QUANTIFICATION OF MONOSACCHARIDE ANHYDRIDES BY LC/HRMS TOF-APPLICATION TO SAMPLES FROM AN URBAN AND A SUB-URBAN SITE INFLUENCED BY SMALL-SCALE WOODBURNING

K.E. YTTRI AND C. DYE

Department for Chemical Analysis, Norwegian Institute for Air Research.
P.O. Box 100, N-2027 Kjeller, Norway.

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INTRODUCTION

Water-soluble organic carbon (WSOC) accounts for 20–70% of the total carbon found in ambient air aerosols. 90% of the WSOC mass has, based on gel-permeation chromatography and HNMR, been assigned to three different groups; namely neutral/basic compounds, mono- and diacids, and polyacids (Decesari *et al*., 2001). Studies that elucidate the nature and amount of the major compounds present in these fractions are needed to improve the understanding of how they influence atmospheric chemistry and climate. Particles originating from wood burning are especially rich in WSOCs, and levoglucosan, which is a monosaccharide anhydride (MA), is so far the most ubiquitous single compound detected. In this study levoglucosan (1.6-anhydro-β-D-glucopyranose) ($C_6H_{12}O_5$) and its isomeric compounds galactosan and mannosan, have been quantified at two sites influenced by small scale biomass burning for residential heating during winter, using a LC/HRMS TOF instrument. MAs are combustion products of cellulose and hemicellulose, which are the major constituents of wood. Although not source-specific, levoglucosan can be used as a general tracer for biomass burning as it can only be emitted into the atmosphere by incomplete combustion.

METHODS

Two sampling campaigns were conducted during November – December 2001 in Oslo (urban site) and during February - March 2002 at Elverum (suburban site). Ambient air aerosols were collected using a PM_{10} unit, having a 50% cut off for aerosols with an EAD (Equivalent Aerodynamic diameter) of 10 µm. At Elverum a Berner impactor segregating aerosols into eight size fractions between 60 nm and 16 µm was operated simultaneously. The aerosols were collected on pre-fired (850ºC, 3.5 h) quartz fibre filters (Whatman Q-MA). The filters were stored at -30ºC before being subjected to analysis. Prior to analysis parts of the filters (1-1.5 cm^2) were soaked in tetrahydrofuran (2 ml) and subjected to ultrasonic bath (30 min). The extracts were filtered trough a syringe filter (0.45 µm) to remove particulate matter and filter parts. Each filter was extracted twice, and prior to analysis the sample solvent elution strength was adapted to the mobile phase by adding ultrarinsed Milli-Q water. The LC/HRMS TOF instrument was operated in negative electrospray mode. Reversed phase C18 chromatography was selected as separation technique for the MAs.

RESULTS

The average ΣMA (galactosan, levoglucosan and mannosan) concentration for Oslo and Elverum was 201 ng m^{-3} and 544 ng m^{-3}, respectively. The campaign in Oslo was conducted 1-2 months prior to the expected peak of emission from wood burning for residential heating, explaining the absence of MAs in some of the samples from this site. The maximum ΣMA-concentration recorded was 614 ng m^{-3} in Oslo and 1240 ng m^{-3} at Elverum. In Oslo, levoglucosan accounted for 79% of the ΣMA, whereas mannosan and galactosan accounted for 20% and 1%, respectively. The corresponding splits at Elverum were approximately the same, with levoglucosan, mannosan and galactosan accounting for 77%, 22% and 1%, respectively. At Elverum ΣMA accounted for 8.6% of the OC concentration and 3.3% of the PM_{10} mass concentration (Se Table 1). Quite high regression coefficients were found between ΣMA and OC as well as between ΣMA and the PM_{10} mass concentration at both sites (Table

2). For the Oslo site modeled concentrations of particles due to wood burning contributing to PM_{10} mass concentration were compared to the observed levoglucosan concentration (Figure 2). The preliminary results look promising; however there are certain discrepancies between the two data sets indicating that there are conditions that the model is not accounting for. A more comprehensive study including a larger set of data is required in order to improve the model. Figure 1 shows that most of the ΣMA is associated with particles in the sub-micron range (80% < 1 µm). The mode diameter (x_c) of the log normal distribution is 561 nm, which corresponds with the findings of Hedberg *et al.* (2002), who reported that the largest mass is found in particles around 500 nm during combustion of birch wood in a wood stove.

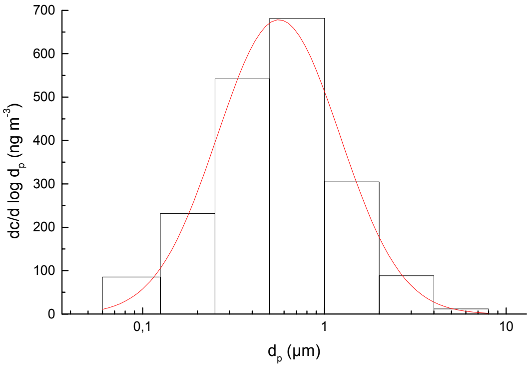
Table 1: Relative contribution of ΣMA to the OC, WSOC and mass concentration in the PM_{10} fraction.

	$\Sigma MA/OC_c$ (%)$^{1)}$	ΣMA/WSOC (%)	$\Sigma MA/PM_{10}$ (%)
Oslo	2.6$^{2)}$	5.4	0.6
Elverum	8.6$^{3)}$	-	3.3

1) Concentration of OC in µg C m^{-3}
2) OC corrected for positive adsorption of organic vapor by a QBQ set up.
3) OC corrected for positive adsorption of organic vapor by a QBT set up.

Table 2: Regression coefficients (R^2) for ΣMA determined against OC, WSOC and mass-concentration in the PM_{10} fraction.

	ΣMA vs OC_c	ΣMA vs WSOC	ΣMA vs PM_{10}
Oslo	0.86 (n = 14)	0.77 (n = 14)	0.74 (n = 24)
Elverum	0.90 (n = 21)	-	0.88 (n = 21)



Figur 1: Particle size distribution of ΣMA measured in ambient air at Elverum, using a Berner cascade impactor. The line is the lognormal fit to the observed data given by bars.

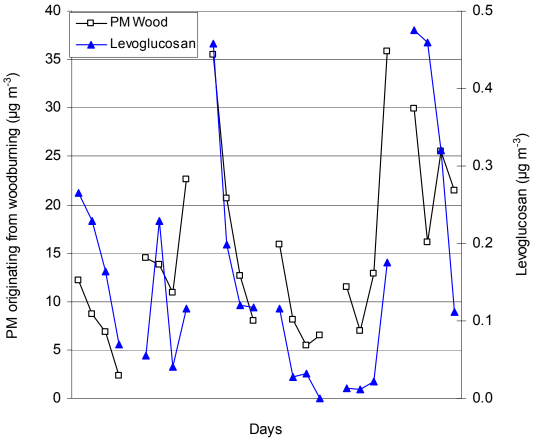


Figure 2: Comparison between levoglucosan and modeled concentrations of particulate matter due to woodburning contributing to the PM_{10} fraction. r_p = 0.63 and R^2 is 0.39.

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