Biogeosciences Discuss., 8, C4231–C4244, 2011
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Biogeosciences Discussions

Interactive comment on "Organohalogen emission from saline environments – spatial extrapolation using remote sensing as most promising tool" *by* K. Kotte et al.

K. Kotte et al.

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Received and published: 8 November 2011

We thank reviewer1 for his very profound and constructive review and will pick up his suggestions during the revision. Most of the following statements will be included in a revised version of the paper.

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1) General comments: The manuscript by Kotte et al. concerns the growing research field of emission of natural organohalogens (VOX) to the atmosphere, which is an interesting subject clearly within the scope of Biogeosciences. The manuscript is (despite some grammatical errors) well written and novel in the sense that not much has been

published on VOX emission from terrestrial saline environments. The manuscript provides some data that clearly shows that the investigated areas may release significant amounts of organohalogens, although the data appear rather preliminary. The largest focus in the manuscript is on remote sensing as a tool to predict landscape changes and the idea is then that these changes may be used to predict VOX emissions within the areas. The mix of presenting novel laboratory data and reflecting on tools for quantifying landscape changes and hence changes in VOX emissions appears at first interesting to the reader. There is a great risk, though, of confusion and wrong conclusions in linking very small-scale lab measurements and very large scale landscape data. I think the authors are aware of this since they discuss future needs of quantifying things like small-scale spatial variation and field measurements of actual VOX-emissions before actual conclusions may be drawn. The question is if this will be clear to a reader who is either not very deep into the subject already or who does not read the paper very thoroughly. There is a clear risk that this will be another paper that is cited for providing general estimates of VOX-emissions from a quantitatively important environment in general instead of what it actually does: Provide evidence that there may be an emission and provide suggestions as to how reliable estimates may be achieved in the future. I think the authors should try to rewrite parts of the manuscript bearing this risk in mind, e.g. by decreasing the focus on their VOX formation measurements.

Response:

- We understand that there is a chance of misconceiving our experiments and statements, which might be based in linguistic characteristics and terms used in this paper. Therefore we will rewrite a few paragraphs to emphasize the pilot character of the study and to focus on the potential of the method. Furthermore it should be noted that the manuscript forms part of a Special Issue: Earth observation for land-atmosphere interaction science". To meet the issues focus we had to concede on the extent of the chemical analytical part.

Specific comments: 2) P. 7527 l. 11. What semi-volatile compounds? Chloromethane seems to be mentioned as an example but would be classified as very volatile I think?

Response:

- e.g. PCDDs and PCDFs

- MeCl is of course not a semi-volatile; the paragraph will be rearranged

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3) P. 7528 l. 27 to P. 7529 l. 1. Please provide (a) reference(s) for this statement.

Response:

- e.g. Huber et al. 2009

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4) P. 7530 l. 2-3. Do you actually know that this extrapolation is possible?

Response:

- To give the statement more character of a thesis we will change the sentence to '... might allow ...' .

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5) P. 7530 l. 16. Do you mean sea or rather salt lake here?

Response:

- Although in popular parlance often named as Aral Sea (russ. Aralskoje more) it is geographically a lake. Sentence will be changed during revision.

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6) Section 2.3 The section on especially the VOX production seems extremely short compared to the value the data obtained are given in the later Results and Discussion

BGD

8, C4231–C4244, 2011

Interactive Comment

sections.

Response:

- As reviewer 1 mentioned this work focuses on the development and application of satellite products. Therefore we don't got into detail on the soil sampling and chemical analysis part. The underlying methods can be looked up in the reference cited, e.g. Huber et al. (2009) and Löw et al. (2011).

Additional Literature: Löw, F., Navratil, P. and Bubenzer, O.: Landscape Dynamics in the Southern Aralkum Desert - Using MODIS Time Series for Land Cover Change Analysis. In: Aralkum - A Man-made Desert: The Desiccated Floor of the Aral Sea (Central Asia), edited by Breckle, S.-W., Wucherer, L., Dimeyeva, L. and Ogar, N.P., Ecological Studies Series, 218, Springer, 83-96, 2012.

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7) P. 7533 l. 2-4. The procedure of freeze-drying and milling the soil samples might not change abiotic formation to a very large degree (although probably some) but the biotic formation will be greatly affected. Since this paper is sent to the Journal Biogeosciences I assume that the authors also expect biotic activity to be important in regards to VOX formation. The authors need to address this issue in detail also within the manuscript, and to discuss to a greater detail how reliable their estimates of emission from these soils are! If the formation experiments only serve as examples that VOX may be formed from these soils and as an example to demonstrate how the subsequent calculations may be performed, the authors should write this very clearly and then put less emphasis on their emission estimates in the Results and Discussion sections.

Response:

- The majority of biogenic VOX-producers (bacteria, algae, archaea) will be suppressed by the preparation method (freezing at -20°C + freeze drying + milling). However, the

BGD

8, C4231–C4244, 2011

microbial residues remain in the sample and will be exposed to geochemical reactions, as it would be the same in unprepared samples.

- Depending on the sample location the generally very low organic content of semi-/arid salt sediments partly originates in algae/bacteria mats. One could question whether spores survive the preparation process and come back to life after adding water to the sample. Based on experiments by Weissflog et al. (2005) one would expect even higher emission rates when using raw samples.

- Anyhow, the production of several VOX under dry condition reveals the relevance of the experiments with regards to the regional climatic condition at the sample sites. Dried out salt flats that cover hundreds of km^2 with surface temperatures of +55°C are no curiosity.

- We agree overall to reviewer 1 that the experiment demonstrates the potential of the applied calculation method and will adjust the manuscript accordingly.

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8) P. 7534 l. 24. Which of the three isomers of DCE?

Response:

- we included data on the trans-1,2-DCE isomer only. The other isomers occurred sporadic.

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9) P. 7536 l. 17. Please define typical. Your observation? Data from literature (I assume it is your data, but there is nothing about sampling at these sites in the Methods section).

Response:

- To bring out the general relevance of terrestrial saline ecosystems as potential VOX

BGD

8, C4231–C4244, 2011

area sources we included some of our own data (provided in table 3), based on similar sampling procedures and analytical methods. Extended data on this samples sites will be discussed in a different paper.

- We will give additional information in table 3 on the sampling locations, including soil characteristics as well as coordinates.

- description of table 3 will be adapted accordingly.

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10) P. 7536 l. 21. Does CHBr3 occur consistently (it does not in Table 3)?

Response:

- CHBr3 does not occur consistently => sentence changed to : "...such as CH3Cl or CH3Br..."

- Explanation: The production of CHBr3 is closely connected to the Br – content of the soil. Thus we find substantial amounts of brominated compounds in saline sediments that are influenced by sea water / sea spray (e.g. Walfishbay/Namibia). Furthermore, inland salt lakes that are feed by ancient marine salt deposits (e.g. southern Russia) often show elevated bromide content and corresponding Br-VOX emission. Saline environments that are mainly feed by erosion processes often show relatively low Br content (e.g. Aral sea, Botswana).

- A separate paper concerning the influence of soil characteristics as well as sequential salt accumulation on VOX production is under preparation.

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11) P. 7537 l. 3. Why especially for southern African environments?

Response:

- This statement refers to the sample locations included in table 3. In contrast to the

BGD

8, C4231–C4244, 2011

Interactive Comment

extreme seasonal climatic variations in Uzbekistan and southern Russia (frost in winter versus heat in summer), the climatic condition in southern Africa provide more favourable/moderate condition for VOX-production throughout the year. Day peak temperature usually varies between 15 – 50°C in southern Africa, whereas in middle Asia and southern Russia temperature can drop to -20°C very easily during wintertime. Experiments on the temperature regime, published by e.g. Wishkerman et al. (2008), indicated increased VOX production rates from $\sim$ 20°C rising, using dry plant material. One should bear in mind that soil surface temperature can rise dramatically in direct sunlight leading to ‘decoupled’ temperature regime between soil and ground level air layers.

- In this sense one can argue that saline sediments of the tropical and subtropical zones generally act as potential ‘all season’ VOX producer. But this has yet to be confirmed.

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12) P. 7537 l. 5-13. I agree that extrapolation from small to large scale is essential. I agree that the remote sensing approach using satellite information might work to estimate changes in landscape. I am however not convinced at all that you can then extrapolate from lab- or even small scale field measurements to general emission rates for a certain landscape. As long as the mechanisms of formation of VOX in these environments are unknown and great variations in VOX-emissions are evident but not understood (as also indicated with the variation in table 2 and 3) in my opinion, one should be careful to conclude that this might actually work in practice.

Response:

- There is no analytical large scale method available with appropriate sensitivity that doesn’t intervene the soil system by sampling. In fact, existing optical methods like DOAS can be used to determine reactive halogens such as BrO. The Open Path FT-IR Spectroscopy might work for some chlorinated organic compounds, but is limited to mid to high concentration in the range of mg/m^3. We also perform chamber experi-

BGD

8, C4231–C4244, 2011

ments and there are airborne measurements as well. However, chamber experiments are difficult to handle in landscapes with little or no infrastructure, whereas airborne measurements often fail due to administrative obstacles and very high expenses. For now there is simply no other option as to recourse on many years of experience in laboratory based VOX analysis of soil, water and plant samples.

- The extrapolation from soil cores to local and regional scale is a common method in remote sensing science. Depending on the heterogeneity of the target landscape and soil structure one has to adjust the sampling grid. Focusing on the former seabed of the southern Aral Sea we are talking about hundreds of km^2 that show extremely homogenous soil structure and geography (see attached photographs for sample regions).

- Remote sensing science always has to deal with the problem of modeling natural systems that are not fully understood. There would not be a single global or regional map available on issues like atmospheric trace gases, surface water quality or land erosion without accepting far-ranging effects from necessary estimations and simplifications.

- But we follow reviewer1 in the way that we can adjust our discussion to more general statements.

- Variations in Table 2+3 can be explained by the grouping of different soil types to one soil class (according to method used) as well as fractional misinterpretation of soil signals by MODIS. To conclude: Mapping specific features like salt quality, organic content or humidity to assign soil sub classes can't be realized without a hyperspectral data approach. Herein the limits of the applied method become evident. To demonstrate the limits of MODIS data we updated figure 5 with our own spectral signature variations of main land cover classes, recorded from pixels covering the soil sampling sites and pixels selected for exercising the image classifier algorithm.

- The overall approach of our study is to describe the phenomenon under different climatic condition, without focusing on chemistry behind the VOX production. A fu-

BGD

8, C4231–C4244, 2011

Interactive Comment

ture more sophisticated emission model will mainly have to rely on geographical and meteorological data plus the information how certain soil types behave under different climatic scenarios. At this stage we can't described all facets of the geochemical system behind the VOX production, but there are a few promising approaches by e.g. Huber, Keppler or Wishkerman to describe the fraction of MeCl/Br and the THM's under moist and dry condition.

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13) Table 2. I believe that presenting emissions estimated from experiments with a few grams of soil with the units g/km2 tends to completely ignore the great spatial variability that may exist even on a small scale (e.g. as was recently described for CHCl3-emissions from temperate forests (Albers et al. 2011)

Response:

- Albers et al. 2011 started a discussion on the spatial variability of MeCl in temperate soils that was long overdue. In contrast to their research sites in Denmark and Sweden we focused on an geographically and geologically extremely homogenous soil system with usually no O, A and B horizon and Corg-contents of around 1% - compare Löw et al., 2011 and attached photographs. Thus a comparison to northern European forest stands seems difficult, also with regards to the climate conditions and hydrology. However, the question on the heterogeneities of the VOX emission is an important issue in saline sediments and has to be discussed in future. For DCE we still have to discover the production mechanism.

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14) Table 3. Something must be wrong with the units (g/m2). Furthermore, it is not clear to me, if the minus-sign indicates no emission (which would in some of the cases be unexpected with the very large emissions at other sites, even if the unit is g / km2 as in table 2) or if it indicates that the study is ongoing, as is indicated in the Table caption.

BGD

8, C4231–C4244, 2011

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Response:

- the “minus-sign“ indicates ‘below detection limit’, except for class ‘water’ and class ‘reed’ where it refers to the absence of data since no samples have been taken there. => will be changed accordingly.

- Units in Table3 must be changed to ng/kg

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15) Table 3. Did you also determine the fourth Br/Cl-trihalomethane (CHBrCl2)? It could be interesting to compare with the others. . .

Response:

- CHBrCl2 was not detected (now included in Table 3)

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16) Table 2 and 3. What are the detection limits of the emissions? It is surprising that you in some cases see no formation while in others a large formation (actually very large compared to any previous published VOX-emissions). What is your suggestion to explain this observation?

Response:

- Detection limits within 0,1 – 0,01 ng/g depending on species and matrix

- see statement to reviewers comment 11 (P. 7537 l. 5-13)

Revised Table 3.

VOX emission of saline soil sediments of different origin using purge-and-trap GC/MS analysis. 24 hour incubation time; moist or dry sediments – ongoing study [ng/kg].

Revised Figure 5:

BGD

8, C4231–C4244, 2011

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Spectral signature variations of main land cover classes (bare area, salt soil and salt crust). Data recorded from pixels covering the soil sampling sites respectively pixels selected for training of the image classifier algorithm. For comparison with laboratory data the image backdrop shows spectral profiles of gypsum, halite, calcium carbonate, sodium bicarbonate, and sodium sulphate in the visible, near, and mid-infrared (400 - 2500 nm). Data source: Metternich and Zinck (2003); recorded by the GER 3700 Spectroradiometer.

Additional photograph:

Top left: halite enriched salt crusts, in the northern part of the transect (close to the remaining water body). Top right: sand dunes in the southwestern transect Bottom left: sparce vegetation, open-worked by saline soils. Bottom-right: emerging thunderstorm on robust salt crusts in the northwestern transect.

Interactive comment on Biogeosciences Discuss., 8, 7525, 2011.

		Uzbekistan Southern Aral Sea	South Russia Volgograd region	Namibia Walfish-bay	Botswana Makgadigkadi Pan
Site description		endorheic basin, partly seasonally flooded	salt dome, seasonally covered with water	dry river mouth, maritime coastline	dry salt pan, seasonally covered with water and grass
GPS		43°58'46 N 59° 0'24 E	49° 7'50 N 46°41'35 E	23° 5'30 S 14°27'35 E	20°32'12 S 25°58'31 E
pH soil crust		8.5 - 10	6.9 – 8.3	7.8 – 9.0	9.5 – 10.3
Conc. range Cl [g/kg]		6.1 - 120	22 - 51	17 - 81	25 - 82
Conc. range Br [mg/kg]		n.d.	112 - 315	43 - 312	64 - 204
Cl/Br (Molar ratio)		-	260 - 450	470 - 990	780 - 990
Chloromethane	CH_3Cl	n.d.	1524 *	1441 *	n.d.
Bromomethane	CH_3Br	n.d.	104 *	116 *	n.d.
Tribromomethane	$CHBr_3$	n.d.	257 *	n.d.	n.d.
Trichloromethane	$CHCl_3$	464	148	362	219
Dibromochloromethane	$CHBr_2Cl$	n.d.	n.d.	n.d.	980
Dichlorobromomethane	$CHBrCl_2$	n.d.	n.d.	n.d.	n.d.
Dichloroethene	$C_2H_2Cl_2$	264	n.d.	2070	827
Trichloroethene	C_2HCl_3	29	n.d.	n.d.	129
Tetrachloroethene	C_2Cl_4	n.d.	n.d.	43	36

Fig. 1. Table 3

BGD
8, C4231–C4244, 2011

Interactive Comment

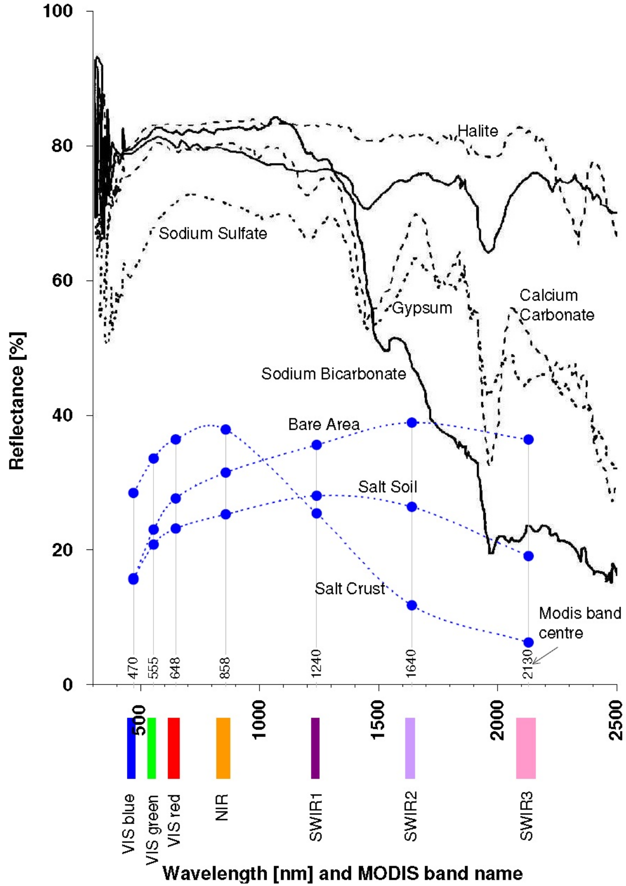

Fig. 2. Figure 5

Fig. 3. Add Photographs