

## Quantification of the volatile organic compounds in the smoke from prescribed burning and comparison with the occupational exposure limits

by Barboni and Santoni

The manuscript reports information on an important environmental research area: emissions from fires and exposure to compounds emitted. Although the topic is important, it seems that the manuscript is a “squeeze of the juice” of experiments whose results were already published. In addition, the experiments present serious drawbacks, which limit the interpretation of results and the generalisation of conclusions (see comments above). The literature cited is quite limited and important references are missing.

A watchful revision of the English is required. The support of a native English speaker is highly encouraged.

### Specific comments:

- Abstract. The personalization of "we" should be avoided in formal writing. Example: “potentially dangerous molecules ... were identified”, instead of “we identified potentially...”. The same in other parts of the manuscript.

- Introduction. Second sentence. Smoke is composed primarily of carbon dioxide, water vapor, carbon monoxide, particulate matter, hydrocarbons and other organic chemicals, nitrogen oxides, trace minerals and several thousand other compounds.

- Lines 17-18. There are many recent references on particle emissions from wildfires.

Examples:

Vicente et al. (2013) Emission factors and detailed chemical composition of smoke particles from the 2010 wildfire season. *Atmospheric Environment*. 71, 295-303.

Vicente et al. (2012) Organic speciation of aerosols from wildfires in central Portugal during summer 2009. *Atmospheric Environment*. 57, 186-196.

Alves et al. (2011) Emission of trace gases and organic components in smoke particles from a wildfire in a mixed-evergreen forest in Portugal. *Science of the Total Environment*. 409, 8, 1466-1475.

- Page 6500. Lines 20-26. VOC also include isoprenoids. See Evtugina et al. (2013) and references therein.

Evtugina et al. (2013) VOC emissions of smouldering combustion from Mediterranean wildfires in central Portugal. *Atmospheric Environment*. 64, 339-348.

- Page 6501, lines 11-12. There are many other studies reporting VOC emissions from biomass combustion. Examples:

Evtugina M., Alves C., Calvo A., Nunes T., Tarelho L., Duarte M., Prozil S., Evtugin D., Pio C. (2014) VOC emissions from residential combustion of Southern and mid-European woods. *Atmospheric Environment*. 83, 90-98.

Akagi, S.K., Yokelson, R.J., Wiedinmyer, C., Alvarado, M.J., Reid, J.S., Karl, T., Crouse, J.D., Wennberg, P.O., 2011. Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos. Chem. Phys.* 11, 4039-4072.

T. Christian, B. Kleiss, R. Yokelson, R. Holzinger, P. Crutzen, W. Hao, B. Saharjo, D. Ward. Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels. *J. Geophys. Res.*, 108 (D23)

J.D. McDonald, B. Zielinska, E.M. Fujita, J.C. Sagebiel, J.C. Chow, J.G. Watson. Fine particle and gaseous emission rates from residential wood combustion. *Environ. Sci. Technol.*, 34 (2000), pp. 2080–2091

G.R. McMeeking, S.M. Kreidenweis, S. Baker, C.M. Carrico, J.C. Chow, J.L. Collett, W.M. Hao, A.S. Holden, T.W. Kirchstetter, W.C. Malm, H. Moosmüller, A.P. Sullivan, C.E. Wold. Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory. *J. Geophys. Res.*, 114 (D19) (2009)

E. Pettersson, C. Boman, R. Westerholm, D. Bostroem, A. Nordin. Stove performance and emission characteristics in residential wood log and pellet combustion, part 2: wood stove. *Energy Fuels*, 25 (2011), pp. 315–323

R.J. Yokelson, T.J. Christian, T.G. Karl, A. Guenther. The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data. *Atmos. Chem. Phys.*, 8 (2008), pp. 4221–4266

- Section 2.1. Tedlar bags have been used by the authors. It is stated that the smoke was drawn into the bags through a heat-resistant Teflon tube. This procedure raises many concerns. Were the smoke particles filtered before the admission of the gaseous sample into the bag? There is a high probability of having condensation of water on the bag walls, since pre-condensation was not carried out. In addition, adsorption of volatile compounds onto the walls is also highly probable. Were the bags reused? In relation to the Tenax tubes, water saturation problems are likely to occur. Analyses of breakthrough times for VOCs were not performed.

In line 3 of page 6504, the term “smoke emissions” is used. Emissions refer to mass of compound emitted by unit of mass of biofuel burnt. I think there is confusion between emission and concentration.

How was it assured that the smoke plume was really sampled? Important measurements to estimate the dilution suffered by the plume were not performed (e.g. CO and CO<sub>2</sub>). A mixture of flaming and smouldering emissions was sampled. The duration of each one of these combustion phases may be highly variable. The flaming phase represents a more complete combustion and, consequently, the major compound emitted is CO<sub>2</sub>. On contrary, the smouldering phase corresponds to combustions efficiencies (which were not determined in

the present study) < 0.9 and to the emission of many hydrocarbons. What do these measurements in fact represent?

- Section 2.2. Should be moved to the end of the experimental part.
- Pages 6505-6506 (Identification and Quantification). Were the standards directly injected into the GC-MS or into the Tenax tubes? The calibration results may be completely different depending on the method. Why was the quantification performed in equivalent benzene, equivalent phenol, ...?
- 1<sup>st</sup> sentence of Discussion. Barboni et al. (2010). Is it 2010a or 2010b? What is the innovative character of the present study in relation to the previous one? After accessing the abstract of the previous paper, I got the idea that it is the same work. This aspect needs clarification.
- It is stated that device 2 enabled the identification of 71 compounds. Why only 14 were quantified (Table 3)? Why was it decided to quantify only the 14 VOC with known STEL and TWA? Why waste information that can be useful for other purposes?
- Page 6507, line 21 and subsequent lines are a reading of table 2.
- Page 6509. Benzene and toluene have been identified as dominant aromatic compounds in emissions of smouldering combustion from Mediterranean wildfires (e.g. Evtyugina et al., 2013). In residential wood combustion experiments, it was observed that, among the VOCs identified, benzene and related compounds were always the most abundant group, followed by oxygenated compounds and aliphatic hydrocarbons (Evtyugina et al., 2014).
- Table 3 presents the concentrations of major VOC and compares these values with STEL and TWA obtained from literature. Since concentrations are in mg/m<sup>3</sup>, it makes no sense to compare with emission factors in g/kg.