Answers to the Reviewers Reports of

Dear Editor,

Please find following the answers to the referee's comments.

We made all the suggested corrections:

1- The English was revised

2- All references were added

3- All questions and comments were taken into consideration.

Best Regards,

Toussaint Barboni

Reviewer: 1

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.

1. **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) ; Vicente et al. (2012); Alves et al. (2011) ;
Evtyugina et al. (2013 and 2014); Akagi (2011); . Christian (2000) ; McMeeking (2009) , Yokelson, (2008).

Answer 1: All the modifications have been made into the document and new references were added

2. **Section 2.1**.

a. 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?

Answer 2a: Smokes were aspirated and absorbed into the bag. The compounds were filtered by a filter cartridge for removing particles of soot. There is a probability that the water was condensed with a low loss of compounds mass because they are compounds of low solubility in water. The bags Tedlar were stored in opaque bags to minimise the impact of U.V. radiation during transportation to laboratory. In the laboratory, we did not observe condensation related to water, no droplet. The use of Tedlar bags was unique.

b. In relation to the Tenax tubes, water saturation problems are likely to occur. Analyses of breakthrough times for VOCs were not performed.

Answer 2b: The tubles Tenax TA allow adsorption of VOCs in a proportion in high relative humidity. The volume of the sampled air does not exceed the breakdown of the combinaison of adsorbent - compounds. For to assure complete retention of VOCs on the adsorbents, trials with different concentration of VOCs (Restek) were carried out by direct injection in GC. The mode of loading cartridges is by doping gas path (vaporization of standard solutions via a GC injector) of a standard gas mixture. There is no saturation of our samples because all the calibration curves were linear (part quantification). See figure 1.

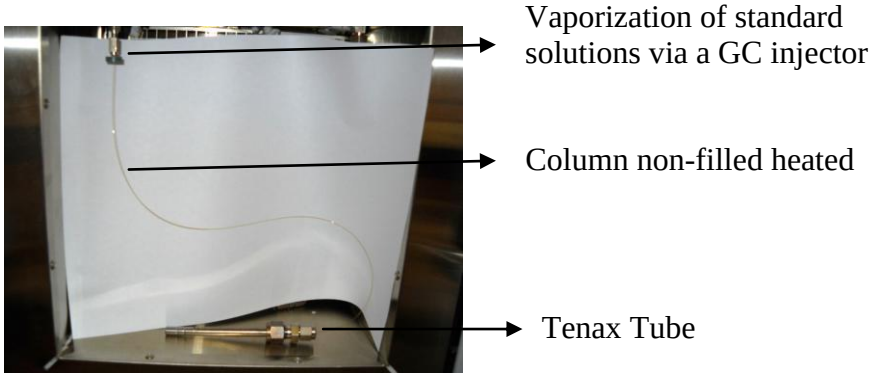

Figure 1. System for the doping tubes

c. 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 CO2). 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 CO2. 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?

Answer 2c. The term "smoke emissions" was removed from the text as it is to quantify the compounds that are inhaled by firefighters. The flaming and smoldering phases are not examined because our goal is to determine or estimate the quantity inhaled by forest fire toxic compounds. Sampling is performed without observation phase combustion. However, given the low intensity and thus the low rate of spread, there are a lot of smokes that are inhaled by firefighters during the smouldering *phase resulting in a higher concentration of compounds in the air.*

3. **Section 2.2.**

Should be moved to the end of the experimental part.

a. 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, …?

Answer 3a. The method of external calibration by gas way was used with commercial compounds (Restek®: benzene, toluene, ethylbenzene, xylenes, styrene, propylbenzene, □-methlstyrene, trimethylbenzene, diphenyl, phenol, o-cresol, 4-methoxyphenol, furfural and naphthalene). The method consists in injecting the compounds at concentration known in the injection chamber GC's at 240°C. GC is equipped with a short column non-filled heated at 240 °C and the end of this column there is a Tenax tube. The doping of the tube is carried by the gas path. Triplicate injections of standards were made for each level (5 points) to obtain curves for external calibration standards. The correlation coefficient (R2) for the linear regression of the curves of external calibration standards, varied between 0.987 and 0.999 ensuring a good correlation between the detector’s response and the concentration of injected products.

b. 1st 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.

Answer 3b. Barboni et al., 2b.
Clarification was provided in the introduction

"However, a preliminary work was realized on the methodology and qualitative analysis of VOCs in smokes (Barboni et al., 2010b). This first study has allowed to identify 79 volatile compounds (> C3) without assessing the toxicity of these pollutants. In the present work, the study was conducted in 3 steps. Firstly, VOCs present in the smoke were identified according the mode of sampling during the prescribed burning. Secondly, identification and quantification of the compounds the most toxic were carried out. Finally, assessed the toxicity of these compounds in relation to the limit values (LVs) of the French government and the American Conference of Governmental Industrial Hygienists (ACGIH)."

c. 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.

Answer 3c. Of the 79 compounds, only 14 compounds have a toxicity known by the agencies (ACGIH or INRS). The study focused on the evaluation of toxicity, our choice is made to quantify these 14 compounds which had a limit of exposure and a toxicity to humans known.

d. 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).

Answer 3d: The ref and the discussion were added.

4. **Table 3** presents the concentrations of major VOC and compares these values with STEL and TWA obtained from literature. Since concentrations are in mg/m3, it makes to sense to compare with emission factors in g/kg.

Answer 4: There was an error in the table.
Table 3
Concentration of major toxic VOCs emitted by vegetation during the prescribed burnings ([a]INRS; [b]ACGIH; [c]NIOSH, [d]OSHA)

compounds	*Concentration (min-max) ($mg.m^{-3}$)*	*STEL ($mg.m^{-3}$) (15 min)*	*TWA ($mg.m^{-3}$) (8 hours)*
benzene	*27-54*	*16[d], 8.1[b], 0.32[c]*	*30[b], 3.2[c,d]*
toluene	*28-42*	*560[c,d]*	*188[b], 375[c,d]*
ethylbenzene	*22-67*	*543[b-d]*	*434[b-d]*
(o+m+p)-xylene	*19-37*	*655[b-d]*	*435 [b-d]*
styrene	*1.0-7.6*	*425[b-d]*	*215[b-d]*
propylbenzene	*tr-4.7*	-	*245[b]*
α-methylstyrene	*< 3.8*	*483[b-d]*	*242[b-d]*
trimethylbenzene	*< 3.8*	-	*123[b]*
Diphenyl	*< 0.8*	-	*1[b-d]*
phenol	*12-29*	*60[c]*	*19[b-d]*
cresols (o+m+p)	*3-14*	-	*22 [b,d], 10[c]*
4-methoxyphenol	*0.2-4.4*	-	*5[c]*
furfural	*3.2-19*	-	*7.9[b]*
naphtalene	*1.2-4.2*	*75[b-d]*	*50[b-d]*

Reviewer: 2

General comments

The main objective of the research introduced in the manuscript is to contribute to the knowledge regarding exposure of foresters to smoke from prescribed fires. To reach the goal authors use data from previous field experiments whose results have already been published and that were focused on identification of compounds present in the smoke during prescribed burning events. In this work authors quantified concentrations of 14 organic chemicals and assessed firefighters' exposure risk to smoke by comparing compound concentrations with threshold limit values (TLVs). Although the topic is relevant, the manuscript seems to have been hastily written; consequently it needs to be improved in several parts. In general, the paper is not well organized; material and methods should be more detailed and some parts need to be moved from different sections. In addition, quality of English needs improving, revision of the text by a native English speaker is recommended.

Specific comments

Introduction:

1. Pag 6506, lines 9-10: Probably objectives should be revised; if I have understood correctly, the aim of this MS is to give information on potential toxicity of vegetation moke; so I suggest emphasizing this aspect. The originality of the present work in relation to the previous one needs more explanation.

Answer 1: Clarification was provided in the introduction

"However, a preliminary work was realized on the methodology and qualitative analysis of VOCs in smokes (Barboni et al., 2010b). This first study has allowed to identify 79 volatile compounds (> C3) without assessing the toxicity of these pollutants. In the present work, the study was conducted in 3 steps. Firstly, VOCs present in the smoke were identified according the mode of sampling during the prescribed burning. Secondly, identification and quantification of the compounds the most toxic were carried out. Finally, assessed the toxicity of these compounds in relation to the limit values (LVs) of the French government and the American Conference of Governmental Industrial Hygienists (ACGIH)."

2. Pag 6506, lines 11-14: Authors say that the study was carried out in 3 steps but I am not able to find where in the text VOCs present in the smoke of burning vegetation were compared with those found in prescribed burning smoke.

Answer 1: In the present work, the study was conducted in 3 steps. Firstly, VOCs present in the smoke were identified according the mode of sampling during the prescribed burning. Secondly, identification and quantification of the compounds the most toxic were carried out. Finally, assessed the toxicity of these compounds in relation to the limit values (LVs) of the French government and the American Conference of Governmental Industrial Hygienists (ACGIH)."

3. **Experimental methods:** I suggest adding a map with location of experimental sites and including coordinates and main species in table 1 so as to make reading easier.

Answer 3: we added

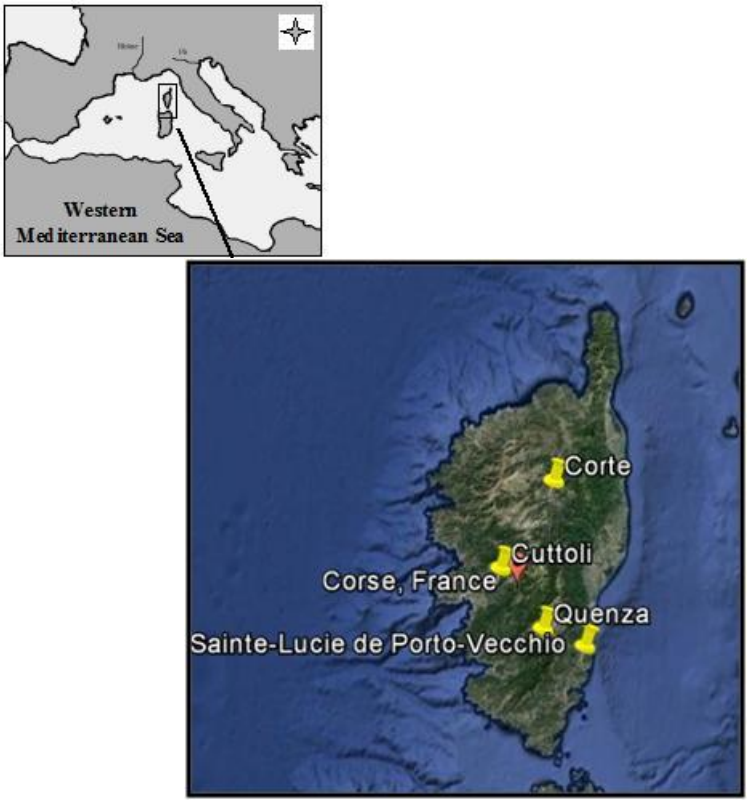

Fig.1 . Location of the study sites on the Corsican (French island).

Table 1

Main characteristics of the experimental plots.

	Plot A	Plot B	Plot C	Plot D
Localities	Sainte Lucie de Porto-Vecchio	Cuttoli	Corte	Quenza
Coordinates	41°42’ N; 09°20’ E	41°59’ N; 08°54’ E	42°18’ N; 09°09’ E	41°46’ N; 09°08’ E
Elevation (m)	0	650	400	805
Main species	*Quercus ilex* L.,*Olea europaea* L., *Arbutus unedo* L., *Cistus monspeliensis* L., *Cytisus triflorus* L., *Erica arborea* L.	*Arbutus unedo* L., *Erica arborea* L., *Cistus monspeliensis* L.	*Leaf of Quercus ilex L.*	*Juniperus nana L.*

Slope (%)	0-30	0-10	0	0-20
Vegetation height (cm)	80-250	80-150	1-10	10-20
Fuel load ($g.m^{-2}$)	1160	1200	1370	1450
Vegetation cover (%)	50-60	50-60	60-70	70-80
Burning area (ha)	0.06	2	0.4	2
Relative humidity RH (%) (min. and max.)	20-23	22-25	24-25	30-35
Temperature (°C)	30-32	22-24	22-25	14-16
Wind velocity ($km.h^{-1}$)	40	20	< 5	< 5

4. Pag 6502 - line 25; pag6503 - line13: substitute “plot” for “site”

Answer 4: we modified

5. Page 6504- Lines 1-15: Have some authors used this kind of device before? If so, please cite reference.

Answer 5: Many authors used this device (Miranda et al.; reisen et al.; Evtyugina et al…). These authors added these references in the manuscript.

6. Move paragraph 2.2 to the end of experimental method section.

Answer 6: ok

7. Pag 6504 line 3: explain the acronym ACGIH. Some other acronyms and abbreviations are not explained, please check the text.

Answer 7: all acronyms and abbreviations are defined.

By authors:

Toussaint Barboni and Nathalie Chiaramonti