

***Interactive comment on* “Quantification of levoglucosan and its isomers by High Performance Liquid Chromatography – Electrospray Ionization tandem Mass Spectrometry and its applications to atmospheric and soil samples” by C. Piot et al.**

**Anonymous Referee #2**

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Overall Comments:

This paper is well written, concise, and likely suitable for publication in AMT. The methods are sound and the comparison to established GC/MS methods for these compounds is appropriate. However, I have outlined a number of issues below that the authors need to address before full publication can be considered. This study will

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likely be useful to other groups doing chemical characterization, especially since this involves the mass spectrometry analyses of water extracts directly. Typically, methods like GC/MS require extraction with organic solvents, which prevents further analyses by techniques like WSOC and ion chromatography. Most importantly, the authors fail to highlight the potential novelty of their technique in the introduction and abstract. Specifically, they have coupled anion-exchanged chromatography to ESI-MS.

Specific Comments:

1.) Page 4542, Lines 15-17:

The authors argue that levoglucosan is a reasonably stable tracer in the atmosphere for biomass burning. However, several recent studies argue that this may no longer be the case. For example, Kessler et al. (2010, ES&T) recently examined the heterogeneous oxidation of pure levoglucosan particles in order to evaluate the effects by atmospheric aging (by OH radicals) on the mass and chemical composition. Substantial volatilization was observed during these experiments arguing that heterogeneous oxidation reactions involving OH might be a sink for levoglucosan in the atmosphere. Furthermore, Hoffmann et al. (2010, ES&T) conducted detailed kinetic studies on the reactivity of levoglucosan with OH, NO<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup> radicals in aqueous solutions to better understand the levoglucosan oxidation in deliquesced particles. The data collected from these studies were implemented into a detailed microphysics and complex multiphase chemical model to investigate the degradation fluxes of levoglucosan in cloud droplets and in wet aerosols (or deliquesced particles). The model calculations revealed that levoglucosan can be oxidized readily by OH radicals during the daytime. The Kessler et al. (2010, ES&T) and Hoffmann et al. (2010, ES&T) studies indicate that levoglucosan may not be as stable in the atmosphere as previously thought. In light of these new findings, I suggest that the authors include these very important studies in their introduction and conclusions. How might these studies effect the authors current work? I think this has to be addressed somehow. See my comment # 3 below for some help with this issue.

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## References:

Kessler, S. H.; Smith, J. D., Che, D. L.; Worsnop, D. R.; Wilson, K. R.; Kroll, J. H. Chemical Sinks of Organic Aerosol: Kinetics and Products of the Heterogeneous Oxidation of Erythritol and Levoglucosan. *Environ. Sci. Technol.* 44, 7005-7010, 2010.

Hoffmann, D.; Tilgner, A.; Iinuma, Y.; Herrmann, H. Atmospheric Stability of Levoglucosan: A Detailed Laboratory and Modeling Study. *Environ. Sci. Technol.* 44, 694-699, 2010.

### 2.) Importance Reference Missing in Introduction

Recently, Iinuma et al. (2009, *Atmos. Environ.*) developed a novel technique for simultaneous determination of atmospherically relevant sugar alcohols, monosaccharides, and monosaccharide anhydrides. Levoglucosan was included in the development of this new method. Specifically, Iinuma et al. (2009, *Atmos. Environ.*) interfaced high-performance anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD). The authors should cite this prior work in their introduction section.

### Reference:

Iinuma, Y.; Engling, G.; Puxbaum, H.; Herrmann, H. A highly resolved anion-exchange chromatographic method for determination of saccharidic tracers for biomass combustion and primary bio-particles in atmospheric aerosol. *Atmos. Environ.*, 44, 1367-1371, 2009.

### 3.) Novelty of New Method:

First, I want to make sure I'm absolutely clear on the type of chromatography the authors have employed here. You are utilizing anion-exchange chromatography, right? If so, why don't you highlight this more clearly in the abstract and in the introduction? The reason I say this is I think this is the most novel (and most important) aspect of the present study. I argue this since LC/ESI-MS is typically assumed to employ reverse-phase chromatography (i.e., separation based on hydrophobicity), especially

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in aerosol research (Hallquist et al., ACP, and references therein). The unique aspect of the present study is that the authors interface anion-exchange chromatography to ESI-MS, where ESI is operated in the negative ion mode. Typically, when employing reverse-phase chromatography, only acidic species (e.g., organic acids and organosulfates) have no problem being observed by ESI-MS operated in the negative ion mode. However, in the latter, neutral species, like alcohols and levoglucosan, are not easily observed. Thus, the benefit of coupling anion-exchange chromatography to ESI-MS could potentially be very powerful in aerosol research. From what I know about the literature, this approach taken by the authors is very unusual but could be very important in detecting novel organic aerosol tracer species in the future. Due to my concern I raised above in comment # 1 about the stability of levoglucosan, I think the authors really want to stress the potential utility of this technique to other organic aerosol tracer species and this technique could potentially be important in elucidating new compounds that have not been previously observed by LC/ESI-MS techniques that have typically employed reverse-phase chromatography. I encourage the authors to make sure there aren't previous studies in the aerosol community employing anion-exchange chromatography to ESI-MS. If there are papers out there on this, then they should include these studies in their references.

4.) Page 4543, Lines 8-10:

I'm not really sure I agree with this statement, especially in terms of expense of the GC/MS technique. LC/MS uses high-purity solvents and similar supplies (i.e., vials, inserts, etc.) that have similar costs to that of the GC/MS. I agree that time can be saved by using LC/MS, but I think it is an overstatement to say that GC/MS is more expensive. Plus, I wouldn't downplay the importance of GC/MS. It has been important in characterizing novel aerosol species (e.g., Hallquist et al., 2009, ACP).

Technical Comments:

1.) Section 2.1.

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Is your ultrapure water 18.2 mega Ohm grade? If so, I would state that clearly.

2.) Section 2.2.

Were aerosol filter samples from Franc stored in prebaked Al foil? If not, are you worried about contamination?

3.) Section 2.3.

What is the injection volume for the LC/MS technique? Please state directly.

4.) Section 2.4.

What is the injection volume for the GC/MS technique? Please state directly. Was it splitless or split injection?

5.) Section 2.4.

How does the current quantification from the GC/MS compare to when using total ion current (TIC) chromatogram peak areas? I'm not convinced it is best to use extracted ion currents (EICs) from GC for quantification. Using peak areas from EICs is usually fine for ESI-MS techniques, but not always for GC/MS.

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Interactive comment on Atmos. Meas. Tech. Discuss., 4, 4539, 2011.

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