

## **A comparison of new and classic methods to estimate the contribution of wood smoke at different sites in Switzerland**

A.S.H. Prevot (1), J. Sandradewi (1), M.R. Alfarra (1), S. Szidat (2), V.A. Lanz (3), N. Perron (1), A. Caseiro (4,5), A. Kasper-Giebl, H. Puxbaum (4), U. Baltensperger (1)

(1) Laboratory of Atmospheric Chemistry, PSI, Villigen, Switzerland  
(andre.prevot@psi.ch)

(2) Department of Chemistry and Biochemistry, University of Bern 3012, Bern, Switzerland

(3) Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research, 8600 Duebendorf, Switzerland,

(4) Institute for Chemical Technologies and Analytics, Vienna University of Technology, 1060 Vienna, Austria,

(5) CESAM and Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal,

Residential wood combustion is increasingly being identified as a major contributor to air pollution at a number of sites in Switzerland and in other countries. A source apportionment method using the aethalometer light absorption parameters is 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<sub>traffic</sub>) and woodburning (PM<sub>wb</sub>) obtained with this model compared fairly well with results from the <sup>14</sup>C source apportionment method. PM<sub>wb</sub> from the model is 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 <sup>14</sup>C results and they are shown to be comparable to literature values from wood burning emission studies using different types of wood (hardwood, softwood). The levoglucosan to PM<sub>wb</sub> ratios varied much more strongly between the different campaigns compared to mannosan to PM<sub>wb</sub> with a range of 1-1.5%. Possible uncertainty aspects for the various methods and markers are discussed.

### **1. Introduction and discussion of available instrumentation**

The main contents of this contribution are currently under discussion in ACPD and all details can be found there (Sandradewi et al., 2008a). Until the conference, some of the methods described here will have been used at additional sites and will be presented. Here we present a short presentation/discussion of the main instrumentation/analyses in use by our lab and collaborators and some general conclusion and discussion.

A classical tracer for biomass burning is potassium. Potassium is released especially under high temperatures in fires mostly as potassium chloride and potassium sulfate and has been often used as indicator of biomass burning (e.g. Khalil and Rasmussen, 2003). For the organic fraction of the particulate organic matter emitted from wood burning, the most commonly used tracer is levoglucosan because it is produced from pyrolysis of cellulose which is available in every type of wood. Examples of application have been discussed by Puxbaum et al. (2007), Schauer et al. (2001), and Simoneit et al. (1999). These two marker methods rely on the quality and variability of available estimation of the emitted concentration of marker / concentration of the totally emitted mass

Recently, several new techniques have been developed to estimate contributions of different sources to particulate matter (see also Baltensperger and Prevot, 2008). These are aerodyne aerosol mass spectrometer, multi-wavelength aethalometer, and  $^{14}\text{C}$ -analyses. These techniques have in common that they take not necessarily only markers into account but use all of the organic mass or carbonaceous material information. The aerosol mass spectrometer allows for the distinction of different sources to the organic matter. Alfarra et al. (2007) could show that there are some key marker fragments ( $m/z60$  and  $m/z73$ ) that could be found both for direct emissions and in ambient air where wood burning is a very important source. Lanz et al. (2007; 2008) could then show that the wood burning spectra and their contribution to organic matter can be extracted with statistical source apportionment methods similar to PMF (positive matrix factorization). They found that in winter wood burning is an important contribution to organic mass in Zürich but also in summer the contribution can be higher than from traffic. Both in summer and winter Lanz et al. (2007; 2008) found that oxygenated (presumably secondary) organic aerosol is the major fraction in OM in Zürich. The  $^{14}\text{C}$  method developed by Szidat et al. (2006; 2007) allows for the distinction of fossil and non-fossil contribution to elemental carbon (EC) and organic carbon (OC). In the case of EC, the non-fossil fraction can directly be related to biomass burning. In the cases of OC, the non-fossil contribution is only an upper limit, because e.g. SOA from biogenic emissions and SOA from gaseous biomass burning might be important as well. The use of multi-wavelength aethalometer for source apportionment uses the fact that wood burning derived particles have a relatively higher ratio of light absorption at lower wavelengths (370-550 nm) compared to the light absorption at higher wavelengths (880-950 nm). Sandradewi et al. (2008b) developed a model on this basis and validated it with  $^{14}\text{C}$  analyses. The method distinguishes the emissions of all carbonaceous material including EC and the organic mass.

## **2. Discussion and conclusions**

The main results of Sandradewi et al. (2008a) showed that at different sites for certain time periods the different tracers correlate fairly well. However, when comparing different stations, significant differences for the various estimations of wood burning versus different wood burning marker concentrations can be found. In an Alpine valley with many poor burning systems, less potassium is found compared to other estimations. At the same location, higher levoglucosan versus PM from aethalometer or versus non-fossil carbon is found compared to measurements in Zurich, where

secondary organic aerosols were important (Lanz et al., 2008). Possible explanations might be different types of wood that were used for burning or the degradation of levoglucosan in the atmosphere which might happen at the same time when SOA is formed. More intercomparisons as those in Sandradewi et al. (2008) should be performed. More measurements of markers and woodburning indicators including all techniques presented should be performed. Also the stability of tracers of levoglucosan needs to be studied e.g. in smogchambers.

## Acknowledgements

This work was part of the AEROWOOD project funded by the Swiss Federal Office for the Environment (FOEN). We sincerely thank the staff of Empa and the environmental offices in Cantons Lucerne, Graubunden, and Zurich for their financial and general support and for providing us with the continuous monitoring data.

## References

- Alfarra, M. R., A. S. H. Prévôt, S. Szidat, J. Sandradewi, S. Weimer, V. A. Lanz, D. Schreiber, M. Mohr, and U. Baltensperger (2007), Identification of the mass spectral signature of organic aerosols from wood burning emissions, *Environ. Sci. Technol.*, 41, 5770-5777.
- Baltensperger, U., and A.S.H. Prevot (2008), Chemical analysis of atmospheric aerosols, 390, 277-280.
- Khalil, M. A. K., and Rasmussen, R. A. (2003), Tracers of wood smoke, *Atmos. Environ.*, 37, 1211-1222.
- Lanz, V. A., M. R. Alfarra, U. Baltensperger, B. Buchmann, C. Hueglin, and A. S. H. Prevot (2007), Source apportionment of submicron organic aerosols at an urban site by linear unmixing of aerosol mass spectra, *Atmos. Chem. Phys.*, 7, 1503-1522.
- Lanz, V. A., M. R. Alfarra, U. Baltensperger, B. Buchmann, C. Hueglin, S. Szidat, M.N. Wehrli, L. Wacker, S. Weimer, A. Caseiro, H. Puxbaum, and A. S. H. Prévôt (2008), Source attribution of submicron organic aerosols during wintertime inversions by advanced factor analysis of aerosol mass spectra, *Environ. Sci. Technol.*, 42, 214-220.
- Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., and Pio, C. (2007), Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, *J. Geophys. Res.*, 112, D23S05, doi:10.1029/2006JD008114.
- Sandradewi, J., A. S. H. Prévôt, M. R. Alfarra, S. Szidat, M. N. Wehrli, M. Ruff, S. Weimer, V. A. Lanz, E. Weingartner, N. Perron, A. Caseiro, A. Kasper-Giebl, H. Puxbaum, L. Wacker, and U. Baltensperger (2008a), Comparison of several wood smoke markers and source apportionment methods for wood burning particulate mass, *Atmos. Chem. Phys. Discuss.*, 8, 8091-8118.
- Sandradewi, J., A. S. H. Prevot, S. Szidat, N. Perron, M. R. Alfarra, V. A. Lanz, E. Weingartner, and U. Baltensperger (2008b), Using aerosol light absorption

measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter, *Environ. Sci. Technol.*, 42, 3316-3323.

Schauer J. J., M. J. Kleeman, G. R. Cass, B. R. T. Simoneit (2001), Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood, *Environ. Sci. Technol.*, 35, 1716-1728.

Simoneit B. R.T., J. J. Schauer, C. G. Nolte, D. R. Oros, V. O. Elias, M. P. Fraser, W. F. Rogge, and G. R. Cass (1999), Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, 33, 173-182.

Szidat, S., T. M. Jenk, H.-A. Synal, M. Kalberer, L. Wacker, I. Hajdas, A. Kasper-Giebl, and U. Baltensperger (2006), Contributions of fossil fuel, biomass burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by  $^{14}\text{C}$ , *J. Geophys. Res.*, 111, D07206, doi:10.1029/2005JD006590.

Szidat, S., A. S. H. Prévôt, J. Sandradewi, M.R. Alfarra, H.-A. Synal, L. Wacker, and U. Baltensperger (2007), Dominant impact of residential wood burning on particulate matter in Alpine valleys during winter. *Geophys. Res. Lett.*, 34, L05820, doi:10.1029/2006GL028325.