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

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INTRODUCTION

Water-soluble organic carbon (WSOC) accounts for 20–70% of the total carbon found in ambient aerosols. Studies that elucidate the nature and amount of the major compounds present in the WSOC fraction 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 (Simoneit,). 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. 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 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

Table 1: Mean, min and max concentrations of monosaccharide anhydrides in the PM_{10} fraction in Oslo (Nov-Dec, 2001) and at Elverum (Feb-Mar, 2002). The MA concentrations are given in units of ng m^{-3}.

	Levoglucosan	Mannosan	Galactosan	ΣMA
Oslo	159 (n.d.-475)	39 (n.d.-155)	2 (n.d.-17)	201 (n.d.-614)
Elverum	421 (134-971)	121 (34-286)	3 (1-7)	544 (187-1240)

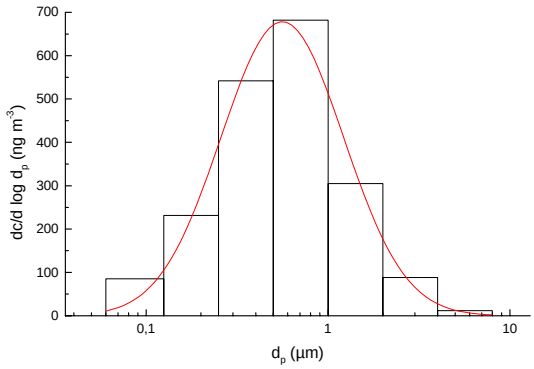
Table 2: Relative contribution of ΣMA to the OC, WSOC and mass concentration in the PM_{10} fraction.

	ΣMA/OC[1)] (%)	ΣMA/WSOC[1)] (%)	ΣMA/PM_{10} (%)
Oslo	2.6	5.4	0.6
Elverum	8.6	-	3.3

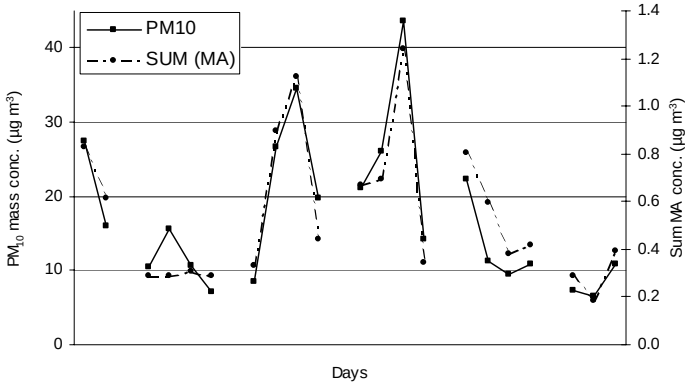
1) Concentration in µg C m^{-3}

Table 3: Regression coefficients (R^2) for ΣMA determined against OC, WSOC and mass concentration in the PM_{10} fraction.

	ΣMA vs OC	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. The mode diameter (x_c) of the log normal distribution is 561 nm. 80% of the ΣMA is associated with particles < 1 µm.



Figur 2: PM_{10} mass concentration and ΣMA concentration at Elverum during weekdays. Average temperature in the sampling period was –5.1°C (-25.7 - 5.6). The high degree of correlation indicates that wood burning is the dominating source.

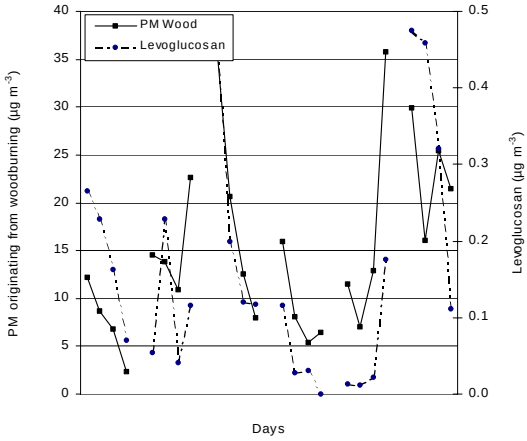


Figure 3: Comparison between levoglucosan and modeled concentrations of particulate matter due to wood burning contributing to the PM_{10} fraction on weekdays in Oslo. The discrepancies between the two datasets indicates that there are certain conditions that the model is not accounting for. R^2 is 0.39 and r_p = 0.63

CONCLUSIONS

Wood burning for residential heating during winter is widespread in Scandinavia. The presence of a reliable tracer as levoglucosan or ΣMA is therefore important in order to verify and potentially improve existing models for small-scale wood burning. As far as we know this is the first time an LC/MS-method has been used to quantify MA. This method benefits from the fact that no extensive derivatisation step is needed and therefore less time have to be spent on sample preparation. The results obtained indicate quite strongly that this approach is a good alternative to the already established GC/MS techniques.

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