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Using the Aethalometer for Source Apportionment of Carbonaceous Aerosols

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Abstract

Atmospheric aerosols are present everywhere on the planet in various concentrations. It has been shown that aerosols affect the climate. Some aerosols, like soot, absorbs light and heat the climate while mineral dust particles scatter light and thereby cools the climate. This contradiction leads to uncertainties of the net effect of aerosols on the climate, it is thus important to characterize the aerosols and their sources. Source apportionment of the carbonaceous fraction of the aerosol is an important tool for evaluate the influence of the sources. It is performed by using multiple measurement techniques to provide a comprehensive picture of the sources. The aethalometer is a real time optical instrument which measures the absorption of light by aerosols. By measuring the absorption at seven wavelengths it is possible to deduce a spectral dependence of the aerosols. It turns out that this dependence differs depending on the constituents of the measured particle, it is thus possible to trace the sources.

Introduction

Aerosols

Atmospheric aerosols consist of a mixture between solid and liquid particles suspended in an air mass. Aerosol originates from both natural and anthropogenic sources. The most important natural sources are windblown dust, volcanic eruptions, sea spray, natural fires, pollen, spores and vegetation (Seinfeld and Pandis, 2006). Among the anthropogenic sources we find agriculture, biomass burning, fossil fuel burning and traffic as the most important contributors (Andreae and Merlet, 2001). The aerosols range in size from nanometers up to micrometers in diameter (Raes et al., 2000). Concentration of aerosols differs a lot on a spatial and temporal scale: the range is from ten to hundreds of particles per cubic centimeter in rural unpolluted sites, up to hundreds of thousands particles per cubic centimeter in polluted areas (Mönkkönen et al., 2005).

Aerosols consists of up by many different compounds depending on the origin of the aerosol. Common compounds are nitrates, sea salts, sulphates, organic matter, mineral dust and soot. The organic matter and soot component of an aerosol is sometimes referred as the organic aerosol (OA). Studies have shown that OA makes up a large fraction (20-90 %) of the particulate mass (Jimenez et al., 2009). If the OA is released directly from its source it is called primary organic aerosol (POA). Spores, pollen and soot can be regarded as POA (Gelencsér, 2004). If the aerosol is built up by volatile organic compounds (VOCs) from vegetation etc. they are regarded as secondary organic aerosols (SOA) (Gelencsér, 2004). The OA is built up by carbon and thereby regarded as the carbonaceous component of the atmospheric aerosol (Gelencsér, 2004). The total carbon content (TC) of the carbonaceous aerosol is then divided into elemental carbon (EC) and organic carbon (OC). EC is basically soot that has been measured with thermal analysis. Soot that has been measured with optical methods, using its light absorbing properties, are called black carbon (BC), which will be discussed more in detail later. Soot is formed from incomplete combustion of biomass and fossil fuels. OC consists of organic molecules and polymers such as alkanes, polycyclic aromatic hydrocarbons (PAH), organic acids, humic acids and cellulose (Pöschl, 2005). For several years it was thought that OC does not absorb light, however recently the term “brown carbon” have been introduced to this field. Brown carbon consists of light absorbing organic matter (other than soot) such as humic-like substances (HULIS), bioaerosols and soil humics (Andreae and Gelencsér, 2006). A major fraction of the brown carbon originates from biomass burning. Given that biomass burning is considered to have a net zero emission of CO_2 biomass burning can be expected to increase and thereby the effects of brown carbon on air quality (Herich et al. 2011).

Climate Effects of Aerosols

Ever since the industrial revolution in the mid 1800’s anthropogenic activities has led to increasing emission of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) into the atmosphere. Earth’s mean temperature has increased with 0.75 °C since the industrial revolution and is accelerating. According to the Intergovernmental Panel on

Climate Change (IPCC) it is very likely that this increase in temperature is a result of human activities (Alexander et al., 2013).

The emission of greenhouse gases causes a perturbation of the radiative flux in the atmosphere of earth. The radiative forcing (RF) is a measure of these changes in radiation (Jacob, 1999). A positive RF results in heating of the climate and a negative RF results in cooling. In figure 1 it is evident that emissions of the greenhouse gases CO_2, CH_4 and N_2O all are believed to contribute to a positive RF.

However, greenhouse gases are not the only constituents of the atmosphere that affect the climate, there are also aerosols. The aerosols affect the climate in a numerous different ways (Andreae and Rosenfeld, 2008). The effects from aerosol on the climate are usually divided into the *direct* and *indirect* effect of aerosols. The direct effect means that aerosols scatter incoming solar radiation; the solar radiation will change direction due to this scattering and a fraction will be sent back to space (Baird and Cann, 2008). Thus, the direct effect gives a net cooling on the climate with an estimated negative radiative forcing of 0.5 ± 0.4 W/m^2 (Solomon et al., 2007). There is one important exception, dark soot which is particles that absorb solar radiation and emit heat instead of scattering the incoming radiation (Menon et al., 2002). Thus, soot particles have a net warming effect on the climate. In a recent report by Bond et al. (2013) the radiative forcing of soot was estimated to + 1.1 W/m^2. This would make soot together with CH_4 the largest climate enhancers after CO_2 (figure 1), however the uncertainty is still very high. The indirect effect of the aerosol on the climate is caused by cloud formation. All cloud droplets are formed by water that condenses on an aerosol particle. By changing size, number concentration and chemical composition of the aerosols the optical properties of the clouds are changed (Ramanathan et al., 2001). A high number of aerosol particles results in more but smaller cloud droplets. This will make the cloud brighter and it will thus reflect more incoming solar radiation and increase the albedo of earth, which has net a cooling effect on the climate (Twomey, 1974). This is called the *first indirect effect*. The *second indirect effect* is also a result of the small cloud droplets which delays precipitation and thereby extends the lifetime of the clouds (Albrecht, 1989). However, as seen in figure 1, the uncertainty of the cloud albedo effect is high.

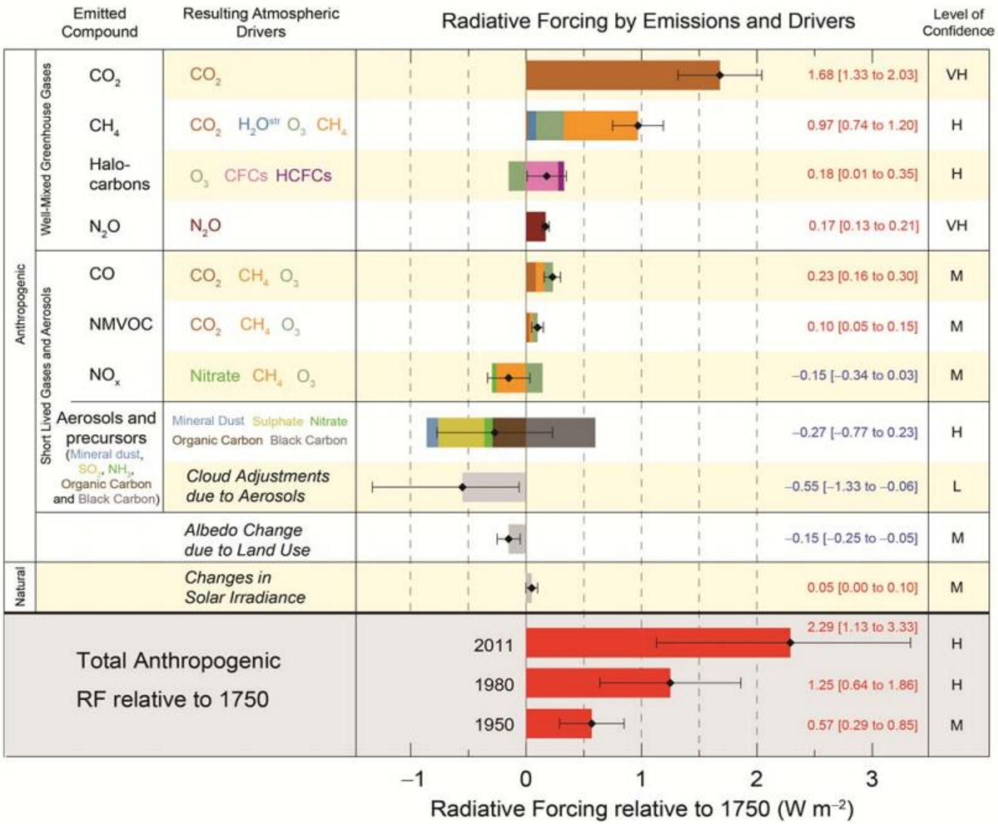

Figure 1. Global average radiative forcing due to anthropogenic activities since the 1750's. A positive radiative forcing warms the climate while a negative forcing cools the climate. Some emitted compounds have bars that are both negative and positive, this means that some fractions of the emitted compound have the potential of one effect (heating or cooling the climate) while other fractions have the opposite effect. Error bars show 90 % confidence intervals. From Alexander et al. (2013).

Health Effects and Legislation regarding Aerosols

Aerosols are also affecting the human health. Numerous studies have shown that even low concentrations of particulate matter (PM) have a negative effect on human health (Pope et al., 1995; Abbey et al., 1999). Exposure to urban PM is estimated to cause 800 000 premature deaths annually on earth. In Sweden this number is around 3500 (WHO, 2002; Forsberg et al., 2005). Cardiovascular and lung diseases are the most common conditions related to PM exposure. Children and people with already reduced cardiovascular and lung functions are particularly susceptible to exposure.

Today there are both global and national legislations regarding the air quality. The main mission of the legislation is to improve air quality for humans. The European union has implemented an air quality directive where every member state should undertake this legislation (European Parliament, 2008). The directive advocates a limit of PM_{10} (particulate matter with an aerodynamic diameter smaller than 10 µm) to 50 $\mu g/m^3$ as a daily average. This limit can be violated maximum 35 days per calendar year. For PM2.5 the limit is set to 25 $\mu g/m^3$ as an annual average. All member states shall designate an authority that has the main responsibility that the directive is implemented in the nation. To create a unity in the air quality measurements and to favor comparisons, the directive also carefully describes how to perform the measurements (European Parliament, 2008).

Source Apportionment

Due to the counteracting effects of aerosols on the climate (direct and indirect effect vs. soot) the level of scientific understanding is low and hence, the uncertainties are high (figure 1). Global scale simulations try to model the climate effect of aerosols. However, in order to evaluate the model robust measurement data are needed. By identifying sources of aerosols and apportioning loadings to the different sources, local and regional measurements need to be performed for developing global models. The most important task is to identify the fraction of the aerosol that has an anthropogenic origin, since this is the fraction we as humans can affect.

Source apportionment of aerosols is not straightforward since the general aerosol consists of many different compounds with different chemical and physical properties. The different compounds may also have different effects for the environment and climate, sometimes even opposite effects such as interaction with light (mineral dust vs. black carbon). Thus, to perform a source apportionment of good quality, it is crucial to use many different techniques to be able to deduce the different compounds and their origin. The most commonly used techniques for source apportionment of the carbonaceous part of the aerosol are presented below.

Thermo Optical Analysis (TOA)

To distinguish between EC and OC Thermo Optical Analysis (TOA) is used. Here, a filter punch with collected aerosols is inserted into a thermal/optical carbon analyzer. On the assumption that OC is more volatile than EC, temporal separation is possible by separation of the two different fractions using a thermal protocol where the sample is heated in different temperature steps and atmospheres. There are well established thermal protocol's, the EUSAAR_2 (European Supersites for Atmospheric Aerosol Research) protocol is for instance widely used in European aerosol research (Cavalli et al., 2010).

Usually OC is first evolved from the sample by 4-5 temperature steps ranging from 200-700 °C during 550-650s. The combustion takes place in an inert atmosphere, usually helium. EC is then evolved in an oxidizing atmosphere ($He + O_2$) in 4-5 temperature steps ranging from 500-900 °C during 300-400s. The evolved OC and EC are fully oxidized to CO_2 in an oxidation oven, and then converted to CH_4 by hydrogen over a zinc catalyst. The CH_4 is then measured quantitatively by a flame ionization detector (FID).

The separation of OC and EC is not trivial. During the combustion of OC, some OC may char and appear as EC. To compensate for this error, a laser is measuring the transmittance of the filter sample during the analysis. As OC starts to char, the transmittance decreases. However, when EC is evolved in an oxidizing environment the transmittance is increasing and when the transmittance signal reaches its initial value (base line) the split point between OC and EC is defined.

TOA is one of the fundamental measurement techniques used in source apportionments. It gives a rough estimate of the influence of various sources on the proportion of the carbonaceous aerosol. High EC loading is an indication of diesel and incomplete combustion, while high OC loadings indicate biomass burning but also SOA and biogenic aerosols.

Organic Tracers

The organic aerosol is built up by a plentitude of chemical compounds. On this basis it is hard to identify the constituents in a quantitative way. However, there can be constituent molecules that are characterizing the aerosol source. These kind of molecules are called organic tracers. Levoglucosan is an anhydride sugar that is created from pyrolysis of cellulose above 300 °C (Simoneit, 2002), its stability in the atmosphere is debated (Fraser and Lakshmanan, 2000; Hoffman et al. 2010) but it has been used in several source apportionments for allocating biomass burning (Gelencsér et al., 2007; Genberg et al., 2011; Yttri et al., 2011). Cellulose itself can be used to apportion POA from biogenic litter (Puxbaum and Tenze-Kunit, 2003). In fungal spores we find tracers like arabitol and mannitol (Bauer et al., 2008). Plants also emits VOC's which can be reactants in SOA formation, here isoprene and pinonic acids can be used as tracers (Kleindienst et al., 2007). To quantify various organic tracers, particles collected on filters are extracted with dichloromethane and methanol during sonication. The samples are then derivatisized before analyzed in a gas chromatograph with mass spectroscopy (GC-MS) (Hyder et al. 2012).

^{14}C-Analysis

Carbonaceous aerosols may origin from biomass and fossil fuel burning. Analysis using ^{14}C can distinguish between the two sources. Since ^{14}C has a halftime of 5730 years we can find the isotope in all carbonaceous aerosols except for those who comes from fossil fuel combustion. The fossil fuel has been conserved for millions of years, thus all ^{14}C has decayed. This technique is well established in modern source apportionment (Gelencsér et al., 2007; Genberg et al., 2011; Yttri et al., 2011). ^{14}C is measured by accelerator mass spectrometry (AMS) (Hellborg et al., 2003). Aerosol particles are collected on a filter, the carbonaceous fraction of the aerosol must then be transformed into graphite in order to perform the measurements with AMS. The atoms of the sample is then ionized and accelerated in the AMS. The atoms can then be separated by their charge and mass.

When using ^{14}C-analysis for source apportionment it is important to consider and account for the anthropogenic activities that have altered the ^{14}C concentration in the atmosphere. The increased combustion of fossil fuels during the 19th and 20th century have caused a "dilution" of the natural ^{14}C concentration by emissions of ^{14}C free CO_2 from these combustion processes. This effect is called the Suess effect. During the 1940's to 1960's detonation of atomic bombs also affected the ^{14}C concentration in the atmosphere. The detonations spread neutrons which can form ^{14}C in the atmosphere.

Aerosol Mass Spectrometry (Aerosol MS)

Aerosol mass spectrometry (Aerosol MS) is a versatile tool for chemical identification and characterization of aerosols. It has a wide field of application, from indoor local measurements to atmospheric global measurements (Canagaratna et al. 2007). The aerosol MS uses an aerodynamic lens inlet to concentrate the aerosols while the ambient gas are reduced. The aerosols then impact on a heated surface and get vaporized. Vaporized aerosols then get ionized by electron impact and are finally analyzed by mass spectrometry. It is also possible to derive aerosol size distributions by the particle time-of-flight from a mechanical chopper to the heated vaporizer. The instrument can be equipped with a laser vaporizer which enables the aerosol MS to detect soot particles, this instrument is then referred as a soot particle aerosol mass spectrometer (SP-AMS) (Onasch et al. 2012).

The aerosol MS operates in real time and generates a mass spectrum showing several large classes of chemical compounds such as nitrate, sulphate, organics, water, ammonium, chloride and potassium. With knowledge of the molecular weight of certain chemical tracer compounds (hydrocarbons, PAH's, levoglucosan etc.) it is possible to determine mass concentrations of these. Thus, the aerosol MS is a powerful tool in source apportionment. However, when using mass spectrums it is important to be aware of that one mass on the spectrum does not need to consist of one chemical compounds. This is because of the existence of chemical isomers, two or more molecules that have the same chemical formula but different chemical structure.

Optical Measurements

In comparison to complex filter measurements and chemical techniques, optical measurement techniques are often rapid, simple and do not demand as much maintenance as other in-situ techniques. In general they are all based on measuring the absorption of light by particles. Common analytical tools are the Particle Soot Absorption Photometer (PSAP), the Multi Angle Absorption Photometer (MAAP) and the Photo Acoustic Soot Spectrometer (PASS). The PSAP is with regard to measurement principle similar to the aethalometer (described below). It measures the absorption of particles on filters over 3 wavelengths (λ= 467, 530 and 660 nm) and has a time resolution of 10 s (Bond et al. 1999). The MAAP instrument was specifically developed to reduce the emerging uncertainties due to sampling artifacts (described below) from black carbon measurements and it measures the absorption of a particle loaded filter at 670 nm. The measurement is corrected in real time for sampling artifacts by measuring the reflectance of light scattered from the filter (Petzold and Schönlinner, 2004). The PASS, however, is not a filter based technique, instead it measures the light absorption of the airborne aerosol. It uses a 3 wavelength laser beam that when illuminating a light absorbing particle makes the particle emit heat. This heat is then causing changes in pressure which is registered by a sensitive microphone. The signal from the microphone is linearly related to the aerosol light absorption coefficient. A major uncertainty related to PASS measurement is that some trace gases also absorb light and thus get registered by the microphone. To avoid this, 3 wavelengths have been carefully selected not to interfere with the most common trace gases in the atmosphere (Lack et al. 2006). On the other hand, the PASS does not have the filter measurement artifacts like PSAP and MAAP. Therefore PASS is often used as a reference when measurements are performed with PSAP or MAAP. PSAP, MAAP and PASS have all been used in order to apportion light absorbing particles (Nguyen et al. 2013; Thornhill et al. 2010; Weimer et al. 2008).

The Aethalometer

Measurement Principles

The aethalometer is a real-time instrument for measurement of aerosol particles and was first described by Hansen et al. (1984). The name “aethalometer” are derived from the greek word “aethaloun” (αιθαλουν) which means “to blacken with soot”. The instrument is continuously measuring the attenuation of a beam of light through a filter (see figure 2). An air flow with constant velocity is directed through the filter and thus particles are loaded on the filter and the deposition rate of black carbon on the filter is proportional to its concentration within the aerosol and gives a corresponding rate of increase of optical attenuation. The optical attenuation through a filter is defined as

$$ATN = 100 \ln\left(\frac{I_0}{I}\right) \qquad (1)$$

where I_0 is the intensity of the incoming light and I is the remaining light intensity after passing through the filter. The aerosol attenuation coefficient of the filter loaded particles b_{ATN} can now be calculated by using the change in attenuation, ΔATN, as a function of the filter spot area A, flow rate Q and time Δt:

$$b_{ATN} \equiv \frac{A}{Q}\frac{\Delta ATN}{\Delta t} \qquad (2)$$

Due to sampling artifacts the aerosol attenuation coefficient b_{ATN} needs to be corrected in order to calculate the “real” aerosol absorption coefficient b_{abs}. The first sampling artifact occurs when the filter is relatively unloaded with particles. The light beam can then be scattered within the filter fibers and thus the intensity I will be affected. The second sampling artifact is due to the “shadowing effect”, which occurs as the filter gets highly loaded with particles, the light absorbing particles in the filter absorbs a higher fraction of the scattered light. As a consequence there is a reduction of the optical path in the filter, which means that lower attenuation coefficients are measured for filter with high particle loading than for filters with low particle loadings (Weingartner et al. 2003). There are several developed methods available for correcting this artifact (Arnott et al. 2005; Collaud Coen et al. 2010; Weingartner et al. 2003; Virkkula et al. 2007; Müller et al. 2011). However, new in-built techniques allow modern aethalometers to correct for this shadowing effect automatically (Magee Scientific, 2013). By measuring the attenuation of two parallel filter spots simultaneously from the same air beam but with different accumulation rates, i. e. different *ATN*, it is possible to derive a “loading compensation parameter” which correct the *ATN* (Magee Scientific, 2013). In modern aethalometers this correction is made for all seven wavelengths in real time.

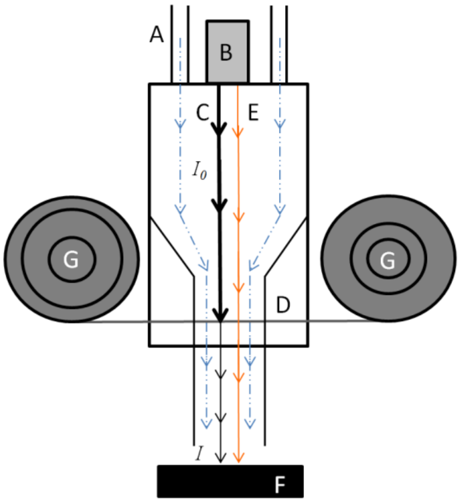

Figure 2. Schematic picture of the aethalometer. Ambient air is pumped into the instrument (A) and is then led through the filter (D). A light source (B) emits a beam of light with one or several wavelengths (depending on model). The initial light beam (C) has the intensity I_0 and I after passing through the filter (D). A reference beam (E) is lead directly to the photo detector (F) and thus not through the filter. The filter is automatically switched to a new spot by rotation of the filter tape (G).

Spectral Dependence

Modern aethalometers measure the attenuation of seven wavelengths simultaneously by using seven different LED-lamps (see Table 1.). This feature makes it possible to study aerosols with different optical properties. For several years it was thought that light absorbing carbon (LAC) was equivalent with black carbon (BC) which has the same optical and compositional properties as soot. This assumption led to that aerosol light absorption was usually measured with a single wavelength assuming BC to be the primary absorber of light. For instance, older models of PSAPs and aethalometers measured at 570 nm and 880 nm respectively (Kirchstetter et al. 2004). However, recently the brown carbon has gained a lot of attention due to the fact that it also absorbs light, and thus may also heat the atmosphere.

Table 1. Wavelengths and corresponding colors used by modern aethalometers.

Wavelength (nm)	370	470	520	590	660	880	950
Color	Ultraviolet	Blue	Green	Yellow	Red	Infrared 1	Infrared 2

It also seems that there is a dependence in absorption due to wavelength (λ). Brown carbon absorbs light more efficiently in the short wavelengths (370-470 nm) while the BC do not show spectral dependence (Kirchstetter et al. 2004). The dependence of aerosol light absorption on wavelength is given by a power law relationship:

$$\sigma = K \cdot \lambda^{-\alpha} \qquad (3)$$

where σ is the spectrally dependent mass absorption effiency, K is a constant, λ is the wavelength of light and α the absorption Ångström exponent. α is measure of strength of the spectral dependence in the light absorption by aerosols. Kirchstetter et al. (2004) measured the attenuation of aerosols sampled on filters from a heavily trafficked road and from firewood burning and compared those with respect to spectral dependence. They found that the firewood burning aerosols had a strong spectral dependence (α=2.5), especially in the UV-blue spectra. Aerosols from the heavily trafficked road showed less spectral dependence (α=1). By using acetone to evolve OC from the filters with firewood aerosols and compare the absorption with and without acetone treatment Kirchstetter et al. (2004) also showed that the high spectral dependence was mainly due to OC. The acetone treatment decreased the α from an average of 2.0 to 1.2.

Source Apportionment using Aethalometer

The fact that there is a difference in spectral dependence in absorption between biomass and fossil, i.e. diesel, aerosols opens up possibilities for using the aethalometer to apportion sources of carbonaceous aerosols. Below are some examples demonstrating how the aethalometer has been used in source apportionment.

Yang et al. (2011) used a two wavelength (370, 880 nm) aethalometer together with levoglucosan measurements for source apportionment in Rochester, US. By simply subtracting the measured light absorbing particle concentration from 370 nm (BC_{370nm}) to 880 nm (BC_{880nm}) Yang et al. (2011) got an indicator (Delta-C) of biomass burning:

$$\text{Delta-C} = BC_{370nm} - BC_{880nm} \tag{4}$$

There was a clear annual trend (r=-0.78) showing that residential biomass burning (Delta-C) increased during the cold winter months and decreased in the summer. They also found good agreement between levoglucosan concentrations and Delta-C values (r=0.89), suggesting that Delta-C is an indicator of biomass burning.

Together with a tapered element oscillating microbalance (TEOM), which measures mass of aerosols, Yang et al (2011) was able to apportion 17.3 % of the $PM_{2.5}$ concentration to residential wood burning during wintertime. This study stresses the fact that a well conducted source apportionment needs to be performed with various methods and instruments.

Several studies on aerosols and trace gases have been made in alpine valleys (Albinet et al. 2008; Gaeggeler et al. 2008; Sandradewi et al. 2008; Weimer et al. 2009), mainly due to the interest of the pollutant emitting villages that are situated in the very bottom of a valley surrounded by steep mountains and hills. This environment creates strong and permanent temperature inversions during the winter. Temperature inversions are created when the ground temperature is colder than the above air mass, warmer emissions of pollutants are not able to raise and be transported away but instead stays as a layer over the emission sources (Jacob, 1999). Sandradewi et al. (2008) conducted a study during the summer and winter periods of 2004 and 2005 in Roveredo, a 2000 inhabitant village in a Swiss alpine valley where about 77 % of the houses uses wood burning for residential heating during winter. The aim of the study was to investigate the variability and diurnal cycles of the aerosol light absorption and the Ångström exponent (α) with a 7-wavelength aethalometer. Compared to Yang et al. (2011) (see above), Sandradewi et al. (2008) used a different method to describe the temporal variability of the aerosol optical properties. They calculated the mean α of all wavelengths (370-950 nm) during summer and winter and could show that the residential wood burning in the winter had significant impact on the α. During the winter campaign α were between 1.2 and 2.0 with strong diurnal cycles whereas the value of α during the summer campaign was 0.96 to 1.13 with weak diurnal cycles. The aerosol absorption coefficient b_{abs} was also increased during the winter measurements, especially b_{abs}(370 nm) which measures in the UV-blue spectra.

Aethalometer data may also be used for modeling long range transport of atmospheric aerosols. Hyvärinen et al. (2011) measured black carbon concentrations with aethalometers or MAAPs at five different sites in Finland. The BC concentration was measured at 880 nm, which is one of the operating wavelengths of the aethalometer that is most efficiently absorbed by BC. They found that the BC concentrations for each station were generally higher during southerly winds. By using a trajectory model Hyvärinen et al. (2011) were able to identify the geographic source region of the measured BC to Central and Eastern Europe. Emission inventory data was then used to deduce strength of different sources of BC.

Conclusions

The aethalometer is a comprehensive and powerful instrument in atmospheric research. To measure real-time aerosol absorption with multiple wavelengths with minimum maintenance is an important strength in the instrument. Modern aethalometers allow direct and automatic correction for sampling and filter artifacts which made manually is a time consuming performance.

The spectral dependence of light absorption by aerosols, especially for aerosols from biomass burning which absorbs efficiently in the UV-blue spectra, is very useful and applicable in source apportionment. This dependence allows for rapid differentiation between contributions of biomass burning and traffic emissions to carbonaceous aerosol. Although, it is worth to note that a high quality source apportionment is not conducted solely by one instrument. A combination of data from aethalometer, organic tracers, aerosol-MS, ^{14}C-analysis and TOA would together enable a comprehensive source apportionment.

Since BC and brown carbon are possible climate enhancers it is of great importance to measure these particles and determine their origin. If these particles have a locally, regionally or globally effect on the climate accurate measurement data are crucial for decisions regarding emission limits, regulations etc.

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