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Atmospheric Chemistry and Physics Discussions

Comparison of several wood smoke markers and source apportionment methods for wood burning particulate mass

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Abstract

Residential wood combustion has only recently been recognized as a major contributor to air pollution in Switzerland and in other European countries. A source apportionment method using the aethalometer light absorption parameters was applied to five winter campaigns at three sites in Switzerland: a village with high wood combustion activity in winter, an urban background site and a highway site. The particulate mass from traffic ($PM_{traffic}$) and wood burning (PM_{wb}) emissions obtained with this model compared fairly well with results from the ^{14}C source apportionment method. PM_{wb} from the model was also compared to well known wood smoke markers such as anhydrosugars (levoglucosan and mannosan) and fine mode potassium, as well as to a marker recently suggested from the Aerodyne aerosol mass spectrometer (mass fragment m/z 60). Additionally the anhydrosugars were compared to the ^{14}C results and were shown to be comparable to literature values from wood burning emission studies using different types of wood (hardwood, softwood). The levoglucosan to PM_{wb} ratios varied much more strongly between the different campaigns (4–13%) compared to mannosan to PM_{wb} with a range of 1–1.5%. Possible uncertainty aspects for the various methods and markers are discussed.

1 Introduction

Biomass combustion is a major global source of particulate matter (PM) in the atmosphere with significant impacts on regional air quality, visibility, ecosystems, human health, and global climate (e.g., Penner et al., 1992; McKenzie et al., 1995; Hobbs et al., 1997; Riebau and Fox, 2001; Wu et al., 2002; Abas et al., 2004; Reid et al., 2005). Large scale forest or savanna fires are mainly due to long periods of dry season or deforestation for land-use. Wood combustion in residential areas is commonly used for heating (and cooking) during cold winter seasons. Wood is an attractive energy source since it is renewable and relatively easy to obtain, unlike fossil fuel which is

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mostly an imported good and has a relatively high price uncertainty. In various regions, the aerosol burden from residential wood combustion in winter contributes significantly to the total organic mass and/or the submicron particulate mass (Ward et al., 2006a; Puxbaum et al., 2007; Szidat et al., 2007; Alfarra et al., 2007; Lanz et al., 2008). Particulate matter from wood combustion contains mostly organic material (Fine et al., 2002; Jordan and Seen, 2005) which causes adverse health effects (Li et al., 2003; Pope and Dockery, 2006; Chow et al., 2006). Therefore source apportionment of the particulate sources is important for developing and implementing action plans for air quality improvement.

The source apportionment methods for discriminating wood burning aerosols from other sources such as traffic or secondary organic aerosols include the usage of radioactive carbon isotope (^{14}C) determination (Currie et al., 1994; Szidat et al., 2006 and 2007) and chemical mass balance receptor models using source-specific emission rates profiles of various tracer compounds (e.g., Schauer et al., 1996 and 2000; Watson, 1984; Hedberg and Johansson, 2006). Recently the use of positive matrix factorization (PMF2) and the multilinear engine (ME-2) applied to aerosol mass spectrometer data allowed for a more detailed source apportionment at high time resolution (Lanz et al., 2007 and 2008).

Specific markers are associated with the presence of wood smoke particulate matter. For example, levoglucosan, a product of thermal degradation (pyrolysis) of cellulose (e.g., Simoneit et al., 1999; Fine et al., 2002), is found in relatively high concentrations in wood smoke particles and is detected even after long-range global transport (Simoneit and Elias, 2001) or in sediment cores (Elias et al., 2001), making it a good and widely used marker of biomass burning aerosol. It is accompanied by other anhydrosugars such as mannosan and galactosan yet at lower amounts. Schneider et al. (2006) and Alfarra et al. (2007) introduced the mass fragment 60 (m/z 60) measured by a quadrupole aerosol mass spectrometer (Q-AMS) (Canagaratna et al., 2007) to be a specific marker for wood burning aerosols. Additionally the Q-AMS provides a qualitative measure of the potassium content in the fine aerosol (particle diameter

≤1 μm). Fine potassium, however, is not a unique wood smoke tracer since it is also found in fine particle emissions from meat cooking (Schauer et al., 1999), among others. In addition to these chemical markers, an optical method using the principle of aerosol light absorption has also been shown to qualitatively measure the presence of wood smoke versus traffic aerosols (Kirchstetter et al., 2004; Hoffer et al., 2006; Sandradewi et al., 2008a).

Sandradewi et al. (2008b) recently introduced a method to quantitatively attribute the particulate matter contribution from traffic exhaust and wood burning, using the different light absorption characteristics of these sources. In this paper we provide a comparison of various markers and some recently developed methods to estimate the wood burning contribution to particulate matter. This includes the aethalometer method, the ^{14}C analyses (Szidat et al., 2007), other wood smoke markers such as m/z 60 and potassium from the aerosol mass spectrometer (Alfarra et al., 2007; Lanz et al., 2008), as well as levoglucosan and mannosan (anhydrosugars) for five different field campaigns during winter time at three different sites.

2 Field measurements and instrumentation

Table 1 summarizes the five campaign periods where data were obtained, along with the site characteristics and the associated main instruments.

The aethalometer (AE31, Magee Scientific) measures the aerosol light absorption at seven wavelengths ranging from 370–950 nm. The real aerosol absorption coefficients were calculated and corrected following the procedure by Weingartner et al. (2003). Data logging took place every 2 min.

The high volume samplers (HIVOL, DA-80, Digitel) collected the aerosol on preheated quartz fiber filters (Szidat et al., 2007) at a flow rate of 0.5 m^3/h. During the Roveredo January and March 2005 campaigns, one HIVOL unit sampled between 6–14 h and a second one between 18-02h to differentiate between the morning and evening periods. In the last three campaigns, sampling was performed for 24 h. The

HIVOLs were equipped with PM1 size-cut inlets except during the Roveredo January 2005 and Reiden February 2006 campaigns where they had PM10 size-cut inlets.

The quadrupole aerosol mass spectrometer (Q-AMS, Aerodyne) characterizes the composition of the submicrometer, non-refractory aerosol particles at a high time resolution. Canagaratna et al. (2007) gives the details of the operating principle of the Q-AMS. A collection efficiency (CE) value needs to be applied in order to determine the absolute mass concentrations of the aerosol components (Alfarra et al., 2004). A CE of 0.5 was applied for all campaigns data, except during the Roveredo November-December 2006 campaign where a CE value of 0.7 was used (Alfarra et al., 2007).

3 Wood burning markers and quantification methods

This section summarizes what kind of markers each methods is using, the assumptions made and parameters used to determine the particulate matter from wood burning activity (PM_{wb}).

3.1 The aethalometer model

The quantification of wood burning PM, PM_{wb}, using an optical method such as the aethalometer takes advantage of the enhanced absorption in the ultraviolet and visible wavelengths region (370–520 nm) due to the abundant UV-absorbing organic compounds contained in wood smoke aerosols. In traffic-related aerosol or diesel soot, a significant lower increase in light absorption is observed at these wavelengths. Sandradewi et al. (2008b) introduced an aethalometer model which is a linear regression of the PM1 carbonaceous material with respect to the aerosol absorption coefficients at different wavelengths of particles from wood burning and traffic allowing a quantification of PM_{wb} and $PM_{traffic}$.

In this paper, we use values derived by Sandradewi et al. (2008b) for the absorption exponent at 470 and 950 nm ($\alpha_{470\,nm,950\,nm}$) of traffic and wood burning to be 1.10 and

1.86, respectively, and apply the aethalometer model on the Roveredo November–December 2005 data. Thus we have the following equations:

$$\frac{b_{abs}(470\,\mathrm{nm})_{woodburning}}{b_{abs}(950\,\mathrm{nm})_{woodburning}} = \left(\frac{470\,\mathrm{nm}}{950\,\mathrm{nm}}\right)^{-1.86} \quad (1)$$

$$\frac{b_{abs}(470\,\mathrm{nm})_{traffic}}{b_{abs}(950\,\mathrm{nm})_{traffic}} = \left(\frac{470\,\mathrm{nm}}{950\,\mathrm{nm}}\right)^{-1.1} \quad (2)$$

$$b_{abs}(950\,\mathrm{nm}) = b_{abs}(950\,\mathrm{nm})_{traffic} + b_{abs}(950\,\mathrm{nm})_{woodburning} \quad (3)$$

$$b_{abs}(470\,\mathrm{nm}) = b_{abs}(470\,\mathrm{nm})_{traffic} + b_{abs}(470\,\mathrm{nm})_{woodburning} \quad (4)$$

$$\mathrm{OM}_{AMS} + BC_{Aeth} = \underbrace{c1 * b_{abs}(950\,\mathrm{nm})_{traffic}}_{\mathrm{PM}_{traffic}} + \underbrace{c2 * b_{abs}(470\,\mathrm{nm})_{woodburning}}_{\mathrm{PM}_{wb}} + \mathrm{others} \quad (5)$$

b_{abs} is the absorption coefficient at a certain wavelength, OM_{AMS} is the organic mass measured by the AMS, BC_{Aeth} is the black carbon measured at 880 nm by the aethalometer. The regression constants $c1$ and $c2$ were calculated to be $2.6\times10^5\ \mu\mathrm{g/m^2}$ and $6.3\times10^5\ \mu\mathrm{g/m^2}$, respectively.

In Roveredo during winter, most of the particulate matter is of primary origin (Szidat et al, 2007; Alfarra et al., 2007) and, therefore, the third term in Eq. (5) is negligible. However, this may not be the case in Zurich and Reiden since more secondary organic aerosol is present at these sites (Lanz et al., 2008).

3.2 ^{14}C method

Punches from the HIVOL quartz filters were analyzed for its organic carbon (OC) and elemental carbon (EC) contents following the procedure in Szidat et al. (2004a). CO_2 from thermal oxidation of OC and EC was cryogenically trapped and measured for ^{14}C

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with accelerator mass spectrometry (Szidat et al., 2004b, Jenk et al., 2007). The total carbon (TC), OC and EC concentrations were determined offline using the thermal optical transmission method of the Sunset Laboratory OCEC Analyzer with a temperature program comparable to the NIOSH 5040 protocol (Birch and Cary 1996; Chow et al., 2001). Combining the results from both methods, we obtained the concentration of EC_{fossil}, $EC_{nonfossil}$, OC_{fossil} and $OC_{nonfossil}$. Unlike $EC_{nonfossil}$ which can be attributed mostly to wood burning sources, $OC_{nonfossil}$ may consist of OC_{wb} (primary emission from wood burning) and $OC_{biogenic}$(secondary organic aerosol from the oxidation of gaseous biogenic volatile organic compounds, and primary biogenic organic particles, which are probably often negligible). To discriminate between the two major $OC_{nonfossil}$ sources, an average literature value of $(EC/OC)_{wb}$=0.16±0.05 is used (Szidat et al., 2006).

In Roveredo, it was not possible to discriminate $OC_{biogenic}$ from OC_{wb} due to the overwhelming contribution of aerosols from the latter. However, in Zurich (urban background) and Reiden (highway) we observed significant $OC_{biogenic}$ contributions (>40%) in several HIVOL samples analyzed for ^{14}C.

3.3 AMS m/z 60 and potassium

Alfarra et al. (2007) reported the presence of mass fragment (m/z) 60 in ambient air with a dominant wood burning contribution in winter, during laboratory wood burning experiments using small stoves (see also Weimer et al., 2008) and in levoglucosan mass spectra. Therefore, this mass fragment was recommended as a suitable marker for wood burning aerosols, especially as it was not observed in mass spectra taken near a highway site in summer (Alfarra et al., 2007). The ratio of AMS organic mass to m/z 60 was computed to be 36 in the Roveredo December 2005 evening periods. Alfarra et al. (2007) showed that this factor was also similar for summer time conditions when open air fires are the main wood burning particle source. Nevertheless, this factor might vary a lot in individual fires during different burning conditions and for different

wood ovens (Weimer et al., 2008). The value in Roveredo can be regarded as an average factor over all burning conditions for mostly simple wood stoves.

The emission factors of potassium during wood burning have been shown to be strongly influenced by the combustion temperature. Wood combustion at low temperature result in less potassium mass per unit fine particles emitted, and vice versa (Khalil and Rasmussen, 2003). The AMS measures potassium yet as a qualitative parameter due to the incomplete volatilization of KCl and K_2SO_4, and the production of K^+ ions by surface ionization. For the Zurich winter campaign in January 2006, a marked degree of correlation (r^2=0.67) between OM_{wb} determined by factor analysis and the measured AMS potassium was reported (Lanz et al., 2008).

3.4 Anhydrosugars (levoglucosan and mannosan)

Levoglucosan is the most abundant anhydrosugar measured in wood smoke aerosol. For the analysis of levoglucosan and other anhydrosugars, filter punches with a diameter of approximately 20 mm were taken from selected HIVOL filters, extracted with Milli-Q water in an ultrasonic bath and analyzed with a HPLC method with a column for carbohydrate separation (Puxbaum et al., 2007; Caseiro et al., 2007). The highest concentration was found for levoglucosan, followed by mannosan yet at a much lower level. Galactosan, glucose and fructose were also detected but at negligible concentrations.

4 Results and discussion

4.1 The aethalometer model versus ^{14}C method

Using Eqs. (1)–(4), we solve for the absorption coefficient at 950 nm due to traffic ($b_{abs}(950\,nm)_{traffic}$). The absorption coefficient and equivalent BC concentration calculated at 950 nm is within 5% difference to those values calculated at 880 nm, which is the commonly used wavelength for BC measurement. The ratio

of $b_{abs}(950\,nm)_{traffic}/b_{abs}(950\,nm)_{total}$ was determined and compared to the ratio of EC_{fossil}/EC_{total} ratio obtained with the ^{14}C method on the selected HIVOL filters. The correlation plot displays a slope=1.1 and r^2=0.8 (Fig. 1a). This confirms that the choice of the absorption coefficients of $\alpha_{traffic}$=1.1 and $\alpha_{woodburning}$=1.86 in Eq. (2) gives a relatively good agreement between the two methods concerning the traffic contribution to BC respectively EC.

Szidat et al. (2006 and 2007) used an average $(OC/EC)_{wb}$ of 6.25 and an average organic mass to OC ratio (OM/OC) for non-urban and wood-smoke aerosols of 2.25, resulting in $(OM/EC)_{wb}$=14.1, which further corresponds to $(PM/EC)_{wb}$=15.2 neglecting the emissions of salts. These emission ratios are highly influenced by the combustion processes and wood types. In Fig. 1b, we compare the particulate matter due to wood burning (PM_{wb}) from the aethalometer model with the $EC_{nonfossil}$ from the ^{14}C method resulting in a correlation slope ($PM_{wb}/EC_{nonfossil}$)=11.7 and r^2=0.7. This is somewhat lower than the expected $(PM/EC)_{wb}$ ratio applied on the ^{14}C method but well within the range of the published ranges of these $(OM/OC)_{wb}$ and $(EC/OC)_{wb}$ ratios (Table 3 in Szidat et al., 2006). Additionally, the comparison between the aethalometer model and the ^{14}C method shows no significant influence from the different inlet size-cuts used among the campaigns.

4.2 Aethalometer model versus AMS markers (m/z 60, potassium)

The time series of PM_{wb} from the aethalometer model show similar trends as the ones for m/z 60 and potassium measured by the AMS (Fig. 2). The slope of the correlation of PM_{wb} to m/z 60 in Roveredo November–December 2005 (Table 2) is comparable to the published value of 36 (Alfarra et al., 2007) obtained with the data from Roveredo in December 2005 during the evening hours when wood burning activity was at its highest.

However, the campaigns in Roveredo March 2005, Zurich and Reiden deliver a much higher PM_{wb} to m/z 60 ratio, i.e. between 50–60. Variations in the PM_{wb} to m/z 60 ra-

tio could be due to the different combustion processes or wood types used between the northern (Zurich and Reiden) and southern (Roveredo) regions of the Alps. Another reason for this discrepancy could be that the organics forming m/z 60 in the ionization of the AMS are not chemically stable, which would explain why we observe a higher PM_{wb} to m/z 60 ratio during early spring (March) in Roveredo when the temperature inversion layer breaks during the day allowing for more vertical mixing and photochemical reactivity. As Alfarra et al. (2007) pointed out, levoglucosan contributes significantly to m/z 60 in the aerosol mass spectrometer. This could thus mean that also levoglucosan is not as stable as commonly thought (see Sect. 4.3). Another possible explanation could be that secondary organic aerosols formed from gaseous woodburning exhaust might as well be associated with increased light absorption at low wavelengths.

Significant correlations ($r^2 \geq 0.6$) between PM_{wb} and AMS potassium were only found for Roveredo in winter and Zurich. The highest ratios between PM_{wb} and AMS potassium were measured during the Roveredo November–December 2005 campaign. This might indicate that the wood stoves in this area indeed are not of high standard and are operated at rather poor combustion conditions with high carbonaceous and thus lower relative potassium emissions (Khalil and Rasmussen, 2003). In Zurich, lower PM_{wb} to potassium ratios suggest that the wood stoves in this region are of better technology and allow for more complete combustion of the carbonaceous material.

4.3 Anhydrosugars versus ^{14}C results

The selected HIVOL filters were analyzed for their anhydrosugars content. Levoglucosan, a widely proposed organic tracer for wood smoke, had the highest concentration, followed by mannosan. The average ratio of levoglucosan to mannosan in the Roveredo filters is computed to be 10.1 (PM_{10} and PM_1 filters combined), while it is 3.3 in Zurich and 3.4 in Reiden. Schmidl et al. (2007) reported a levoglucosan/mannosan ratio of around 14–15 for hardwoods and 3.6–3.9 for softwoods burned in a domestic tiled stove. Thus, if the wood type were to be the only determining factor, then the levoglucosan to mannosan ratio in Roveredo could be attributed to the significant

use of hardwood, while the ratio in Zurich and Reiden would point to combustion of softwood. Indeed, based on a statistical report from 2005, approximately 95% of the firewood used in Roveredo are of hardwood type such as beech, chestnut, birch, etc. (H. P. Lötscher, personal communication). In contrast, approximately 60% of the forest wood in canton Zurich are softwood (Source: http://www.wald.kanton.zh.ch), which suggests that the households in this region have easier access to softwood than to hardwood.

For comparison of the levoglucosan and mannosan data with the ^{14}C results, the Roveredo campaigns data is treated as one group (representing regions south of the Alps), and Zurich and Reiden as a second group (representing regions north of the Alps). Figure 3a and b show high correlation coefficients ($r^2 \geq 0.8$) between the levoglucosan concentration and OC_{wb} and EC_{wb}. The values of the correlation slopes between the two data groups differ from each other by a factor of 3. However, they are well within the range of published values from several wood combustions studies summarized in Table 3. The relatively wide range of emission ratios can be attributed to the different wood types burned and the combustion process (e.g. Johansson et al., 2004; Engling et al., 2006; Schmidl et al., 2007). Fine et al. (2002) reported values for the levoglucosan to OC ratio of 0.14 for hardwood and 0.04 for softwood typical of the southern US. Assuming that the wood type is the only determining factor, then the levoglucosan/OC_{wb} ratio of 0.19 in Roveredo is comparable to that of hardwood while the value of 0.06 in Zurich and Reiden is comparable to that of softwood.

Mannosan which is almost one order of magnitude lower in concentration than levoglucosan is compared with OC_{wb} and EC_{wb} in Fig. 3c and d. The correlation coefficients r^2 are around 0.5, except for the one of mannosan versus OC_{wb} in Roveredo (r^2=0.8). No significant differences are observed in the slope values among Roveredo, Zurich and Reiden. If one uses all data for the correlation, r^2 between mannosan and OC_{wb} is 0.7 and r^2 between mannosan and EC_{wb} 0.5. A possible explanation for this is that the levoglucosan emission is more dependent on burning conditions and fuel types than mannosan. Possibly levoglucosan is also less stable concerning chemical

degradation in the atmosphere. Chemical processes such as acid-catalyzed polymerization and hydroxyl radical reactions could partly explain the absence of levoglucosan in aerosols known to originate from biomass burning (Holmes and Petrucci, 2006, Gao et al., 2003).

Note that more HIVOL filters were analyzed for anhydrosugars than for ^{14}C content, therefore the statistical analysis in this subsection is limited to the number of HIVOL filters analyzed with the ^{14}C method.

4.4 Anhydrosugars (levoglucosan, mannosan) versus aethalometer model

The anhydrosugar concentrations are compared with PM_{wb} from the aethalometer model in Fig. 4. The ratio of PM_{wb} to levoglucosan and PM_{wb} to mannosan in terms of the correlation slopes are summarized in Table 4. The levoglucosan to PM_{wb} ratios vary among the three Roveredo campaigns but are generally higher than in Zurich and Reiden. This could be due to the already discussed variation and uncertainties in the levoglucosan emissions (Sect. 4.3), but also in the choice of α_{wb}=1.86 used in Eq. (1). The levoglucosan to PM_{wb} ratios computed in Zurich and Reiden are similar to each other, i.e. 0.04 and 0.05 respectively. The mannosan to PM_{wb} ratios are similar for all five campaigns, i.e. 0.011–0.015. However, lower correlation coefficients ($r^2 \leq 0.5$) were observed in the Roveredo November–December 2005 and Reiden campaigns.

5 Conclusions

We applied the aethalometer model which uses the aerosol light absorption at different wavelengths for quantification of particulate matter from traffic and wood burning ($PM_{traffic}$, PM_{wb}) at three sites in Switzerland: a village in an Alpine valley with high wood burning activity, an urban background site and a highway site.

The results of the aethalometer model agree statistically well with the ^{14}C source apportionment method. The PM_{wb} from the model showed similar time series as m/z

60 and potassium measured by the AMS. However, differences in the correlation slopes and correlation coefficients may be influenced by wood combustion processes, the wood type used, and aging processes of the wood smoke. The wood smoke tracers from the AMS data (m/z 60, potassium) may be influenced by the atmospheric stability of the organics forming m/z 60 which is unknown at this point, and the incomplete volatilization of KCl and K_2SO_4, and the production of K ions by surface ionization.

The results of the comparison between the anhydrosugars and ^{14}C method could be explained by the different wood types used. However the possible influence of various wood burning conditions or technology among these study sites should not be neglected. Additionally, recent studies suggest that levoglucosan may not be so stable in the atmosphere, changing its concentration in the atmosphere with time. The ratios of levoglucosan/mannosan, levoglucosan/OC_{wb}, levoglucosan/EC_{wb}, mannosan/OC_{wb} and mannosan/EC_{wb} are comparable to published values from recent biomass combustion emission studies.

The ^{14}C method and aethalometer model as source apportionment methods have uncertainties due to the choice of emission ratios or constants used, e.g. the OM/OC or OC/EC ratios used in the ^{14}C method, or the wood burning absorption exponent (α_{wb}) chosen for the aethalometer model.

In spite of some variability in these correlations which are not fully understood yet (especially the comparison with wood smoke markers), the potential of using an aethalometer for wood smoke particulate mass determination is worth further research considering it is reasonably priced, gives a high resolution data output (minutes), and requires minimal attention in the field. Furthermore, studies on wood smoke in smog chambers could provide information on the atmospheric stability of m/z 60 and levoglucosan. Additionally, smog chamber studies are needed to determine how secondary organic aerosols from wood combustion affect the aerosol light absorption measured by the aethalometer.

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Table 1. Campaign details with site characteristic and instrumentation.

Campaigns	Site characteristic	Instrumentation
Roveredo 3–24 January 2005 Roveredo 1–16 March 2005 Roveredo 24 November–15 December 2005	Village in an Alpine valley with~77% households using wood stoves in winter	aethalometer, HIVOL*
Zurich 6–25 January 2006	Urban background	aethalometer, HIVOL*, Q-AMS
Reiden 27 January–15 February 2006	Highway	

* High volume filter samplers; selected HIVOL filters were analyzed for the fossil and non-fossil fractions of OC and EC using the ^{14}C method and for their anhydrosugar content.

Table 2. Slope and correlation coefficient (r^2) values for Fig. 2. The slopes are given in bold when r^2 was at least 0.5.

Campaign	PM_{wb} versus m/z 60	PM_{wb} versus AMS Potassium
	Slope (r^2)	
Roveredo November–December 2005	**32.2** (0.65)	**16.8** (0.72)
Roveredo March 2005	58.2 (0.49)	9.6 (0.26)
Zurich January 2006	**59.4** (0.88)	**8.9** (0.67)
Reiden February 2006	**51.3** (0.60)	8.2 (0.30)

Table 3. Emission ratios of levoglucosan, mannosan, EC, and OC from different types of biomass combustion compiled from recent studies.

Levo/Mann	Levo/OC	Levo/EC	Mann/OC	Mann/EC	
2.5–14.6	0.08–0.3	0.2–1.5	0.01–0.1	0.01–0.4	Schmidl et al., 2007[a]
	0.06–0.2	0.3–2.2			Szidat et al., 2006[a,b]
	0.01–0.1	0.01–0.3			Mazzoleni et al., 2007[c]
4.8–5.6					Ward et al., 2006b[d]
0.1–52.3	0.04–0.7		0.01–0.2		Engling et al., 2006[e]
1.9–12.3	0.05–0.2	0.3–2.1	0.01–0.03	0.09–0.2	This study

All values are reported in [w/w]
[a] softwood and hardwood combustions in a domestic tiled stove
[b] and references therein
[c] residential and agricultural fireplace with various wood types
[d] Montana wildfire
[e] wood combustion experiment with various fire and combustion processes, excluding grass, sage and needles.

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Table 4. Summary of slope and r^2values from Fig. 4 for PM_{wb}, levoglucosan and mannosan.

Campaign	Levoglucosan / PM_{wb} Slope (r^2)	Mannosan / PM_{wb} Slope (r^2)
Roveredo January 2005	0.13 (0.9)	0.013 (0.8)
Roveredo March 2005	0.10 (0.9)	0.010 (0.9)
Roveredo November–December 2005	0.06 (0.7)	0.011 (0.5)
Zurich January 2006	0.04 (0.9)	0.013 (0.9)
Reiden February 2006	0.05 (0.4)	0.015 (0.1)

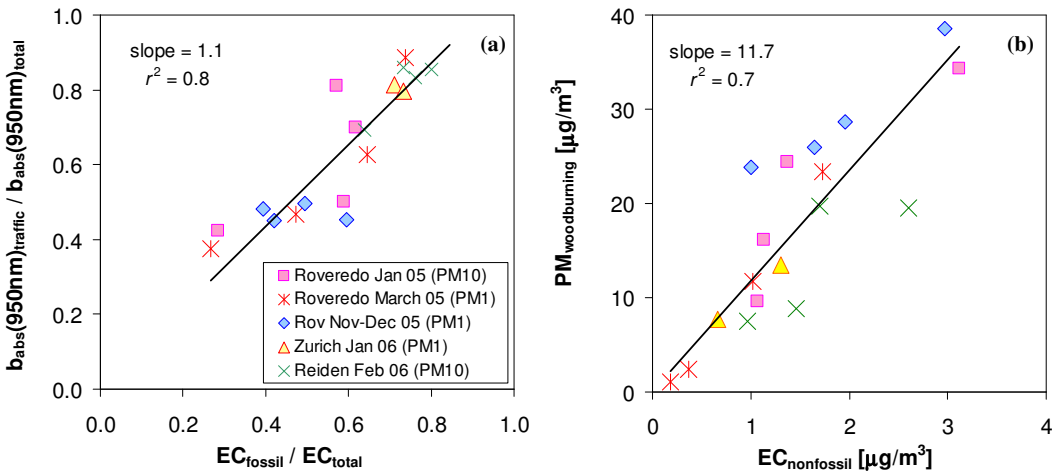

Fig. 1. (a) Correlation of the fractional light absorption at 950 nm from traffic as determined by the aethalometer and the fractional EC_{fossil} as determined by the ^{14}C method, and **(b)** correlation of the wood burning mass determined by the aethalometer and $EC_{nonfossil}$ determined by the ^{14}C method. Data are from five different campaigns at three different sites.

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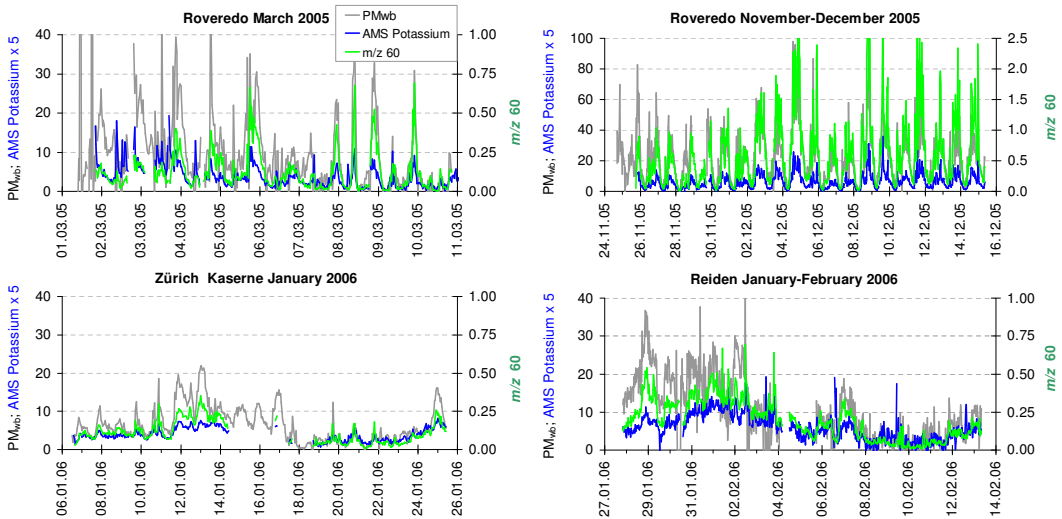

Fig. 2. Time series of aethalometer PM_{wb}[μg/m^3], AMS m/z 60 [μg/m^3] and AMS potassium for four winter campaigns. Note that AMS potassium is scaled up for graphical purposes.

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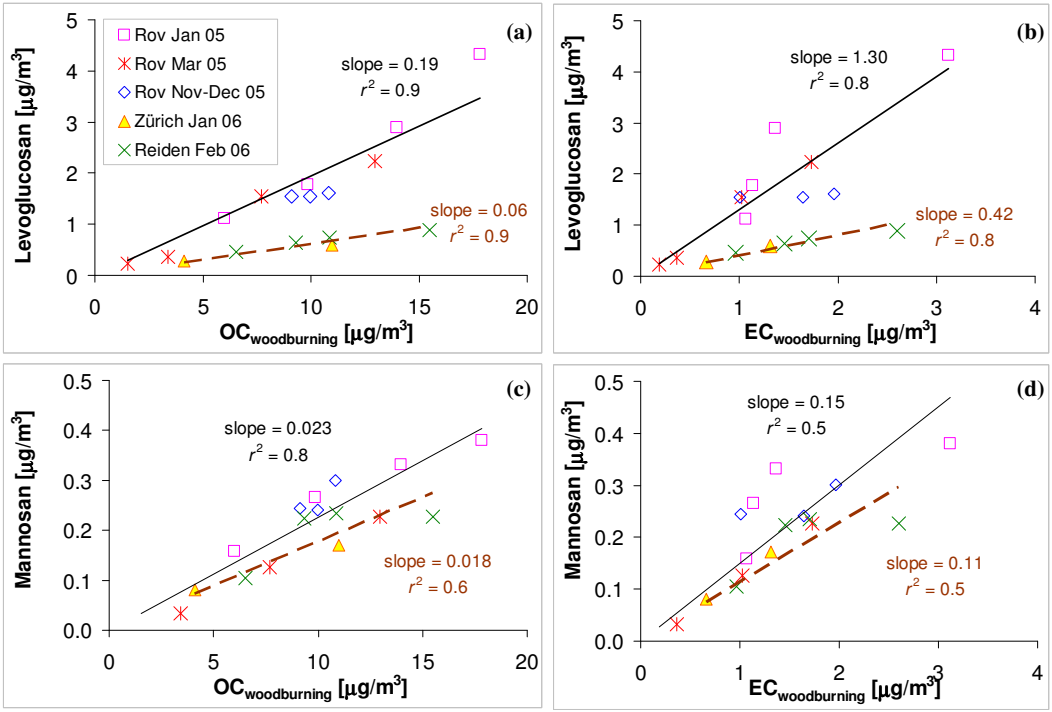

Fig. 3. Scatterplots of anhydrosugars versus ^{14}C results: (a) levoglucosan versus $OC_{woodburning}$, (b) levoglucosan versus $EC_{woodburning}$, (c) mannosan versus $OC_{woodburning}$, and (d) mannosan versus $EC_{woodburning}$. In Roveredo the contribution of $OC_{biogenic}$ to OC_{total} in winter was relatively small (<10%) so that $OC_{nonfossil} \approx OC_{woodburning}$, while for the Zürich and Reiden winter data it was not negligible thus $OC_{nonfossil} = OC_{woodburning} + OC_{biogenic}$. For EC the situation is more straightforward, i.e. $EC_{nonfossil} = EC_{woodburning}$. The solid black line indicates the correlation for the Roveredo data. The dashed brown line relates to the Reiden and Zurich data.

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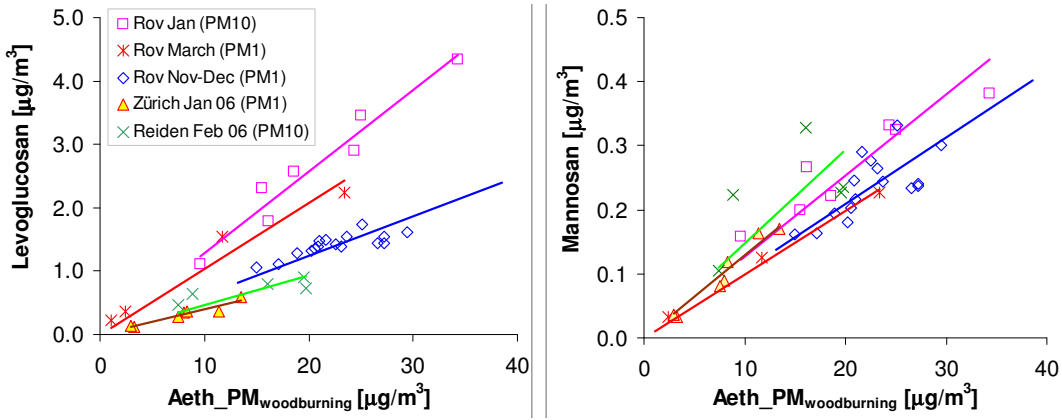

Fig. 4. Correlation of aethalometer PM_{wb} with **(a)** levoglucosan, and **(b)** with mannosan.

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