the number of available active sites decline. This could then have caused the relatively slow but significant adsorption of soot at the glass surface between 5 min and 24 h time of exposure.

The characterization tests of soot adsorption on to the surface in contact show comparable results for both the funnel and filtration unit, with higher relative adsorption

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

at lower sample concentration and lower sample volume. The results suggest that the funnel and filtration unit contain similar to the borosilicate glass active sites that get saturated by adsorption of soot with time of exposure. When comparing time of exposures between 5 and 30 min, no difference in influence on the adsorption was shown, which suggests that the detected adsorption occurs within 5 min. When the sample volume was kept constant, samples with a higher concentration (0.5 to 2.0 $\mu\text{g/ml}$) contain a larger amount of soot compared with those of lower concentration (below 0.5 $\mu\text{g/ml}$). If the absolute amount of adsorbed soot is equal in the two cases, this could explain the higher relative soot adsorption at concentrations below 0.5 $\mu\text{g/ml}$ compared with tests at concentrations between 0.5 and 2.0 $\mu\text{g/ml}$, in the characterization tests.

When comparing filtrations operated by vacuum and pressure no apparent difference in resulting OD is detected. This implies that vacuum and pressure are equal in performance.

The results from tests with ambient samples at 0.3 OD show a better precision (5%) compared to synthetic samples at 0.3 OD (9%). An explanation can be that the surface of the soot in the ambient samples collected outdoors could have a more hydrophilic nature.

The collection efficiency of the PCMB main filter (82 to 88%) with rain samples showed improved efficiency compared to quartz filters (50 to 80%) used by Ogren et al. Additional the use of PCMB filters enables scattering correction of the absorption measurements by subsequent chemical analysis of the sample composition. The maximum collection efficiency of 2% measured in the test of the pre-filter showed that the pre-filter only collected a few of the soot particles and thus will meet its purpose to remove large objects such as insects and plant debris but let the soot particles through to be collected by the main filter.

The precision for the method was better than 10% as relative standard deviation. The overall loss of soot due to adsorption during collection and filtration was $22\pm 2\%$. One of the aims with the characterization of the soot loss was to come up with a mathematical formula to correct for the detected soot in the rain sample. Then the

determination of the amount of soot adsorbed to the funnel and bottle would not have been necessary to perform for every sample, and by that reducing the work effort by a factor of three. But with the high variability that these results show the conclusion is that it is better to continue to analyse the fractions in the funnel and bottle.

5 The loss of soot during collection of ambient samples (31% at MCOH and 27% at NOC for bottle and funnel combined) is lower compared to the tests performed with synthetic samples in the laboratory (bottle 30% and funnel 7%). An explanation can be that the surface of the soot in the ambient samples could have a more hydrophilic nature, due to interactions with other particles, trace gases and repeated cloud processes
10 in the atmosphere.

6 Conclusions

A new method to measure soot in rain water have been developed and characterized. The detection limit for the method was 0.025 OD. Assuming a filtration volume of 30 ml gives a detection limit of 2 ng/ml expressed as a concentration. The precision for
15 the method was better than 10% calculated as relative standard deviation. The overall loss of soot due to adsorption during collection and filtration was $22 \pm 2\%$. At MCOH the average soot concentration in rain was $0.048 \mu\text{g/ml}$ and at NOC $0.081 \mu\text{g/ml}$. The higher soot concentration in Nepal can be explained by emissions from cities present in the region, while MCOH is a remote station surrounded by ocean. The synthetic samples showed a higher adsorption compared to the ambient samples. An explanation
20 can be that the surface of the soot in the ambient samples collected outdoors could have a more hydrophilic nature and by that not equally easy adsorbed.

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25

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



MISU (Stockholm, Sweden) and MCOH for the help with collecting and analyzing samples. Leif Bäcklin and Lennart Granat (MISU) selected and designed the prototype equipment for rain collection and filtration after which Leif Bäcklin built instrument for rain collection, filtration and also the upgraded soot photometer. The latter after instructions from Jost Heinzenberg. We thank
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References

- Bond, T., Theodore, L., Anderson, T., and Campbell, D.: Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, *Aerosol Sci. Tech.*, 30, 582–600, 1999. 239
10 Heintzenberg, J.: A Processor-Controlled Multisample Soot Photometer, *Aerosol Sci. Tech.*, 8, 227–233, 1988. 239, 241, 242
- IPCC: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp., 2007. 238
15
- Kopp, C., Petzold, A., and Niessner, R.: Investigation of the specific attenuation cross-section of aerosols deposited on fiber filters with a polar photometer to determine black carbon, *J. Aerosol Sci.*, 30, 1153–1163, 1999. 239
20
- Ogren, J. and Charlson: Wet deposition of elemental carbon and sulfate in Sweden, *Tellus B*, 36, 262–271, 1984. 239
- Ogren, J., Charlson, R., and Groblicki, P.: Determination of elemental carbon in rainwater, *Anal. Chem.*, 55, 1569–1572, 1983. 239
- 25 Ogren, J. A. and Charlson, R. J.: Elemental carbon in the atmosphere: cycle and lifetime, *Tellus*, 35B, 241–254, 1983. 239
- Ogren, J. A., Groblicki, P. J., and Charlson, R. J.: Measurement of the removal rate of elemental carbon from the atmosphere, *Sci. Total Environ.*, 36, 329–338, 1984. 239
- Petzold, A., Schloesser, H., Sheridan, P. J., Arnott, W. P., Ogren, J. A., and Virkkula, A.: Eval-

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

uation of multiangle absorption photometry for measuring aerosol light absorption, *Aerosol Sci. Tech.*, 39, 40–51, 2005. 239

Ramanathan, V., Crutzen, P., Kiehl, J. T., and Rosenfeld, D.: Aerosols, Climate and the Hydrological Cycle, *Science*, 294, 2119–2124, 2001. 238

5 Ramanathan, V., Chung, C., Kim, D., Bettge, T., Buja, L., Kiehl, J., Washington, W. M., Fu, Q., and Sikka, D. R.: Atmospheric brown clouds: Impacts on South Asian climate and hydrological cycle, *Proceedings of the National Academy of Sciences of The United States of America*, 2005. 238

10 WHO: Health risks of particulate matter from long-range transboundary air 15 pollution, WHO Regional Office for Europe, 2006. 238

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck**Table 1.** Ion composition of synthetic rain water (ion matrix).

Ion	$\mu \text{ eq} / \text{ dm}^3$
F ⁻	100
For ⁻	100
Ac ⁻	100
MSA ⁻	10
Cl ⁻	600
NO ₃ ⁻	400
SO ₄ ⁻²	660
Na ⁺	500
NH ₄ ⁺	300
K ⁺	60
Mg ⁺²	400
Ca ⁺²	700

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Table 2. Ambient soot adsorption on materials tested for construction. Number of tests: 5

Material	Relative mass units of soot adsorbed	95% confidence interval
Borosilicate glass	1	–
Polyethen	1.30	0.86–1.97
Stainless steel	1.80	1.18–2.73
Teflon	2.13	1.40–3.23

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Table 3. Ambient soot adsorption in funnel and bottle at Maldives Climate Observatory – Hanimaadhoo. Number of samples: 48

	Soot mass (μg)			Mass fraction (%)			Soot conc. in rain ($\mu\text{g}/\text{ml}$)	Rain volume (ml)
	Rain	Funnel	Bottle	Rain	Funnel	Bottle		
June–September								
Average	14.38	0.90	2.06	83	5	12	0.048	324
90 Percentile	28.32	1.58	4.33				0.101	834
75 Percentile	14.31	1.00	2.75				0.056	396
25 Percentile	4.12	0.37	0.85				0.028	94
10 Percentile	1.88	0.22	0.62				0.021	65

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[⏪](#)
[⏩](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

Table 4. Ambient soot adsorption in funnel and bottle at Nepal Climate Observatory. Number of samples: 18

	Soot mass (μg)			Mass fraction (%)			Soot conc. in rain ($\mu\text{g}/\text{ml}$)	Rain volume (ml)
	Rain	Funnel	Bottle	Rain	Funnel	Bottle		
June-September								
Average	21.82	2.80	3.46	69	13	17	0.081	325
90 Percentile	48.67	4.53	5.00				0.135	736
75 Percentile	38.41	3.46	4.05				0.100	525
25 Percentile	8.92	1.71	2.10				0.058	101
10 Percentile	4.18	0.88	1.42				0.041	55

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

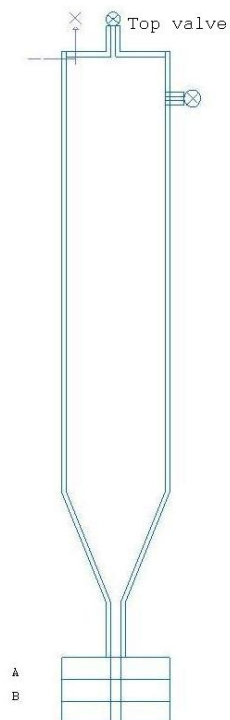
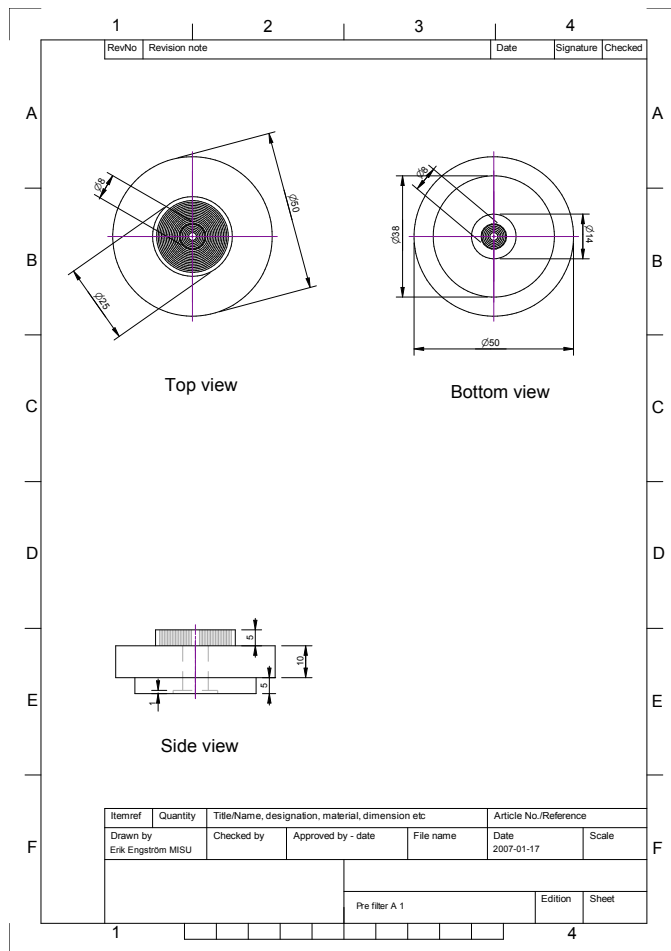
**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Fig. 1. A schematic drawing of the filtration unit. Position A: Prefilter. Position B: Main filter.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck



Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Fig. 2. Filterholder A for pre-filter.

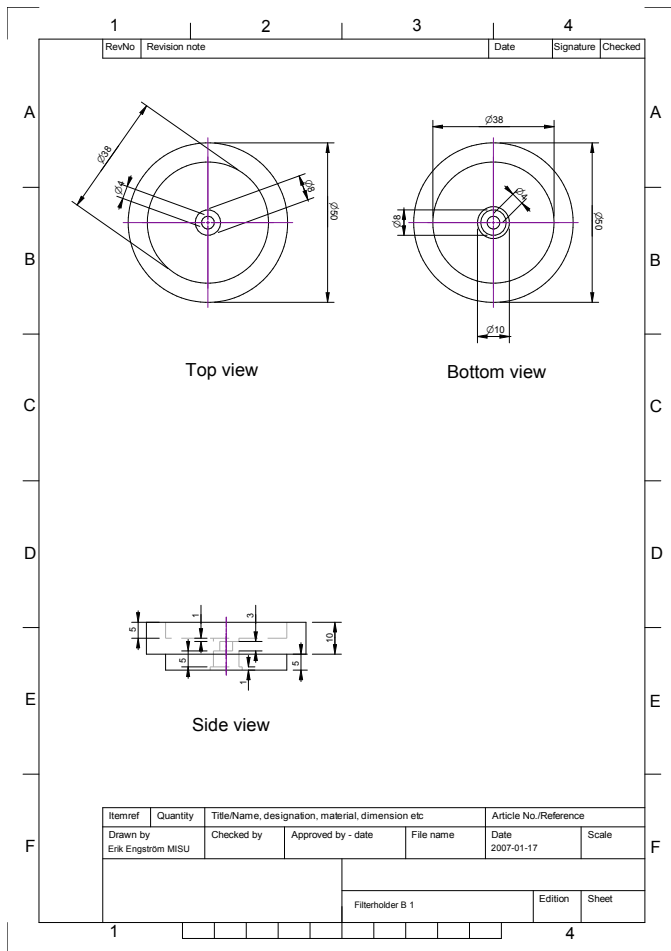


Fig. 3. Filterholder B for main-filter.

Determination of water-insoluble light absorbing matter

J. E. Engström and
C. Leck

[Title Page](#)

[Abstract](#) [Introduction](#)

[Conclusions](#) [References](#)

[Tables](#) [Figures](#)

[⏪](#) [⏩](#)

[◀](#) [▶](#)

[Back](#) [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)

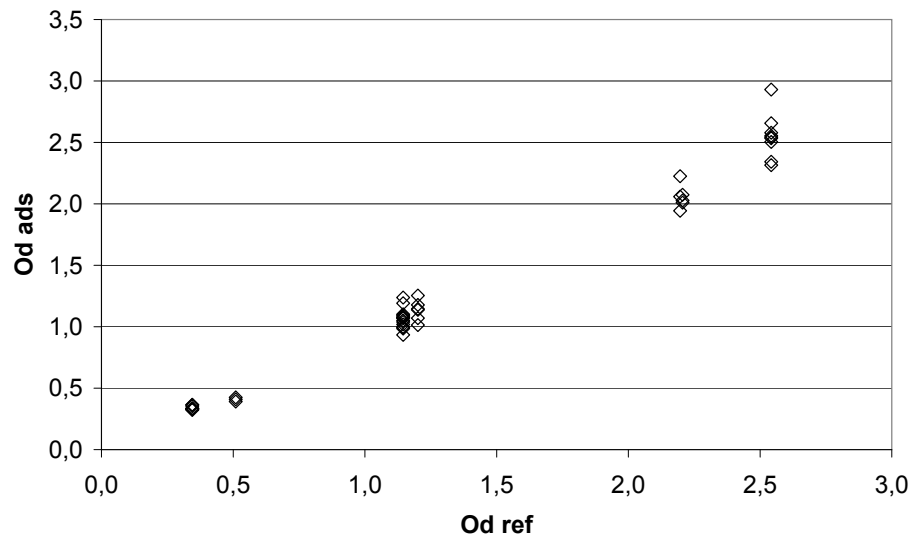
Determination of water-insoluble light absorbing matterJ. E. Engström and
C. Leck

Fig. 4. Soot adsorption to the glass funnel. Soot in the reference sample and in the sample exposed to the funnel showed as optical density of the filter. Synthetic sample volume was set to be constant at 30 ml. Time of exposure varied between 5 and 30 min and soot concentration between 0.2 and 1.7 $\mu\text{g/ml}$.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

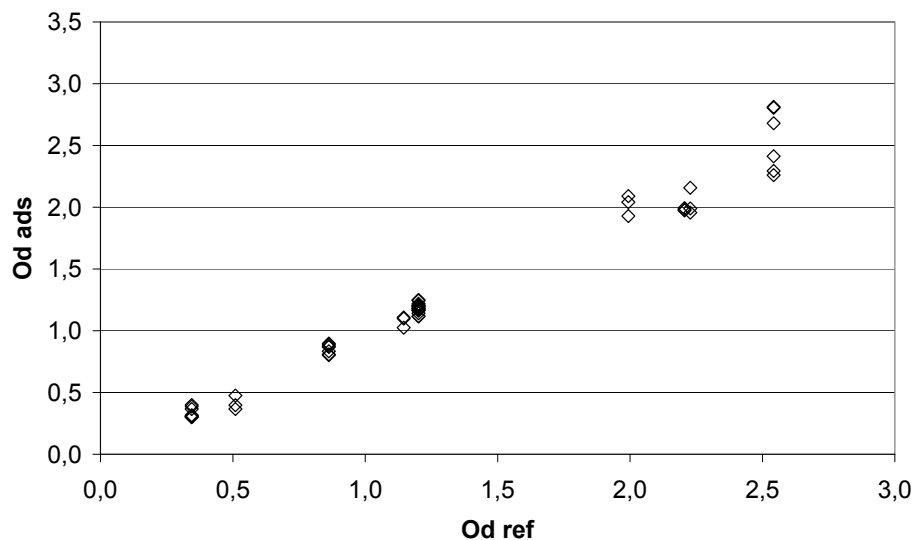
**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Fig. 5. Soot adsorption of the filtration unit. Soot in the reference sample and in the sample exposed to the funnel showed as optical density of the filter. Synthetic sample volume was set to be constant at 30 ml. Time of exposure varied between 5 and 30 minutes and soot concentration varied between 0.2 and 1.7 $\mu\text{g}/\text{ml}$.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

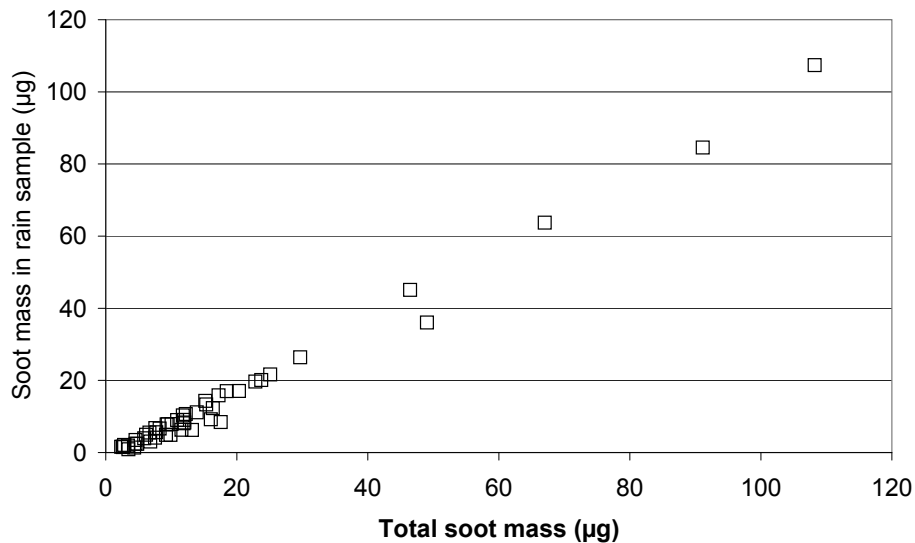
**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Fig. 6. Soot mass in rain sample after exposure to funnel and bottle as a function of total soot mass in rain water at the Maldives Climate Observatory – Hanimaadhoo.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

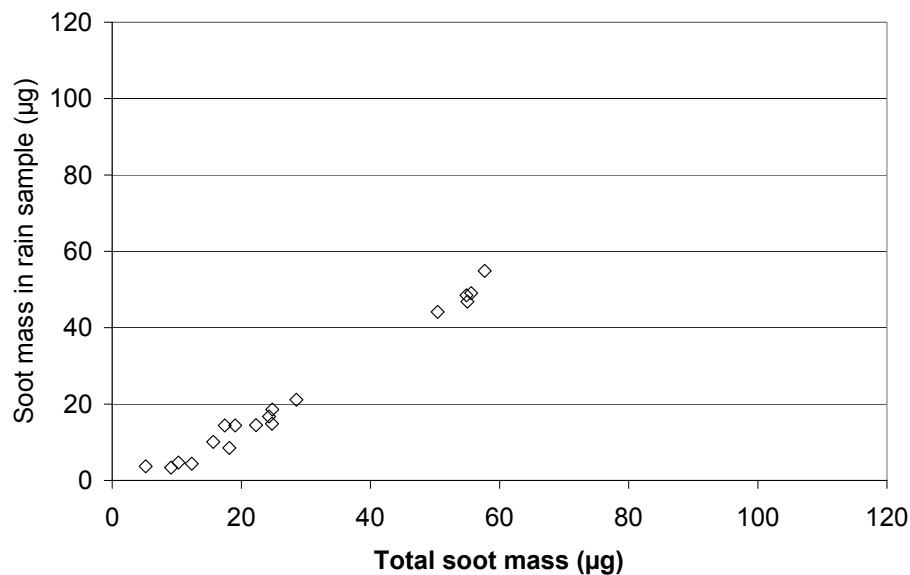
**Determination of
water-insoluble light
absorbing matter**J. E. Engström and
C. Leck

Fig. 7. Soot mass in rain sample after exposure to funnel and bottle as a function of total soot mass in rain water at Nepal Climate Observatory.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)