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Interactive Comment

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

#### T. Krause et al.

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## Thanks you for your comments

1) The Western Australian Wheatbelt is covered with hundreds of salt lakes featuring multifarious geochemical characteristics, most prominently acidic to alkaline conditions. Our sampling strategy involved collecting sediment samples from lakes that were postulated sources of fine particles, e.g. Lake Stubbs (Junkermann et al., 2009; Kamilli et al., 2013; Kamilli et al., 2014) and sources for reactive halogen species in conjunction with DOAS measurements (Holla, 2013). Furthermore, we tried to sample an even amount of highly acidic, slightly acidic and circumneutral lakes to investigate the variation in hypersaline environments. The samples were immediately frozen, then transported to Germany, freeze-dried in the laboratory and stored under dry and cool

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conditions for about 6 months prior GC-MS measurements. Blanks were run at the beginning and end of a daily experimental series. These aspects will be added to the final paper.

- 2) The lakes vary not only in their elemental composition as presented in the manuscript but there are also other factors that need to be considered. On the one hand, iron speciation depends on the pH of the lakes. In circumneutral lakes iron was found mostly as iron sulfides in the sediment, whereas its mobility as dissolved Fe2+ increased under acidic conditions. Furthermore, under slightly acidic conditions above a pH of about 4 Fe2+ is readily oxidised to Fe3+ at the salt lake surface (Lake Golf and Lake Springfield). On the other hand, the input of organic carbon and rain water to the lakes prior to sampling pronouncedly affects their chemistry and emission potentials. For example, Lake Hatter Hill turned from a salt pan in 2011 into a brackish lake supporting aquatic plants in 2012. These are periodic changes specific to some lakes depending on location and catchment area. We would like not to add an in-depth discussion on different lakes and unique characteristics to this paper as it would go beyond the scope of the discussion.
- 3) The sediment samples from the Dead Sea and samples from Australia showing low furan emissions had low organic carbon concentrations and a high pH in common. Furthermore, temporal variations and meteorological conditions have an impact on the chemistry, including iron speciation and organic carbon composition. Further investigations of hotspots will follow.
- 4) The distribution of halogenated furans in samples from 2011 and 2012, respectively, is not a result of methodology as all samples were processed equally. With overall low 3-chlorofuran emissions the identification and quantification of this compound was restricted by the limit of detection (0.05 ng/g) as well as interferences with other gases. The absence of 3-chlorofuran from sediment samples in 2012 is either statistical, attributed to a slight sensitivity loss not noticed for other compounds or increased interferences. Furthermore, annual rain events in Western Australia are not consistent

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and the conditions of the salt lakes changed between the sampling in 2011 and 2012, which might explain the absence of halogenated furans in the water samples in 2011. Nevertheless, the quoted sentence should be made clearer that traces of these unique compounds have been found in a few samples as compared to all samples.

"[..]even traces of halogenated furans (3-chlorofuran and 3-bromofuran) were found in some Australian samples. 3-Chlorofuran was found in 3 sediments and 4 water samples, respectively, whereas 3-Bromofuran was detected in 3 water samples."

- 5) We will contact the editor about the size of the figures for the final paper and add an explanation for the error bars into the caption. Lake Boats was chosen as an acidic lake that emitted several halogenated compounds we hope to present soon.
- 6) The model reaction is one possible reaction mechanism for the natural formation of furans based on iron chemistry. As shown in Fig. 4A iron seems to play a key role during the incubation experiments. Benzene is indeed a possible precursor for phenol and catechol (Zhang et al., 1995) and the degradation of all three compounds by OH radicals result in the formation of furan (Huber et al., 2010), albeit benzene degradation experiments were conducted within the gas phase (Berndt and Boge, 2001). This connection between benzene and phenol/catechol as a link between model reactions and natural samples will be added to the final paper to make the paragraph clearer.
- 7) Simple extrapolation of incubation data to calculate local or even global fluxes are not uncommon but mostly too simplistic for a sound assessment. A genuine conversion would need a good model to account for various meterologic parameters. With this regard, time resolved air sampling within a PTFE chamber above selected Australian salt lakes from 2013 will give further insights into the importance and natural emission rates of furans. Furthermore, furans, especially highly alkylated furans, are atmospherically reactive even on par with monoterpenes (Bierbach et al., 1992; Villanueva et al., 2009) and should be considered as potential SOA precursor over the lakes. Nevertheless, the nature and mechanistics of the particle formation is still unresolved and will

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need further investigation in the future (Kamilli et al., 2014) with furans being a working hypothesis along the way, which will be made more clear in the final paper.

8) Thanks for these suggestions. We will correct the sentences and rephrase them were necessary.

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