

## Reply to referee 1

### General comments

This paper investigates the mineralization of five BVOCs in four different soils. By using BVOCs labelled with  $^{14}\text{C}$  the paper clearly shows the mineralization process of BVOCs occurring in the different soil types. The methodology is adequately described and the experimental procedures are well written, as well as the introduction, results and discussion sections. The fact that soil microbes can metabolize soil BVOCs is already known but, as the authors say, there are still not many studies directly proving microbial degradation of BVOCs. The authors say that one important value of this study is that the incubated soils were exposed to realistic environmental concentrations of BVOCs, not like the other studies, where higher concentrations were used. It would be interesting for the readers to have a table where one could see the real initial concentration (not a range), together with the concentration measured of these BVOCs in the environment (in this experiment or in the literature, if some atmospheric BVOC measurement is missing), the amount of BVOC metabolized to  $\text{CO}_2$  and the amount of BVOC extracted at the end of the incubation, for each BVOCs and soil incubated. This information would help to evaluate the main points of the paper: that some BVOCs can be degraded completely in soil (by giving the recovered BVOCs at the end of the experiment one could see how much was incorporated in the microbial biomass or how much was adsorbed to soil particles) at the relevant environmental concentrations measured. Regarding this point, for the BVOCs that were measured in the atmosphere (not methanol), the highest atmospheric concentrations shown in Table 4 (around 3 ng/L in the coniferous forest, measured at 10 cm above soil) would be still 21 times lower than the minimum concentration used in the incubations (64 ng/L). There are of course technical difficulties, as the authors say, to measure mineralization at the very low atmospheric concentration, thus that table would highlight to what extent the authors have narrowed this challenge.

We have considered carefully to make an additional table with the data suggested by the referee. We are afraid that such a table will increase confusion rather than make things clearer, since very different things would be compared in the table (environmental BVOC-concentrations, BVOC concentrations during incubation, mineralized fraction of BVOC and extractable  $^{14}\text{C}$ ). We do understand the desire to compare environmental and experimental concentrations. However, this is a difficult task, since we do not know how much of the BVOC we add that is in the air phase as we already discuss in the manuscript (see also our response to the specific comment concerning "page 5, line 138"). After all, we have decided to compare the two concentration types in Table 4, where environmental concentrations were already shown. We have also included comparable literature data, if available:

**Table 4.** Atmospheric concentrations of relevant BVOCs (mean  $\pm$  standard deviation, n=3) measured 10 cm above soil surface (coniferous, beech and Arctic bare sites) or 5 cm above the canopy (Arctic heath site) the day of soil sampling. Methanol could not be analyzed with the applied methods. Comparable literature data are included, when available.

Name	Atmospheric concentration (ng L <sup>-1</sup> )			Initial headspace concentration during incubation (ng L <sup>-1</sup> ) <sup>***</sup>
	Coniferous*	Beech	Arctic**	
Oxygenated monoterpenes	0.00 <sup>e</sup> $\pm$ 0.00	0.00 $\pm$ 0.00	0.01 $\pm$ 0.01	504
Hydrocarbon monoterpenes <sup>d</sup>	3.36 <sup>a,f</sup> $\pm$ 0.32	0.37 <sup>b</sup> $\pm$ 0.12	0.71 <sup>c</sup> $\pm$ 0.10	260
Benzaldehyde	1.01 $\pm$ 0.03	1.14 $\pm$ 0.08	0.00 $\pm$ 0.00	286
Acetophenone	0.44 $\pm$ 0.06	0.59 $\pm$ 0.03	0.01 $\pm$ 0.01	350
Chloroform	0.10 <sup>g</sup> $\pm$ 0.02	0.06 $\pm$ 0.00	0.06 $\pm$ 0.00	340
Methanol (literature data)	0.3-284 (Seco et al., 2007)			64

\*n=2 due to loss of a sample, except for chloroform (n=3). \*\*One sample from the bare soil, two from the Arctic Heath.

\*\*\*Assuming all added BVOC is present in headspace, although most will likely be adsorbed to soil or dissolved in water. <sup>a</sup>Mainly pinenes, camphene, carene and p-cymene. <sup>b</sup>Mainly camphene,  $\alpha$ -pinene,  $\delta$ -terpinene and carene. <sup>c</sup>Mainly  $\delta$ -terpinene. <sup>d</sup>Comparable literature values but from a different ecosystem type go from 0.5-50 ng L<sup>-1</sup> (Barney et al., 2009). <sup>e</sup>Air samples taken at the interface between litter and atmosphere have shown concentrations of 60-390 ng L<sup>-1</sup> (Ketola et al., 2011). <sup>f</sup>Air samples taken at the interface between litter and atmosphere have shown concentrations of 10-24300 ng L<sup>-1</sup> (Ketola et al., 2011). <sup>g</sup>Comparable literature data go from 0.08-2.1 ng L<sup>-1</sup> (Albers et al., 2010).

The mineralization extent is clearly an important parameter, but since it is relatively easy to read out of the curves in Figure 3, we did not include them in a table. We can see the need to be able to find the exact data, however and also the benefit of comparing with extraction data, although these play a minor role in the manuscript. We will therefore include a supplementary table with these data in the revised manuscript:

Table S1. Supplementary mineralization parameters from the mineralization experiment shown in Fig. 3. Mineralization extent is the accumulated liberation of <sup>14</sup>CO<sub>2</sub> at the end of experiment (144 h, except chloroform (21 d)). Final extraction is the amount of <sup>14</sup>C extractable with methanol at the end of experiment. All data are average of three replicate incubations. nd = no data.

	Mineralization extent (%)				Extractable <sup>14</sup> C (%)			
	Conif.	Beech	Heath	Bare	Conif.	Beech	Heath	Bare
Chloroform	36	30	44	47	nd	nd	nd	nd
Methanol	93	90	98	85	1	1	0	1
p-Cymene	81	66	87	48	8	7	4	5
Benzaldehyde	60	53	59	57	4	4	2	1
Acetophenone	43	41	37	46	6	4	3	4
Geraniol	46	42	42	33	19	17	16	25

## Specific comments

Page 4, line 115: Table 1 instead of Table 2

Reply: The reviewer is correct, Table 1 and 2 should exchange numbers.

Page 5, line 137: As suggested in the general comments, it would be nice to have a table with the initial concentrations for each BVOC and soil type, the corresponding atmospheric concentrations, etc.

These are now gathered in table 4 (see response to “General comments”)

Page 5, line 138: This range 0.8-11 ug/Kg soil FW, is environmentally realistic? Regarding monoterpenes White (1991) reports 12-47 ug/g soil DW in the organic horizon and 0.03 to 0.23 ug/g mineral horizon of Ponderosa pine forest. That would be much higher than the values in this experiment, at least for the organic layer. Is there any information for other BVOCs? But I guess it's very difficult to find this information. . .

Reference: White, C.S., 1991. The role of monoterpenes in soil-nitrogen cycling processes in ponderosa pine results from laboratory bioassays and field studies. *Biogeochemistry* 12 (1), 43–68.

This point raised by the reviewer is relevant and something we have given a great deal of thought when designing the experiment. First of all, BVOC measurements around or below the soil surface are very scarce in the literature and for the few studies that exist about BVOC concentrations in soil, very different methods have been used, making it impossible to compare. For example in the reference mentioned by the referee, BVOCs were extracted with an organic solvent from the solid matrix after homogenization, hence representing only sorbed/bound BVOC as well as compounds in root material if any remained in the soil, while others measured the concentration in soil air, hence excluding sorbed/bound BVOC. Our focus in the study was the possible uptake from the atmosphere rather than degradation of sorbed/bound residues, although in nature it will all be connected, of course. Based on atmospheric concentration measurements, the concentration of many BVOCs seems in general lower than what is possible to analyze with <sup>14</sup>C-mineralization experiments. We therefore used the lowest concentration possible, which for some of the compounds is not far from realistic and under all circumstances much more realistic than what has been used in previous degradation studies. Furthermore, a fraction of the BVOC we add will be sorbed and/or dissolved in soil water, hence making actual atmospheric concentrations in the experiment even closer to those in nature. However, the exact concentration in atmosphere and soil during incubation is not easy to calculate and furthermore it will change rapidly due to the rapid degradation.

In the manuscript, we already state the following, which we believe sums up these considerations (lines 136-139 and 319-323):

*“The BVOC concentrations used for incubation corresponded to 43-73 ppbv (64-504 ng L<sup>-1</sup>), assuming all BVOC was present in the headspace of the flasks. Most of the BVOCs were, however likely dissolved in water or adsorbed to the soil, so recalculating to a soil basis (0.8-11 µg kg<sup>-1</sup> f.w. soil) may be more appropriate.”*

And:

*“The concentration of BVOCs in the atmosphere is very low, also at the sites where we sampled soil (Table 4). Mineralization experiments cannot be carried out at such low concentrations but we used BVOC concentrations that are much more realistic than those used in previous degradation studies. Furthermore, similar atmospheric concentrations as we used for incubations have been observed in nature for methanol (Seco et al., 2007), chloroform (Albers et al., 2011) and monoterpenes (Barney et al., 2009).”*

Page 6, line 170: Table 2 instead of Table 1

Reply: The reviewer is correct, Table 1 and 2 should exchange numbers.

Page 8, line 208-213: It is very nice to read the investigations about the transfer rate of CO<sub>2</sub> in the supplementary information Fig. S1.

Reply: Thank you. We did consider to include it in the manuscript itself, but ended up placing it in the supplementary, where the interested reader will hopefully find it...

Page 11, line 280: This 5% is then adsorption to soil? Again, a table to compare values between soils and BVOCs would be useful in my opinion

These 5% could be sorbed/bound mother compound or (more likely) microbial metabolites, containing <sup>14</sup>C due to utilization of the <sup>14</sup>C-BVOC. Regarding the Table, we have made a supplementary table (see response to "General comments").

We will add the following sentence:

*"These 5% could be sorbed/bound mother compound or (more likely) microbial metabolites, containing <sup>14</sup>C due to utilization of the <sup>14</sup>C-BVOC."*

Page 11, line 298: what do you mean by dissipation? Do you mean you recovered all the p-cymene added with the extraction? By dissipation we mean degradation in the sense of disappearance, or in other words that we could not recover the compound by extraction. The word "degradation" would probably be easier to read, but since we only measure that the compound is gone, we used the word "dissipation". To clarify, we will change the sentence as follows:

*"In all soils, p-cymene dissipation was complete at the end of the experiment,"*

Will be changed to:

*"In all soils, p-cymene degradation was complete at the end of the experiment, since we could not extract any <sup>14</sup>C with methanol."*

Page 13, Table 4: Assuming the 3 columns represent the sites where BVOCs were measured at 10 cm surface, where is the Arctic heath site?

As explained in the footnotes of the Table, this is an average of one sample from the bare soil and two from the Arctic Heath. We did take more samples, but they were unfortunately destroyed during transport, and since there was no major difference in compound composition and concentration between the three samples (which may also be expected since there is no forest canopy and the sites are located just 300 m apart) we decided to treat it as one sample type.