

## ***Interactive comment on “Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide” by F. Ziska et al.***

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We grateful acknowledge the reviewers for their effort and suggestions improving our paper ‘Global sea-to-air flux climatology of bromoform, dibromomethane and methyl iodide’. We answered all comments step-by-step.

Answer to Anonymous Referee #1

The in situ observations are mapped on a global 1x1 degree grid through a regression with latitude and longitude to construct a background field as described in sections 3.4 and 3.5. If observations are available within a 1x1 degree grid cell, these data are instead taken from an objective mapping technique (section 3.3, if I understood this correctly, this point wasn't made fully clear). As a result of this different treatment,

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there are structures in the climatologies, that represent the availability of data, not real features (seen e.g. in Fig. 4).

>We have chosen a combined technique that we thought was most appropriate for the sparse data treatment. Thus we have mapped the in situ data on the 1x1 grid by objective mapping which gives the best available value for the grid point and then only the missing values were filled with the regressions of the in situ data. We will clarify the text in section 3.3. We believe that within the current knowledge the combined technique represents a better approach than just the regressions, but we will take this into account in our revision and follow the reviewers' suggestions to publish different data tiers, as addressed in the next section.

While I understand that this approach has been chosen to provide the best possible available information, I still find this problematic for the use in global models. My suggestion would be to make available different tiers of the data sets: E.g., Tier 1 could contain only the incomplete data from the objective mapping (similar to Fig. 1), Tier 2 could contain the results from the linear regression with latitude and longitude only, while Tier 3 could contain the merger of both, as for the current data set. Anyway, I would encourage the authors to make these data publically available as a supplement to this paper.

>We thank the reviewer for this suggestion, because this will aid the community with data access and we will provide the different tiers as additional supplements for the ease of access for the community and make this clear in the description of the different tiers. We will provide three files with several columns and 360x180 rows. All files will provide lat and long of the grid points in the first two rows and the fist file further provides the incomplete data from the objective mapping for the three compounds for ocean and atmosphere (six columns), missing data and land will be filled with NaN. Results from the linear regression with latitude and longitude grid points for ocean and atmosphere and three compounds for Robust Fit and OLS fit (12 columns) will be provided in file 2. And file three will contain the merger of both.

C3115

While it seems very reasonable to use different latitude regions for the oceans and the atmosphere, there is the risk that this introduces some inconsistencies for the sea-to-air concentration gradients. E.g., consider a hypothetical situation where concentrations in ocean and atmosphere are in equilibrium but each change with latitude. Calculating regressions over different latitude regions for ocean and atmosphere could then introduce artificial sea-to-air concentration gradients. I am slightly concerned that the pronounced concentration gradients for bromoform seen at about 60S (minimum) and 60N (maximum, Fig. 6) could be related to the particular choice of latitude ranges for the regressions. I suggest to double-check that these features are real and robust and not an artefact due to the regressions used.

>The reviewer is right that this treatment causes concentration gradients, which are related to the latitudinal bands chosen for the interpolation. Therefore, we recalculated the sea-to-air concentration gradient with unique latitude ranges for ocean and atmosphere and compared them with the concentration gradient used in the paper (attached as Figure 1). Figure 1 is equivalent to Figure 2 of the paper. The trend of the OLS or RF regressions with the new latitude ranges has not changed much. The most difference is seen in the equatorial area (Figure 1); a downward trend of the OLS regression in the northern hemisphere and negative concentrations occur both regression techniques in the southern hemisphere for. The regression techniques seem slightly robust. The total global emissions have changed marginal; RF reduced from 1.5 to 1.14 GmolBr/yr and OLS increased from 2.5 to 2.56 GmolBr/yr. The data base is so sparse and ship expeditions with combined data sets of atmosphere and ocean are even less, thus the main intention was to get comprehensible concentration maps which are related to the oceanic and atmospheric features in a climatological sense. And indeed these extrapolations already produce possibly non existing features, which we address in the paper. We believe the regression in the different latitudinal bands as better compromise between data and approach and that our approach although it does not reproduce the accurate concentration gradients better reflects the data pool and extrapolation based on the physical and biogeochemical provinces. For dibromo- $\Delta$ -methane and methyl

C3116

iodide the different approaches yield less variance and obtain a good agreement to already existing estimates.

Given the importance of emissions from coastal and shelf regions compared to the open ocean, I feel that more details should be given how coastal and shelf regions are defined and how sensitive the results are to the particular definition. Is the shelf just the region 2 degrees away from the land, or is it based on water depth or some other parameter? Also more information is needed if and how the coastal and shelf data are further divided into different latitude regions (Sec. 3.2). Most of the current discussion is limited to open ocean.

>The coast is defined as the first grid point next to a land grid point and the second grid point is characterized as the shelf grid point. The others belong to the open ocean water and atmosphere regime. We will clarify this in section 3.2 p. 5609 l.4-6: Considering the compounds distribution, all data are divided into coastal, shelf and open ocean regimes. The coastal area is defined as all first  $1^\circ \times 1^\circ$  grid points next to the land mask, while the shelf regime is marked as all second grid points neighboring the coastal one. The other grid points belong to the open ocean water and atmosphere regime. The data base in coast and shelf regions are very sparse. For this reason, these areas are only divided into northern southern hemisphere (p.5611 l.4). No effort has been undertaken in this paper to parameterize the concentrations on depth or anything else. This own topic will be pursued in detail in following investigations of individual cruise data.

Specific comments of Reviewer #1 p.5603, l.6: "In input of . . .": make clearer that this refers to previous studies, not the current study.

>Sentence will be changed to: Previous studies showed that the input of marine halogens to the stratosphere is based on observations and modeling studies using low resolution oceanic emission scenarios derived from top down approaches.

p.5603, l.18: "global concentration gradients": you mean sea-to-air concentration dif-

C3117

ferences?

>We mean global sea-to-air concentration gradients. We will complete this in the sentence.

p.5604, l.20: I suggest to move this sentence towards the end of the paragraph

>We agree and move the sentence to the end of the paragraph.

p.5606, l.19: remove parentheses around "bromoform, . . ."

>This will be done.

p.5610, l.1: "The data classification. . .has been linked. . .": what specifically does that mean?

>We used the same data classification described for CHBr3 for CH<sub>2</sub>Br<sub>2</sub> and CH<sub>3</sub>I because of the similarity in source regions including coastal, upwelling and planktonic source areas (see Fig.1 in the paper). Since we distributed ocean and atmosphere data roughly in physical and biogeochemical provinces, this distribution also roughly reflects the knowledge about the other compounds sources, which connects the data classification of CH<sub>2</sub>Br<sub>2</sub> and CH<sub>3</sub>I to the one of CHBr3. We will make this clearer in the revised version.

p.5610, Sect. 3.3: More information is needed here or should be made clearer. There is a correlation length for the Gaussian weighting (3 degrees in open ocean, 1 degree for shelf and coast) and also a cut off length? Sorry, this was confusing to me – and may be relevant for my general point 1 above.

>We will try to clarify this in the revised version and will change Section 3.3 into: The original, irregular measurements from the HalOcAt database are transferred to a uniform global 1°x1° grid using a Gaussian interpolation. Based on this technique the value at each grid point is calculated with the measurements located in the defined Gaussian range. The Gaussian Bell radius is 3° for the surface open ocean water and

C3118

atmosphere data and 1° for the coast and shelf region. The wider radius for the open ocean regimes are caused by the higher homogeneity of the data in this region. This kind of interpolation takes the spatial variance of the measurements into account. The smaller the distance between a given data point and the grid point, the greater it is weighting in the grid point calculation (Daley, 1991). For grid points where no measurements are available within the Gaussian Bell area no concentration data can be calculated directly and a linear regression needs to be applied.

p.5611, l.13: remove the word "vertical"

>We will remove it.

p.5611, II.15-20: please provide more information for the RF method

>We will add into the paper: The second method for calculating regression coefficients is the Robust Fit (RF) technique which is especially used for not normally distributed values. A regression analysis is robust if it is not sensitive to outliers. The calculation of the robust coefficients based on the iteratively reweighted least squares process. In the first iteration each data point has equal weight and the model coefficients are estimated using ordinary least squares. In the following iterations, the weighting of the data points is recalculated so that the distant data points from the model regression from the previous iteration are given lower weight. This process continues until the model coefficients are within a predefined range. Our calculations based on the most common general method of robust regression the "M-estimation" introduced by Huber (1964).

p.5611, last paragraph: in addition to the RMS you may also consider the uncertainty for the trends. If the uncertainty is large, it may be better to use just a mean or median, instead of a trend. By the way: Have you considered a continuity criterion for the trends in adjacent regions, or could there be sharp breaks between adjacent regions?

>Any continuity criterion or uncertainty calculations of the trend would introduce more

C3119

complexity in the current approach, which we know is a first simple and not completely realistic approach since we also do not consider other possible influencing factors as f.e. seasonality. Sharp breaks are meant to be avoided also by the choice of our latitudinal range. Given the intention of our climatological concentration maps as first overview, introducing little complexity, we think, that the method of the paper can later be improved by the consideration of a hopefully continuous growing data base.

p.5612, Sect. 3.6: to fully appreciate the functional dependence of the flux on wind speed, SST, pressure and salinity it would be helpful to have also the equations included how the equilibrium water concentration  $Ca$  is related to atmospheric mixing ratios (via pressure) and how the Schmidt numbers depend on temperature and salinity. This would then help to better understand the relationships shown in Fig. 3.

>We will partly include the equations: The calculation of the atmospheric mixing ratio from ppt into pmol/L:  $Ca=Ca(ppt).\cdot pressure/(temp+273.15)/83.137$   
The Henry Constant:  $H= \exp(-4973.0/(temp+273.15)+13.16)$  The Schmidt number equation based on the mean of the references of Schroeder/Le Bas (1915), Wilke and Chang (1955), Hayduck and Laudie (1974), e.g.:  $Sc_{CHBr3}=kinem\_viscosity/(0.0000000193.\cdot (temp.^2)+0.0000001686.\cdot temp + 0.0000040342)$

>The kinematic viscosity depends on temperature and salinity.

P.5612, eq. (2): This is not dimensionless, i.e. it depends on the units for  $U$  (I guess m/s). Provide units or (if possible) write in dimensionless form.

>The units will be provided.

p.5616, l.27: "as reported in the literature": replace by relevant citation We will add the references Laturnus et al. 1998 and Bondu et al. 2008 instead.

p.5619, l.24: in what sense is this an "upper limit"?

>We will delete the words 'upper limit' in the text., since we are now aware that further

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refinement of the data and the possible underrepresented contribution of outliers may increase the flux further: Thus we will revise the text accordingly.

p.5621, l.21 and 27: do you interpolation or extrapolation?

>We interpolate.

p.5624, l.11: "less than 1%": I don't understand. 1% with respect to what? And why?

>We fit (by using objective mapping) the measurements onto the  $1^\circ \times 1^\circ$  grid which involves a decrease in the concentrations of the observations. And this reduction is on average less than 1%. We will change the sentence into: Fitting the in situ measurements onto our  $1^\circ \times 1^\circ$  grid (by using objective mapping) leads on average to a reduction of the initial atmospheric mixing ratios and oceanic concentrations of less than 1 %.

p.5625, Sect.5.3: Are TransBrom data part of the climatology, or is this a totally independent data set? Other point: is this really "short time" variation, or also small-scale?

>The Transbrom data are part of the climatology. The data have high spatial and temporal resolution.'

p.5626, l.6: missing ":"

>We will add it.

p.5633, l.27: If Quack et al. (2013) is still "in preparation" it should not be included in the references list.

>The paper is still in submission. We will take it out from the reference list and clarify possibly missing points in this manuscript.

Figs. 6 and 7: The concentration gradients in Fig. 6 look surprisingly similar for RF and OLS. One can identify differences, but overall the differences are small, even for bromoform. With that I have difficulties to understand why the sea-to-air flux as shown in Fig.7 is almost a factor of 2 larger for OLS than for RF for bromoform.

C3121

>The Figure 6 only shows a zonal mean of the concentration gradient and Figure 7 a total (source-sink) global flux. The differences between OLS and RF are not so small in Figure 6. The concentration gradient calculated with OLS technique shows in the southern hemisphere a lower sink compared to RF. Further, the source regions are all enhanced in OLS. In total it is not unrealistic that OLS fluxes have a factor of nearly two.

Fig.7: Can't see any "gray shaded" area.

>We agree, they are really small and hard to see, we try to improve it by the alignment of punctuated lines.

Answer to Anonymous Referee #2

There are instances where over generalizations of interpretations are provided, specifically when describing similarities between different chemicals. For example, some have suggested that CH<sub>2</sub>Br<sub>2</sub> and CHBr<sub>3</sub> share common pathways for emission, etc. and in a number of instances (e.g., lines 374, 434, 440) the authors comment on the similarity in concentration or flux distributions for these chemicals. But in many instances I have to disagree with the authors and suggest that the distributions for these two gases often appear quite different, despite their assertions otherwise. I'd recommend that the authors avoid over-general comments related to similarities in distributions, and instead focus their comments on specific regions.

>We will revise the text accordingly and add more information to CH<sub>2</sub>Br<sub>2</sub> and reduce over generalizations of interpretations and discuss the second compound also in more detail to clarify similarities and differences.

Section 5.2, I think conclusions about seasonally-varying fluxes are highly suspect, given that only annual mean air and water concentrations are being considered here. These seasonal variations are only driven by seasonal changes in the variables driving exchange, if I'm reading the manuscript correctly. It would seem that seasonal changes

C3122

in water concentrations are highly likely, and, therefore, I presume that such variations could significantly alter our understanding of how the fluxes actually vary with season. I recommend removing this discussion or very clearly emphasizing in this section that these conclusions regarding seasonal variations in flux do not consider one critically important part of the equation (seasonal concentration variations).

>We thought that this had been clarified in 'Variability of the climatological sea-to-air fluxes' and in section 5.1, but we will now put more emphasis on this in section 5.2. The temporal variability of the SST is considered in the concentration gradient, used in the sea-to-air flux calculation, by computing a new equilibrium concentration for every 6 hour time step from 1989-2011. We will add in the end of section 5.2: However, the results do not consider a seasonal varying influence of neither the water nor the air concentration on the emission because the current sparse investigations do not allow a suitable parameterization of the VSLS. See also our comment below.

Section 5.3 is interesting, but needs some comment on the amount of data going into the climatology in this region; is the agreement the result of their being very little data other than that from the Quack et al., 2012 cruise going into the climatology here? Regarding timescales and potential influences of covariations in exchange and concentrations on flux estimates, the information on line 603-606 needs to come in the methods section of the manuscript, not in results and discussions.

>Amount of data going into will be included and information on line 603-606 will put in the method section.

Regarding this (and the point made above regarding section 5.2), are there no longer-term measurements that help one assess seasonality for these gases in water or marine atmosphere that could potentially be extrapolated to broader regions as a sensitivity test?

>As mentioned in the text (Section 5.1), longer-term measurements in the ocean are published in Orlikowska and Schulz-Bull, 2009 (measurements are from the Baltic Sea)

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and in Archer et al. 2007 (measurements are from the English Channel). Both studies are not representative/ useful for extrapolating neither seasonally nor globally. Longer-term marine atmospheric measurements are from the ongoing program NOAA/ESRL (Montzka et al., 2003). A map of the 14 ground-based stations is published in Hossaini et al. 2013. May be it would be possible to use these data as a sensitivity test, however, most of the stations are in the northern hemisphere and therefore not sufficient for a global estimate.

Differences between the two regression techniques are described, and the ordinary least squares is indicated correctly as being more influenced by outliers. One must remember that the true emission magnitude could be driven by the outliers, to some extent, and even the OLR technique would underestimate the influence of those outliers (e.g., line 685). Hence I'm not convinced that it can accurately be described as an upper limit estimate (as you indicate on line 673)... some discussion of this is given in lines 590-592, but be specific about which study you mean by the work "there" (line 592).

>We will delete the words 'upper limit' and 'there' (l.585) in the text. We are aware that further refinement of the data and a possible underrepresented contribution of extreme values may increase the flux further: Thus we will revise the text accordingly.

Details: Not clear if fluxes in sampled grids are from observations or from regression results (which are used for non-sampled grids)...

>This will be revised according to the detailed suggestions by reviewer 1. Tier 1-3

Lines 688-690 conclusions here don't appear to be any that can be drawn from evidence provided in this paper... I'd recommend removing them or attributing them properly.

>We will change the paragraph into: Our global sea-to-air flux estimates can be used as input for different model calculations. The existing uncertainties can be reduced

C3124

by enlarging of the HalOcAt data base with more measurements, especially in ocean waters, common calibration techniques and more basic research into the underlying source and sink processes.

Units on RMSE in tables C1 and C2?

>The units for the RMSE in table S1 and S2 is mentioned in the text.

Seems to me that the first two paragraphs on p. 17 make the same points, perhaps one was meant to be deleted?

>We checked and will revise.

Quote fluxes in comparable units throughout the paper and in Tables and figures (moles or grams of halogen or compound...)

>We tried to use mol consistently and check again all tables and figures.

Standard of English needs improving.

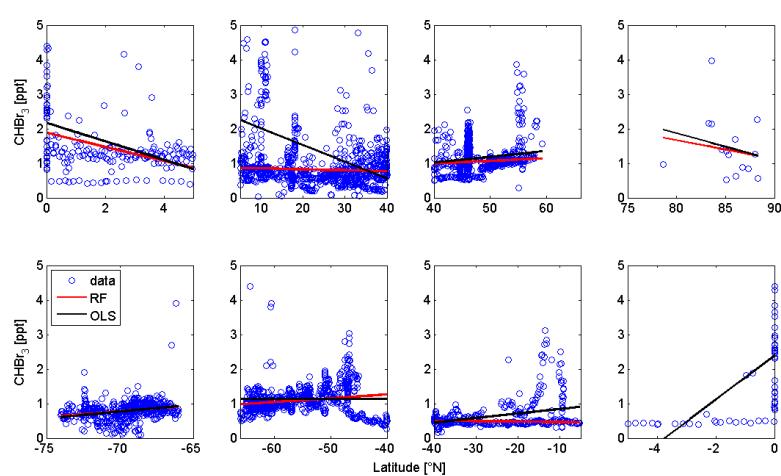
>We will let it check again from a native speaker.

Line 127, I'm not convinced that iodine affects stratospheric ozone. Lines 382-387, are these differences robustly determined by measurements in multiple seasons and/or from multiple groups so that we can be sure they are the result of one groups.

>Current model results of Tegtmeier et al. 2013 suggest an overall contribution of 0.04 ppt CH<sub>3</sub>I mixing ratios at the cold point and a localized mixing ratio of 0.5 ppt. However, this is low but not a negligible part in the stratospheric ozone loss budget. For this reason we would not change the statement. (Tegtmeier, S., Krüger, K., Quack, B., Atlas, E., Blake, D. R., Boenisch, H., Engel, A., Hepach, H., Hossaini, R., Navarro, M. A., Raimund, S., Sala, S., Shi, Q., and Ziska, F.: The contribution of oceanic methyl iodide to stratospheric iodine, *Atmos. Chem. Phys. Discuss.*, 13, 11427-11471, doi:10.5194/acpd-13-11427-2013, 2013)

C3125

C3126



**Fig. 1.**

C3127