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Interactive comment on "Model reactions and natural occurrence of furans from hypersaline environments" *by* T. Krause et al.

Anonymous Referee #2

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This is a very interesting manuscript describing the abiotic formation of furans from a) model compounds and b) natural sediments and water samples from salt lakes in Australia as well as the Dead Sea. Atmospheric furans are not your mainstream VOCs that you typically hear about, especially in the context of natural formation and emission. Furans are 5-member heterocyclic compounds, and I'm surprised to learn that these compounds, including halogenated furans, might form naturally in hypersaline soils. This is perhaps less surprising when one considers that the precursor compounds are typically other aromatic substances, such as catechol. Production of furans has been noted previously from plant matter and even soils, presumably from such aromatic precursors. Whereas Huber et al. (2010) showed abiotic formation of furan from catechol under Fenton-like conditions with Fe(III), this paper shows a similar production using a different iron complex (bispidine Fe(II) complex), which presumably is a better model

for natural iron complexes in soils. This paper then goes on to demonstrate the emission of furans from salt lake sediments and water under controlled incubations in the laboratory.

The first set of experiments seems straightforward and well conceived, demonstrating the optimal conditions in which furans are formed with the model compounds. Figure 2 illustrates that optimal furan production conditions for 0.5 mM catechol occur at 12.5 uM Fe (2+) complex, 2mM H2O2, a pH of 4.6, and at 40 C.

The second set of experiments on natural sediments and lake waters is less clear. The results provide an ambiguous picture of what conditions lead to furan production, and I have some lingering uncertainty about the relationship between the first set of experiments and the second. These issues are summarized with the following questions/comments.

1. Some methodology questions: What was the sampling strategy? The supplement provides a useful and interesting set of field data, but it is unclear if the sampling strategy was intended to be random, representative of the site, or at sites expected to yield highest emissions. Were blank tests conducted? How long were samples stored before analysis?

2. What is unique about the emission hotspots? It is indeed impressive that most sites showed emission, but what I find even more striking is the highly non-random and geographic nature of emissions. The very high outlier emissions are associated with a few lakes in particular. Looking briefly at the supplementary table, the following sites stand out:

a. Lake Springfield: very high for all furans and alkyl furans.

b. Lake Hatter Hill: extremely high for methyl and ethyl furans

c. Lake Strawbridge: very high for methyl and ethyl furans (2011 and 2012)

d. Lake Golf (surface): very high for furans, methyl and ethyl furans

3. The corresponding question is: why do other sites, including all of the Dead Sea samples, show relatively low emissions? Is it primarily related to organic carbon content? I think some analysis of the geographic distribution of 'hotspots' would be worthwhile.

4. It is exciting that halogenated furans were discovered in some of the samples, but Line 10 needs some revision ". . .even traces of halogenated furans (3-chlorofuran and 3-bromofuran) were found in these samples". This suggested to me that most or all samples showed trace amounts, whereas the presence of these compounds was in fact quite rare. Detectable levels of 3-chlorofuran were found in only 3 of 49 Australian lake sediments in 2011, with none in 2012 nor in the Dead Sea samples. 3-bromofuran was also not found in any sediment samples. In the water samples, these compounds were found in the Australian water samples in 2012, but not 2011. Can the authors explain this? Is it because of the samples themselves or because of differences in methodology/detection limits? In any case, the rarity of these halogenated furans should be made a bit clearer.

5. The figures appear very small in my copy - - I hope that the final version will be easier to view. Error bars need to be explained in the captions. Figure 5a should probably be separated from the rest of Fig. 5, as it refers to one site (Lake Boats), whereas the other subplots include all sites. Also, the choice of Lake Boats (0-2 cm) should be described more clearly in the text - - why was this specific site chosen for further analysis?

6. Could the link between the first and second set of experiments be made more explicit? There appears to be a tacit suggestion that the first set of experiments explains what is occurring in the second set, but this is not fully fleshed out. I also did not understand the interpretation of Figure 5c, which shows a link between benzene and furan emissions. Does this suggest that the observed furans may emanate from the degradation of benzene rather than from the process demonstrated in the first set of experiments?

7. Can the production rates observed in the laboratory incubations be converted into potential natural emission rates in the field? I wonder if the rates of furan production could really be large enough to affect ultrafine particle formation, as suggested.

8. I have a number of minor comments also below:

a. p17440, Line 6-7: what does it mean to say that "the turnover numbers of the active iron species increased"?

b. p17440, Line 14: 'assumed' should perhaps be 'speculated'

c. p17441, Line 28-29: confusing sentence

d. p17442, Line 13-14: confusing sentence: "One of the most prominent salt lakes is the Dead Sea being part of this study on the natural occurrence of furans".

e. p17442, Line 24: "Supplementary" should be "In addition"

f. p17444, Line 6: "long time storage" should be "long term storage"

g. p17444, Line 11: "comprised" should be "consisted of"

h. p17446, Line 11: "connected via two stainless steel needles" Please explain this.

Overall, this manuscript presents an intriguing set of results from a creative research group that has led the way in demonstrating novel abiotic production mechanisms for various VOCs. On the whole, the paper is well organized and concise. I believe that addressing the concerns/questions above would allow this manuscript to have a broader impact by making it more accessible to those who are unfamiliar with atmospheric furans or skeptical of their natural formation.

Interactive comment on Biogeosciences Discuss., 10, 17439, 2013.