Atmos. Chem. Phys. Discuss., 12, C8257–C8261, 2012
www.atmos-chem-phys-discuss.net/12/C8257/2012/
© Author(s) 2012. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical characterization and stable carbon isotopic composition of particulate polycyclic aromatic hydrocarbons issued from combustion of 10 Mediterranean woods" *by* A. Guillon et al.

Anonymous Referee #2

Received and published: 16 October 2012

The manuscript presents measurements of concentrations and d13C values of polycyclic aromatic hydrocarbons in wood burning aerosols. These measurements are difficult to do (especially for d13C) and the authors achieve good reproducibility. Since the use of stable isotopes in aerosol source apportionment is a promising research field, where data on aerosol sources are urgently needed, this data set is an important contribution to the literature.

However, some of the conclusions the authors draw from the data are in my opinion not justified. Moreover, the manuscript needs to be seriously rewritten in order to be con-

sidered for publication in ACP, especially the methods section. This section is chaotic and unorganized, often repeating things in different places. In my opinion, it is nearly unintelligible for non-experts in the extraction of PAHs. Since you are aiming for a broad audience in ACP, this section should be made much clearer with a better structure and less jargon. I will provide suggestions how to do this. Lastly, the manuscript needs to be corrected by a native speaker, there many grammatical errors and very cumbersome formulations that make the reading unnecessarily difficult.

Major comments:

1) Reorganization of the methods sections 2.4, 2.5, 2.6 Section 2.4 is generally called 'analytical procedure' and covers a diverse set of subsections, starting with "validation on standard reference materials" for a method that has not been described yet. Section 2.5 is its own section even though 13C measurements are also a part of the analytical procedure. Moreover, part of the validation of 13C measurements (validation of HPLC fractionation) are already covered in section 2.4 before the method is even introduced. Method description and quality assurance measures are intermingled throughout section 2.4 and 2.5, which in my opinion is confusing for the reader. Finally, there is also separate Section on quality assurance (2.6), which repeats part of the information given before and adds new information.

I suggest to restructure the section as follows: 2.4 Analytical procedure 2.4.1 Quantification of PAHs Extraction Purification GC/MS analysis Method evaluation (internal, syringe standards) 2.4.2 determination of isotopic composition (if any procedure is the same as in quantification section this could just be stated and need not be repeated) Extraction Purification GC/IRMS analysis Method evaluation 2.4.3 Application to SRM

This is just a suggestion, but any structure that clearly separates the method description and method evaluation would be ok.

2) In the introduction it is stated that the PAH compounds are highly reactive (p20633, line 24), but that their isotopic compositions are conserved during transport (line 29).

ACPD

12, C8257–C8261, 2012

Interactive Comment

Since chemical reactions usually result in isotopic fractionation, should the isotopic compositions not be affected as well? Please discuss

3) page 20635, line 25: 1 cm2 was used for OC/EC; page 20636, line 1: 1.5 cm2 was used for OC/EC; which is true?

4) Pg 20637, line 4ff: different cell sizes were used to "optimize the volume of solvent against the volume of occupied by the filter". If the volume of the filter was the criterion, then why were big punches of blank filters (16.62 cm2) extracted in the small volume when big punches of filters for GC-IRMS (16.62, see page 20635) were extracted in the big volume?

5) Section 2.5.2: It is said that the "method for isotopic composition was described and validated elsewhere". Since these manuscripts are not accessible it is important to summarize the results of the validation. Did you test for any isotopic fractionation of the extraction/purification method? Was there any fractionation that needs to be corrected for? Even once the methods papers are available it is still very convenient for the reader to have a short summary of the main method paper results.

6) Page 20643, line 20: Why did the recovery yields of internal standards change with the different SRMs?

7) Section 2.3.2 This section is quite long and very unstructured. Please separate the (1) description and discussion your own results from (2) the comparison of the results to measurements of others and from the (3) interpretation the results in terms of (3a) variation between wood species and (3b) discrepancies and/or similarities between this data set and other data sets. For few of the diagnostic ratios is it entirely clear to me if the authors think they vary because of experimental conditions, wood types, burning conditions, regional differences. This gives the impression that there is just a large variability in certain diagnostic ratios without clear cause even though this might not be so. Please avoid all sentences that are structured in the manner: "... diagnostic ratios a, b, c, d are in the range of x-y, y-z, k-d, r-s, respectively." Replace them with

ACPD

12, C8257–C8261, 2012

diagnostic ratios of a are in the range of x-y, of b in the range of y-z . . .", if you really need to discuss them in the same sentence. Try focus the discussion at one diagnostic ratio as much as possible before jumping to another one.

8) Page 20650, line 5: I do not agree that these two diagnostic ratios show significant differences between American and European woods. Sure they are variable but the differences within a region (e.g. Rogge and Fine) are larger than the differences between the regions. The only conclusion remains that these ratios are apparently very affected by experimental design and cannot be used at all.

9) Page 20651, line 23ff: I think it is quite an exaggeration to say that "molecular isotopic compositions . . .are specific for each species". For example the d13C values of cypress (1) and cypress (2) overlap with the range of values measured for cork oak (including twigs) for most of the compounds and also the values for Morrocan coal fall in the range of the two experiments of Cork oak twigs (1) and (2). The main misconception here is assuming that the experimental uncertainties alone determine the ability to distinguish wood species. However, one must also take into account the total reproducibility of burning one wood species repeatedly. If for example the first burning of cork oak twigs gives d13C value of -30.3 permil for fluo, whereas the second burning gives -28.7 permil, all wood that falls within that range (including uncertainties) cannot be distinguished, in this case Juniper. Pease be careful with general statements like that, especially since many woods are measured only once. But considering that repeated burnings of the same wood can easily result in differences of 1 permil or more (see cypress 1 and 2; oak twigs 1 and 2) a difference of 1 permil might be indicative of what you can separate. However, the general message that 13C isotopes are much more useful to differentiate sources than molecular fingerprints or diagnostic ratios is still clear and a nice result.

Minor comments: (Please note again that the manuscript needs to be thoroughly edited for grammar and formulations, beyond what I am correcting here)

ACPD

12, C8257–C8261, 2012

Abstract , line 18: It is not at all clear what these numbers refer to, wood combustion or vehicular exhaust. Page 20635, line 20: Please describe in more detail how the field blanks were taken Page 20636, line 22: Please delete the sentence “A large range ..” It seems out of place here Page 20643, line 16: “ambient particles” instead of “natural particles” Page 20644, line 3: “show” instead of “traduce” Page 20644, line 5: “accurate conditions” is not a valid expression

---

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 20631, 2012.