Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2016-209-RC1, 2016

Atmospheric Measurement Techniques Discussions
Open Access
EGU

Interactive comment on "Atmo-metabolomics: a new measurement approach for investigating aerosol composition and ecosystem functioning" *by* Albert Rivas-Ubach et al.

Anonymous Referee #2

Received and published: 2 October 2016

Overview: This manuscript describes a metabolic-approach for the analysis of atmospheric aerosol. The approach includes GC/MS, LC/MS and direct injection FT-ICR-MS measurements. To demonstrate the potential for this method to contribute toward an improved understanding of natural metabolites associated with aerosol, the authors studied the composition of aerosol collected in the spring and the summer. Key results include: the finding that plant-related metabolites (namely organic acids and carbohydrates) are higher in the spring than summer; the summer samples included metabolites associated with oxidative stress; and summer aerosol composition included a higher fraction of high molecular weight compounds than spring with a higher O/C ratio.

Printer-friendly version

Discussion paper

The manuscript contains very valuable laboratory method information that is well-referenced. However, the details about the advanced statistical analysis are deficient. The introduction and methods sections are well-written, but the results and discussion section seems to be presented poorly. Given the inadequate description of the statistical approach, I found the results section to be especially difficult to understand. Another aspect for further consideration is placing this work into the context of the current literature on aerosol chemistry. There's quite a bit of similar work without a so-called "metabolomics" approach that is relevant.

Specific suggestions: * The literature review of atmospheric aerosol composition is weak and outdated. Since the authors claim to be the first to apply metabolomics techniques to aerosol, which are not necessarily different from other composition measurements, it would be nice if they would acknowledge the vast literature of GC/MS, LC/MS and FT-ICR-MS results aimed at understanding aerosol composition. * Lines 102 - 106: How important is the carbon and nutrient deposition of aerosols to ecological systems? * Lines 145 - 148: The atmospheric system is quite complex and the goals of this manuscript are quite broad. I suggest some refinement of the manuscript goals with a focus on a well-defined portion of the atmospheric system, since this work doesn't address larger spatial sampling, research flight measurements, or multiphase measurements. * Line 187: I often see this statement in manuscripts, but it is not a realistic resolving power for environmental samples. Can the authors cite a paper demonstrating the successful measurement of a complex mixture with a resolving power and actual resolution of 1,000,000? * The organization of sections 2.3 - 2.5 is a little bit strange. Specifically, a description of the GC/MS sample prep (in 2.3) is given followed by LC/MS analysis (2.4), which is in turn followed by the GC/MS analysis (2.5). * Line 346: How were both positive and negative ionization performed with LC/MS? Were they done in separate runs or using fast polarity switching? * Line 371: Was negative mode ESI performed? Why was negative ESI not performed for atmospheric aerosol characterization? * Lines 381 - 383: Both fragment ions and exact mass were used to assign metabolites. Were these measurements made in single runs LTQ MS/MS and FT-MS

in tandem or something else? * Line 418: Why was S/N > 7 used as a threshold? How was the S/N determined? * Lines 473 - 476: How many data points were used for this analysis? How were the sub- sets of data selected for analysis? Some discussion on the QA filtering procedures and selection of data for statistical analysis is greatly needed. * Line 487: In what sense is the statistical significance? * Lines 489-496: What do these compounds indicate? How were they identified? * Lines 501-504: This approach from Kim et al. is highly speculative. It's also not an appropriate approach for atmospheric aerosol. Did you extra proteins? How did you verify protein-like components? * Lines 517 - 520: What is the meaning of this observation? * Aerosol sampling information is vague and seems to imply that the authors are unfamiliar with standard sampling techniques for atmospheric chemistry. How did you assess the total carbon concentrations, filter artifacts, and other recovery issues? * Sampling flow rates are expected to change with diurnal cycles (e.g., temperature & pressure); how was this recorded or accounted for? * Lines 535 - 537: The purpose of the study was to assess the sensitivity of different mass spectrometry instruments. But, I didn't understand how that was accomplished? Did you define method detection limits or find any limitations in your approach? More discussion on this would be appreciated. * How does you approach differ from the existing approaches to canopy measurements or other ecological studies focused on atmospheric-biosphere exchange? * Lines 584-587: Which solvents did you use to sequentially extract the filters? How did you evaluate the results of various solvent combinations? * Lines 590-591: What was quantified in your study? * Lines 596 - 600: How was the absorption extract recovery assessed? * Line 623: "match" or assign? * Lines 706-710: Please clarify how the "metabolic fingerprint" was defined/classified? * Table 1: Fingerprint information is unclear. Please add some explanation in the body of the paper. * Figure 1: What about aqueous phase processing of VOCs or aerosol? * Figure 3: How were common inorganic ions removed from the samples before Di-FT- ICR-MS? * Figure 5: I assume this is the list of "metabolic fingerprint" species. Please clarify. * Figure 7: How were the species in (a) subsetted from the whole dataset?

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-209, 2016.

Printer-friendly version

Discussion paper