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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.

C. Piot et al.

christine.piot@lgge.obs.ujf-grenoble.fr

Received and published: 12 December 2011

We thank the reviewer for their relevant comments, which were all taken into consideration in the corrected manuscript (indicated in blue color).

Responses to referee comments are detailed below and cited after the referee comments.

C2349

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Interactive Discussion

Discussion Paper



General comment

In the corrected manuscript, we emphasized more clearly the usefulness and novelty of such an approach that relies on water extraction and allows the detection of the 3 isomers.

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, NO₃, and SO₄²⁻ radicals in aqueous solutions to better understand the levoglucosan oxidation in deliquesced particles. The data collected from these studies were implemented into a detailed micro-physics 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.

This important point has also been mentioned by reviewer 1 and we tried to address this impact of atmospheric decay of levoglucosan in more detail page 2 line 32 to page

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Discussion Paper



3 line 4.

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.

This section was rewritten and this citation was added in the corrected manuscript page 3 line 32-page 4 line 2.

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 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

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4, C2349–C2354, 2011

Interactive
Comment

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Interactive Discussion

Discussion Paper



other organic aerosol tracer species and this technique could potentially be important in elucidating new compounds that have not be 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.

We thank the reviewer for his help in emphasis better the novelty of our method. We tried to reinforce it in the corrected manuscript. Page 4 lines 3-5: "Liquid Chromatography coupled with Electrospray Ionisation-tandem Mass Spectrometry (ESI-MS/MS) was also proposed by Palma et al., (2004). But also in this case their analytical conditions do not allow the quantification of levoglucosan isomers." Page 4, line 6: "coupling anion-exchange chromatography". Page 11, lines 26-29: "Finally this work has shown that anion-exchange chromatography coupled with an ESI-MS/MS detector allow the quantification of neutral species like anhydrous sugars. And in the future this method could be used to quickly characterize and quantify other organics tracers in aerosol sampling."

Technical Comments:

1.) Section 2.1. Is your ultrapure water 18.2 mega Ohm grade? If so, I would state that clearly.

Yes we use 18.2 mega Ohm grade and this technical information has been added in the corrected manuscript page 4 lines 24-25.

2.) Section 2.2. Were aerosol filter samples from Franc stored in prebaked Al foil? If not, are you worried about contamination?

Contamination is estimate by blank filter like described in the corrected manuscript page 5 lines 7-11: "samples were packed in aluminum foil, sealed in polyethylene bags and stored at -20°C. Blank filter samples were performed in order to estimate the

AMTD

4, C2349–C2354, 2011

Interactive
Comment

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Interactive Discussion

Discussion Paper



Interactive
Comment

contamination and the mean concentration was subtracted to the ambient samples. Concentrations of biomass burning tracers were always above the detection limits of the two analytical methods used."

3.) Section 2.3. What is the injection volume for the LC/MS technique? Please state directly.

The injection volume was already mentioned in the manuscript page 5 line 31.

4.) Section 2.4. What is the injection volume for the GC/MS technique? Please state directly. Was it splitless or split injection?

More details of GC/MS conditions were added in the corrected manuscript page 6 lines 27-29: "This fraction is then analysis by a HP 6890 Gas Chromatograph coupled with a HP 5973 Mass Selective detector (Agilent Technologies). 1 μ L sample is injected in splitless mode in an Optima 5 MS column (Macherey-Nagel)."

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.

The quantification of GC-MS with EICs allows a better sensibility and separation of compounds. In particular, it allows the separation between levoglucosan and levoglucosan-d7 (the internal standard used for the quantification). Levoglucosan and levoglucosan-d7 are quantified in the m/z 204 and 206 respectively. Examples of chromatograms obtained for these two m/z and used for the quantification are presented on the new version of figure 1.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/4/C2349/2011/amtd-4-C2349-2011-supplement.pdf>

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