

Dear Editor,

We are pleased to submit the revised version of the manuscript (acp-2018-1172)

**"Emission of volatile halogenated organic compounds over various Dead Sea landscapes".**

First we want to deeply thank the two reviewers for the effort they invested in reviewing this paper and for its thorough and constructive review. The review helped us better support our findings, improve the presentation of the results and give a more complete, clear and concise discussion. We seriously considered all of the reviewers' comments. We hope that our important scientific findings will be found acceptable, following the revisions that we have made to the manuscript, as described in the following. We open this response with a general description of the major revisions in the manuscript, followed by detailed point-by-point responses to each of the reviewers' comments.

Sincerely,

Eran Tas

### **General major revisions according to the reviewers' comments**

- All discussions and conclusions are supported by statistical tests.
- Title: We now use "landscapes" instead of "landforms" in the title.
- Abstract: We report the mixing ratios and flux ranges for all investigated volatile halogenated organic compounds (VHOCs).
- We present a figure comparing the measured mixing ratios of all investigated VHOCs instead of the original Table 2. A revised version of this table is included in the Supplementary Information (Table S3).
- Fluxes in the original Table 4 (now Table 2) as well as the related discussions are now reported along with information about their statistical significance. Table 2 has been moved to Sect. 3.1.

- Fluxes in Fig. 3 (originally Fig. 2) as well as the related discussions are now reported along with information about their statistical significance. The figure has been revised to allow easier information extraction.
- A new figure has been added (Fig. 4) to demonstrate the spatial distribution of the VHOC fluxes in the studied area.
- Fig. 5 (originally Fig. 3) has been revised and the original figure is included in the Supplement (Fig. S1).
- Correlation values between mixing ratios in Table 4 (originally Table 5) are reported along with their corresponding statistical significance. These values are now also provided individually for different site types (bare soil, coast, etc.).
- Correlation values between fluxes in Table 5 (originally Table 6) are reported along with their corresponding statistical significance.
- The following has been added to the Supplement: average lifetime and primary removal pathways for the VHOCs (Table S1); a tabulated comparison of the mixing ratios measured in this study and the corresponding values reported for the marine boundary layer (revised original Table 2 (now Table S3)); all sampling footprints (Table S4); analysis of potential anthropogenic influence during the measurements (Sect. S5; also discussed in the main text); in situ measured meteorological parameters during the air sampling (Sect. S6).

In the following, all of the reviewers' comments (in italic red font) are followed by our detailed responses.

### **Response to comments by reviewer #1**

*Interactive comment on “Emission of volatile halogenated organic compounds over various landforms at the Dead Sea” by Moshe Shechner et al.*

*Anonymous Referee #1  
Received and published: 16 January 2019*

1. *This is a study of concentrations of short-lived halogenated gases from a unique area, the Dead Sea. Given the interest in these chemicals and the uniqueness of this location, this paper has the potential to be an interesting contribution. It certainly includes a thorough review of the available literature and the authors have very thoroughly considered their new results in light of previously published work. However, I'm concerned about a number of aspects of the interpretation of the measurements, which are described below. The most significant is an inadequate consideration of uncertainties in most aspects of the work. This leads to an extended discussion throughout the paper of effects that I'm not convinced are real.*

*In Table 2, comparisons are made between concentrations measured at these Dead Sea sites with reported concentrations in the marine boundary layer (MBL) (as medians, from Ozone Assessment Reports), and measured concentrations enhancements are taken to imply significant local emissions. But this seems an inappropriate conclusion. I would expect that the influence of the marine boundary layer on what is being measured in the Dead Sea valley is diminished by the time air moves from any distant sea (Red or Mediterranean) to this valley owing to vertical mixing within the lower atmosphere. Perhaps instead, any enhancement relative to the MBL suggests only that fluxes are non-zero in this region too, and are perhaps comparable (or larger) than suggested for the marine boundary layer and coastal ecosystems? Drawing conclusions from concentration differences in the Dead Sea area vs the MBL is tricky and not especially informative, given that concentrations are influenced by dynamics in addition to flux—this seems worth mentioning, but isn't yet in this regard. Also, why aren't MBL fluxes also shown in Figure 2?*

**Answer:** Thank you for this comment. The only reason that we compared concentrations at the Dead Sea to those of the MBL was to suggest irregularly high local emissions in the Dead Sea area, rather than from either the Red Sea or the Mediterranean Sea, whose contributions to the local concentrations are indeed expected to be negligible. Considering the relatively large distance from the Mediterranean Sea (~90 km) and the Red Sea (160 km), we believe that these elevated concentrations imply local emissions from the Dead Sea area itself. We did not intend to indicate significant contributions from the Red or Mediterranean seas, and to clarify this, we now state the following: "Overall, the measurements at the Dead Sea boundary layer revealed higher mixing ratios for all investigated VHOCs than their expected levels at the Mediterranean Sea and Red Sea MBL, indicating higher local emissions from the Dead Sea area" (lines 333-335). We agree that comparing the mixing ratios at the Dead Sea to those measured at the MBL is tricky, but we think that it provides some understanding of how this area can contribute to VHOC loading relative to nearby marine environments. Taking this and the next comment into account, we now present the comparison of mixing ratios to those in the MBL in a figure without including enrichment factors.

We do not include MBL fluxes in Fig. 3 (originally Fig. 2) because reported fluxes in the MBL were measured under very different conditions, which also resulted in remarkably large differences in their magnitudes. For instance, fluxes of VSLs have been found to be significantly different in magnitude over the coastal area, open ocean, shelf and upwelling (Carpenter et al., 2009). Moreover, we also compare the measured fluxes with those measured over various landscapes, such as bare soil, soil mixed with salt deposits, and vegetation, because in the case of fluxes, we find it more suitable to compare the reported fluxes more selectively in the text.

2. *I also find it very difficult to internalize the information given in Table 2 as presented. I'd recommend the presentation of these results, if retained, also (or instead) as a figure. Furthermore, I'd suggest that any enhancement factor should also consider the reported range in the marine boundary layer concentrations so that the reader can better understand the degree to which the Dead Sea region concentrations actually are anomalous (regardless of reason, flux or meteorology). In addition, for some of these gases there are some well documented temporal, seasonal, and latitudinal variations in MBL concentrations that aren't well considered by the "annual average for 2012". As a result, I suspect that some of the EF's (CH<sub>3</sub>Br, perhaps also CH<sub>3</sub>Cl, CHCl<sub>3</sub>, and CH<sub>2</sub>Br<sub>2</sub>) are not accurate representations.*

**Answer:** We agree, and the results presented in former Table 2 are now included as Figure 2 in the new manuscript. Table 2 is now presented in the Supplement, but instead of showing the enrichment factors, we explicitly show the reported measurements for the MBL as compiled by Carpenter et al. (2014). We agree that presenting enrichment factors is problematic because of the sensitivity of the concentrations to season, latitude, meteorological conditions, investigated area within the MBL, etc., particularly for the specified species (CH<sub>3</sub>Br, etc.). Therefore, we do not include emission factors in the new version, and we think that presenting the results vs. the information compiled for the MBL in a graphical way, including a range for the MBL mixing ratios, is a reasonable way to compare the two data sets. Factors which may lead to biased comparison between mixing ratios measured at the Dead Sea and those measured in the MBL are now discussed: "It should be noted, however, that while Fig. 2 implies elevated VHOC emission from the Dead Sea, comparison of mean or median mixing ratios of VHOCs for the Dead Sea with those for the MBL is not straightforward, considering that VHOC mixing ratios in the MBL are sensitive to several factors, including season and latitude. Moreover, the measurement height can play a significant role in affecting the mixing ratios due to decreasing mixing ratios with height over areas where local emissions occur. Hence, we also compared the measured fluxes and mixing ratios with their corresponding values measured in coastal areas, where the highest mixing ratios in the MBL were generally measured due to stronger emissions." (lines 347-355). We also refer specifically to differences in sampling heights with respect to Fig. 5: "Note that differences in sampling heights at different sites can lead to a biased comparison between mixing ratios at different sites; nevertheless, in most cases, differences across measurement sites were larger than across vertical heights." (lines 592-594).

3. *On fluxes, the text seems to inaccurately reflect what the figure indicates once uncertainties are considered. One example: "Figure 2 presents the measured fluxes of all VHOCs studied. On average, the net fluxes of all measured species, except C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I, were positive at most of the investigated sites", and my review of Figure 2 indicates a much lower occurrence of positive flux: only 13 of 36 panels (excluding CH<sub>3</sub>I and C<sub>2</sub>HCl<sub>3</sub>) show positive fluxes where the standard error does not encompass zero. Another example can be found in section 3.2.1, lines 417-419. It is necessary to consider the uncertainty on the average here in drawing conclusions. Furthermore, I would estimate that the standard errors are likely underestimated as a result of the fairly small number of measurements used to estimate fluxes in this work.*

**Answer:** We have addressed this comment by rigorously taking statistical significance into account throughout all of the analyses and discussions, and in drawing the related conclusions. Fluxes in Table 2 (originally Table 4) are presented along with  $p$ -values that indicate their statistical significance, for a specific species at a specific measurement site, by applying a one-sample t-test. Note that considering the small number of measurements, these  $p$ -values are presented in four different categories:  $p < 0.05$ ,  $0.05 < p < 0.1$ ,  $0.1 < p < 0.15$  and  $p > 0.15$ . For our analyses, only  $p$ -values  $< 0.05$  are considered, indicating that a specific site is a net source or sink for a specific species, while the other two  $p$ -value categories (excluding  $p > 0.15$ ) are used only to indicate a moderate likelihood of the fluxes being either positive or negative, possibly due to the small number of measurements. Note that in several cases, correlation analyses of both flux and mixing ratios strongly support the emission of species from a specific site, although the corresponding flux is reported as insignificant in Table 2; for instance, remarkably high correlations were found for  $\text{CH}_3\text{I}$  with  $\text{CHCl}_3$  and  $\text{C}_2\text{HCl}_3$  at the coastal sites near the seawater ( $r = 0.99$ ,  $p < 0.05$  in both cases), based on the flux correlation analysis (Sect. 3.3, lines 883-887), also supported by the concentration correlation analysis (Sect. 3 lines 887-895). Nevertheless, these coastal sites were found insignificant as a net source for  $\text{CHCl}_3$  ( $0.05 < p < 0.10$ ), and for this reason we think that presenting also  $0.10 < p$ -values  $< 0.15$  and  $0.05 < p$ -values  $< 0.10$  contributes, particularly for future studies in this field, even though these are not taken into account by our analyses.

Note that we also tested the  $p$ -value calculations assuming that EGD-SD and TKM-SD, as well as BARE-MSMR and BARE-MSD, are the same emission source, considering their similar characteristics (see Sect. 3.1). In the case of the SD sites, this assumption resulted in a lower evaluated  $p$ -value in only a few cases, affecting the  $p$ -value category (ranking; see Table 2). The statistical tests related to the information presented in Table 2 are described in its caption (see lines 495-497). This table was moved to Sect. 3.1 to support the reports on measured fluxes at the Dead Sea, based on the statistical analysis that is incorporated in the table. We have extensively changed the text in Sect. 3.1 and in Sect. 3.2.1–3.2.3 as a result of taking into account the uncertainties associated with the measured fluxes, based on the statistical analysis. In addition, the two specific comments given as an example by the reviewer were addressed (lines 419-421 and lines 549-552). Overall, however, the conclusions drawn based on the fluxes that are presented in Table 2 were not changed significantly. This is mainly because there is a general correlation between the incidence of positive fluxes associated with  $p$ -values  $\leq 0.05$  and that of the fluxes which were considered positive in the original version of the manuscript. We have double-checked the standard errors, provided by us as standard mean errors, and we find them to be accurate.

Regarding the correlation analyses, each correlation value (i.e., Pearson correlation coefficient ( $r$ )) in Tables 5 and 4, (originally Tables 6 and 5, respectively) is reported along with the corresponding  $p$ -value to indicate whether the correlation is significantly different from zero, based on Student's t-test. In the case of correlation coefficients,  $p$ -values are also reported in four different categories:  $p < 0.05$ ,  $p < 0.1$ ,  $p < 0.15$  and  $p > 0.15$ . For the analyses, only  $p$ -values  $< 0.05$  were considered, indicating that a specific correlation is significant or not significant, respectively, while the other two  $p$ -value categories (excluding  $p > 0.15$ ) were used only to indicate moderate likelihood of the fluxes being either positive or negative, taking into account the small number of available measurements.

The revisions resulting from taking into account the uncertainties for the analyses are included in sections 3.1–3.3, and in the following, we present the related revisions in the summary section, showing their overall effect on our findings and conclusions.

1. In the original version: "Overall, our measurements indicate a higher incidence (in 65–85 % of measurements) of positive fluxes of brominated than of chlorinated VHOCs, except for  $\text{CHCl}_3$ , for which the incidence of positive net fluxes was also relatively high (65 % of measurements)." (lines 756-759).

In the revised version: "Overall, our measurements indicate a generally elevated incidence of positive fluxes of brominated vs. chlorinated VHOCs compared to previous studies" (lines 910-911). Hence, this statement is valid based on the flux uncertainties, namely, considering a measured flux as positive only if the related measurement site was identified as a statistically significant ( $p < 0.05$ ) source for the specific species (for which the flux was measured). In the revised version we do not specify the percentage of this positive flux, but the reader can find this information in Table 2, in several different statistical significance categories. We have removed the text on the incidence of  $\text{CHCl}_3$  considering the relatively low incidence of positive flux from sites which were identified as a source for  $\text{CHCl}_3$  ( $p < 0.05$ ).

2. In the original version it was mentioned that: "The four investigated site types, the cultivated and natural vegetated, the bare soil and the coastal sites, are identified as potential net sources for all VHOCs investigated, except for the emission of  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{HCl}_3$  from the vegetated sites. Hence, this study reveals strong emission of VHOCs over at least a few kilometers from the Dead Sea" (lines 763-767).

In the revised version: "Three of the investigated site types – bare soil, coast and agricultural field – were identified as statistically significant ( $p < 0.05$ ) sources for at least some of the investigated VHOCs. The fluxes, in general, were highly variable, showing changes between sampling periods, even for a specific species at a specific site. The coastal sites, particularly at a short distance from the sea (SD sites) where soil is mixed with salt deposits, were sources for all of the investigated VHOCs, but not statistically significantly for  $\text{CHCl}_3$ . Further from the coastal area, the bare soil sites were sources for  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHCl}_3$ , and apparently also for  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_3\text{I}$ , and the agricultural vegetation site was a source for  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBrCl}_2$ . Our measurements reinforce reports of  $\text{CHCl}_3$  and  $\text{CHBrCl}_2$  emission from bare soil, but indicate that such emission can also occur under relatively low soil organic content. To the best of our knowledge, we report here for the first time strong emission of  $\text{CHBr}_2\text{Cl}$  and emission of  $\text{CH}_2\text{Br}_2$  from hypersaline bare soil, at least a few kilometers from the Dead Sea. We could not identify the contribution of either natural or agricultural vegetation to the emission of the investigated VHOCs." (lines 915-928).

3. In the original version: "Measurements at a bare soil site suggested a decrease in VHOC emission rates for 1–3 days after a rain event, while the gradual increase in VHOC emission more than three days after the rain event suggests that these VHOC emissions are, at least partially, biotic-induced." (lines 777-779).

In the revised version: "Rain events appeared to attenuate the emission rates of VHOCs at the Dead Sea. Measurements at a bare soil site suggested a decrease in VHOC emission rates for 1–3 days after a rain event." (lines 935-937). We do not include the hypothesis about biotic-induced VHOC emission, because it is less strongly supported if we consider measured flux as positive or negative only for measurement sites identified as statistically significant ( $p < 0.05$ ) sinks or sources for the specific species (for which the flux was measured).

4. In the original version: "Trihalomethanes, including  $\text{CHCl}_3$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBr}_3$  and particularly  $\text{CHBrCl}_2$ , are associated with the highest number of sites at which their flux was, on average, positive, while  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBrCl}_2$  showed relatively high incidence of positive fluxes, with values of 65 %, 80 % and 85 %, respectively." (lines 780-783).

In the revised version we do not include this sentence as is, because this cannot be supported, if uncertainties in a measurement site as source are taken into account. In the revised version, we focus more on the common mechanisms/controls for the emission of brominated trihalomethanes: "Both flux and mixing ratio correlation analyses pointed to common formation and emission mechanisms for  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBrCl}_2$ , in line with previous studies, for the agricultural watermelon-cultivation field and bare soil sites. These analyses further strongly suggest common formation and emission mechanisms for  $\text{CHBr}_3$  with these two trihalomethanes." (lines 938-942).

5. In the original version: "The overall average net flux of the trihalomethanes decreased according to  $\text{CHBr}_2\text{Cl} > \text{CHBr}_3 > \text{CHBrCl}_2 > \text{CHCl}_3$ ." (lines 790-791).

In the revised version we further support this point by using the flux magnitude: "The overall average net flux of the trihalomethanes decreased according to  $\text{CHBr}_2\text{Cl} > \text{CHCl}_3 > \text{CHBr}_3 > \text{CHBrCl}_2$ , while  $\text{CHCl}_3$  showed the lowest incidence of positive fluxes among all trihalomethanes." (lines 944-946). Again, this finding of relatively elevated emission of brominated trihalomethanes (compared to previous studies) is generally supported by both the original and revised analyses.

6. In the original version: "We identified the SD sites as a probable source for all methyl halides, whereas vegetated sites appear more likely to act as a net sink for these species." (lines 796-797).

In the revised version: we realize that this sentence should be revised based on both the original and updated analyses: "We identified the coastal sites as a probable source for all methyl halides, whereas neither agricultural field nor natural vegetation site were identified as net sink or net source for these species, except for the agricultural field being a net sink for  $\text{CH}_3\text{I}$ ." (lines 949-951)

7. In the original version: "Comparing the proportion of Br and Cl in the soil for the various sites with proportions of measured positive flux of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  are in line with reports by Keppler et al. (2001) about emission of methyl halides via abiotic oxidation of organic matter in the soil. Similar calculations in our study demonstrated much higher efficiencies of  $\text{CH}_3\text{I}$  emission than those reported by Keppler et al. (2000), pointing to emission of  $\text{CH}_3\text{I}$  via other mechanisms. The high correlation of

CH<sub>3</sub>I emission with that of CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub>, particularly at the SD sites, together with findings by Weissflog et al. (2005), of various chlorinated VHOCs emission, including CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub>, from salt lake sediments, suggests that the Dead Sea, particularly the SD, sites probably act as an emission source for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I via similar mechanisms. Weissflog et al. (2005) reported that the emission of chlorinated VHOCs in their study was induced by microbial activity. Keppler et al. (2000) reported the involvement of an abiotic process in the formation of alkyl from soil and sediments, and the observed correlation between methyl halides and both CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> may indicate that the two processes occur simultaneously." (lines 797-810).

In the revised version: The flux- and concentration-based correlation analyses in the revised version strongly support these findings, even though the coastal sites were not identified as statistically significant net sources for CHC<sub>3</sub>I ( $0.05 > p < 0.1$ ; see Table 2). The revised text refers to the statistical significance of the analyses and we have removed some experimental details about the related analyses to shorten the discussion: "Our analysis demonstrated, however, much higher efficiencies of CH<sub>3</sub>I emission than of CH<sub>3</sub>Br and CH<sub>3</sub>Cl emissions as a function of halides in the soil, compared to those reported by Keppler et al. (2000), pointing to emission of CH<sub>3</sub>I via other mechanisms. The strong correlation between both fluxes and mixing ratios of CH<sub>3</sub>I, CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub>, particularly at the SD sites, strongly suggests that the coastal area of the Dead Sea acts as an emission source for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I via similar mechanisms, although these sites were associated with only moderate statistical significance ( $p \leq 0.1$ ) as a net source for CHCl<sub>3</sub>. The emission of CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> from these sites is in line with findings by Weissflog et al. (2005) of emission of various chlorinated VHOCs, including CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub>, from salt lake sediments. Weissflog et al. (2005) reported that the emission of chlorinated VHOCs in their study was induced by microbial activity. Keppler et al. (2000) reported the involvement of an abiotic process in the formation of alkyl from soil and sediments, and the observed correlation between methyl halides and between CH<sub>3</sub>I and both CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> may indicate that the two processes occur simultaneously in the coastal area of the Dead Sea." (lines 951-965).

**4. *Inferences about flux from measurements as a function of height have a certain spatial influence function. Please indicate what that might be for the sampling heights you have chosen.***

**Answer:** All measurement sites were carefully selected to ensure a sufficiently large homogeneous fetch, and the measurement height was chosen to ensure that the footprint falls within this homogeneous fetch, except for the SD sites where direct emission and uptake from the seawater can potentially affect the samples (lines 236-240). For EGD-SD-s and EGD-SD-w, the footprint included the seawater: "Based on the wind direction, in both cases, the sampling footprint included both the seawater and a narrow strip of bare soil mixed with salty beds (estimated at about 60% of the footprint) very close to the seawater." (lines 667-669). According to our calculations, the 80% footprint in the studied area ranged from ~100–950 m, which was, in all cases, significantly smaller than the fetch of any site (see Table S4). In some cases, the 90% footprint was ~2 km, but taking into account the wind direction for these specific cases (Table S6), the footprint was still smaller than the fetch, except for the samplings at the COAST–EGD, as described above. Based on this and the next



comment, we realized that information was missing in the text about footprint and measurement height selections. Therefore, we have added the following text: "By default, the differences in height between the canisters increased exponentially with height, considering the typical decrease in the vertical gradient of emitted species in the surface layer (Stull 1988). All canisters were placed high enough above the ground to ensure that all sampling was performed within the inertial sublayer, except for the lowest canister at TMRX-ET. In all cases, the sample footprint fell inside the target fetch, except for the sampling at COAST-EGD, for which the sample footprint included a narrow strip of the seawater (estimated at about 40% of the footprint)." (lines 233-240).

*5. Consideration of the C<sub>2</sub>HCl<sub>3</sub> results (an implied sink, perhaps from elevated mixing ratios in the broader Red Sea region) may indicate that the fluxes you are deriving here for naturally-emitted gases are actually not representative of the local regions you intended them to represent. How is the reader to assess this? Also, what has determined the different heights at which samples were collected on these masts? Sampling heights in a region with local emissions should have a large, but not discussed, impact on measured mixing ratios—which are being compared among sites and to MBL results.*

**Answer:** Our analyses suggest that in general, the investigated sites act more like a sink for C<sub>2</sub>HCl<sub>3</sub>, with the coastal sites probably also being a source for this species, based on the mixing ratios and flux correlation analyses (Tables 4 and 5), and the measured positive fluxes from these sites (Table 2). We cannot rule out that the sink for this species reflects its emission from the Red Sea, the Mediterranean Sea, or an anthropogenic source upwind. However, it is not likely that emission from the Red or Mediterranean Sea impacts the measured fluxes at the Dead Sea due to the following: (i) we added correlation and wind direction analyses, including for C<sub>2</sub>Cl<sub>4</sub>, which strongly support the origin of C<sub>2</sub>HCl<sub>3</sub> from an anthropogenic source (see Sect. S4); (ii) the Red Sea and the Mediterranean Sea are located 160 km and 90 km from the Dead Sea, respectively, while mixing ratios of the investigated VHOCs at the Dead Sea are typically significantly higher than those in the MBL, and therefore probably also compared to those over the Red Sea and Mediterranean Sea; (iii) prevailing wind direction during the (different) measurement periods was from the north and in only a few cases, from the northwest (Table S6), whereas the Red Sea and Mediterranean Sea are located to the south and west of the Dead Sea, respectively; (iv) there is no reason to assume that the Dead Sea is an efficient sink for VHOCs transported from the Red Sea and the Mediterranean Sea, whereas there are efficient sinks for these species along the trajectories of the air masses. Therefore, it is not likely that the Dead Sea acts as a significant sink for VHOCs which are transported from these seas.

The Dead Sea probably acts more as a sink than a source for C<sub>2</sub>HCl<sub>3</sub>, but based on the above, this is more likely be the result of emission from inland anthropogenic sources in Israel. In any case, deposition of C<sub>2</sub>HCl<sub>3</sub> or any other species cannot contribute to the emission fluxes at the Dead Sea—the latter, and not deposition, being the focus of this study.

Pursuant to this comment, we include the following: "Only COAST-EGD and COAST-TKM-SD sites were found to be statistically significant sources ( $p < 0.05$ , see Table 2) for C<sub>2</sub>HCl<sub>3</sub>, suggesting that the elevated mixing ratios for this species in the Dead Sea area result mostly from local anthropogenic emissions. This possibility is supported by the high correlations with C<sub>2</sub>Cl<sub>4</sub> (Table S5). Emissions from a more

distant natural source, such as the Mediterranean Sea or Red Sea, are unlikely given their large distance away (~90 km and ~160 km, respectively)." (lines 488-493).

To address the comment about sampling heights, we include the following: "By default, the differences in height between the canisters increased exponentially with height, considering the typical decrease in the vertical gradient of emitted species in the surface layer (Stull 1988). All canisters were placed high enough above the ground to ensure that all sampling was performed within the inertial sublayer, except for the lowest canister at TMRX-ET. In all cases, the sample footprint fell inside the target fetch, except for the sampling at COAST-EGD, for which the sample footprint included a narrow strip of the seawater (estimated at about 40% of the footprint)." (lines 233-240).

In the revised version, we discuss the impact of measurement height as well as of additional factors, including season and latitude, on differences in mixing ratios between our study and the MBL: "It should be noted, however, that while Fig. 2 implies elevated VHOC emission from the Dead Sea, comparison of mean or median mixing ratios of VHOCs for the Dead Sea with those for the MBL is not straightforward, considering that VHOC mixing ratios in the MBL are sensitive to several factors, including season and latitude. Moreover, the measurement height can play a significant role in affecting the mixing ratios due to decreasing mixing ratios with height over areas where local emissions occur. Hence, we also compared the measured fluxes and mixing ratios with their corresponding values measured in coastal areas, where the highest mixing ratios in the MBL were generally measured due to stronger emissions." (lines 347-355).

*6. I find the results in Figure 3 intriguing, although not much is made of it in the text. While it may be that no generalizations are possible related to all gases, there are some interesting similarities that might be worth discussing, especially to understand if these co-variations are consistent with the discussions related to co-variations in fluxes as what was intended in Table 4.*

**Answer:** First, note that Fig. 5 (originally Fig. 3) has been revised according to a comment made by reviewer #2 (we removed the data for VHOCs that did not show any seasonal variation), and the original figure is presented as Fig. S1 in the Supplement. The only case for which we suspect that there was a clear seasonal effect on VHOC mixing ratios is CH<sub>3</sub>I, where both flux and mixing ratio measurements clearly indicated higher emission in spring vs. winter, apparently in line with findings by Sive et al. (2007), and accordingly we have added the following: "While no clear impact of season on mixing ratios was observed, for most sites, differences between two measurement sets resulted in consistent differences in mixing ratios, such that one measurement set resulted in higher mixing ratios for all or most species than the other. This suggests that other factors play a significant role in emission rates of all or most VHOCs in the studied area. Only the CH<sub>3</sub>I results indicated moderate statistical significance ( $0.05 < p < 0.1$ ) for higher mixing ratios in the spring vs. winter, in agreement with seasonal trends for its flux, as discussed above." (lines 598-604).

We further add, in Sect. 3.2.3 on lines 763-766: "As discussed in Sect. 3.2.1, the mixing ratios of CH<sub>3</sub>I also tended to be higher in magnitude in spring compared to winter, with moderate statistical significance ( $0.05 < p < 0.1$  in both cases) (Figs. 3, 5)."

Considering this comment, we have modified Table 4 (originally Table 5), and the correlations between mixing ratios are now provided individually for different site types, similar to Table 5 (originally Table 6), and also for all site types except for SEA–KDM (this site explores the effect of air transported over the seawater on the mixing ratios). These analyses indeed enabled us to further strongly support apparent common emission sources and/or controls between brominated trihalomethanes (Sect. 3.3, lines 846-882) and between  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_3$  and  $\text{CH}_3\text{I}$  (Sect. 3.3, lines 883-895), as well as between methyl halides (Sect. 3.3, lines 883-886).

*7. Table 4 is also very hard to extract information from... and as before, I'm concerned that any identification of positive flux amounts don't take into account uncertainties on those estimations. If uncertainties were not considered, then it seems that much of the discussion related to incidences of positive flux and rankings by chemical etc. that follows should be reconsidered.*

**Answer:**

We have realized that the information on the ratios between flux and mixing ratio (defined as F:C in the original version) does not contribute significantly to the manuscript, and based on this comment, we have removed the F:C information from the table (now Table 2). We believe that this makes the table easier to extract data from.

As explained above, we include in the revised manuscript  $p$ -values, indicating the statistical significance of the related measurement site being a source for a particular species. Only  $p$ -values  $\leq 0.05$  were considered statistically significant in the analyses in the revised manuscript. The resulting differences in our conclusions and findings are summarized in our response to comment #3. Overall, they were not significantly changed by taking into account statistical significance.

*8. Table 5 and 6 need a consideration of correlations that are and are not significant, given the number of measurements included in each determination. Given the small number of samples considered here, I'd estimate that correlations of  $< 0.1$  are in fact indicative of no evidence for a correlation, not a correlation described as "low".*

**Answer:** We agree. All correlations in Tables 4 and 5 (originally Tables 5 and 6) are now reported with a corresponding  $p$ -value, based on Student's t-test, to indicate whether the correlation is significantly different from zero. Similar to the revisions we made to Table 2, we consider four different categories of  $p$ -values:  $p < 0.05$ ,  $p < 0.1$ ,  $p < 0.15$  and  $p > 0.15$ . Only  $p$ -values  $< 0.05$  are considered statistically significant in the analyses in the revised manuscript.

**Response to comments by reviewer #2**

***General Comments***

*The manuscript by Shechner et al. presents ambient measurements and fluxes for short-lived halocarbons at multiple sites around the Dead Sea. The unique characteristics of the Dead Sea make it a very interesting location to study the emissions from and detail the characteristics of this source for atmospherically important halocarbons. The paper contains an abundance of information, but I feel some key details are lacking that are needed to fully assess the author's interpretations. Additionally, the paper is very long and becomes difficult to follow in*

*terms of the main points trying to be conveyed in the various sections of the paper. My opinion is that the paper could be distilled down in length and the key points be fleshed out a bit more cleanly. Additionally, I feel there are some significant improvements that could be made in dissemination of the information in both graphical and tabular form. While there is merit to the manuscript, I feel as though there are an array of issues that should be addressed before it is in an acceptable format for publication.*

*I will present a general list of issues here and elaborate on them in the Specific Comments section.*

*Urban and other source influences – it would be useful to provide some context to the potential of urban emissions, for the solvents like  $\text{CHCl}_3$  and  $\text{C}_2\text{HCl}_3$ , but also including things like wastewater treatment facilities and other agricultural activities that could influence the area.*

*The first time a chemical constituent is introduced, it should be spelled out – there are several places this occurs throughout the manuscript. For example, L72 chloroform ( $\text{CHCl}_3$ ), L73 chloroethane ( $\text{C}_2\text{H}_5\text{Cl}$ ), L112 iron ( $\text{Fe}$ ), L115 potassium bromide ( $\text{KBr}$ ), nitric acid ( $\text{HNO}_3$ ), etc. – please address.*

*Percentages – there are spaces between the number and the percent sign. The most common convention is to not have a space between a number and the percent sign.*

*I would recommend either referring to the suite of halocarbons as VHOCs or VSLS, but not going back and forth between them.*

*From the measured fluxes, can you estimate the local/regional source or sink strength of the Dead Sea? How do your results play in to the scale of the source strength of the Dead Sea for these gases?*

*It would be useful to present some quantitative information in the abstract, such as mixing ratios and fluxes.*

*There are no uncertainties propagated through any of the fluxes. I would be useful to include the atmospheric lifetimes and primary removal sources for the compounds in the manuscript.*

*The manuscript seem to try and agree with all previous studies. Tables are difficult to read and digest. Plots within the figures are too small making it difficult to extract information from them.*

*Flux section could be moved to SI*

*A more thorough overview of the site, including meteorology, would be useful to help set the stage for the reader.*

**Answer:** We have addressed all of the above according to the specific comments below and have revised the discussion to make it more concise. We have also added

information in Sect. 2.1.1 regarding anthropogenic emission sources in the studied area, including agricultural fields, and mention that to the best of our knowledge, there are no wastewater facilities in the area of the Dead Sea. The reader is further referred to a sensitivity analysis which investigates, as suggested below, the potential impact of anthropogenic activity on the measured mixing ratios, based on the ratio  $[C_2HCl_3]/[C_2Cl_4]$  (see Sect. S4). We further include a description of the meteorological conditions in the area of the Dead Sea (Sect. 2.1.1), and a summary of the meteorological measurements in Sect. S6.

In the revised version, we rigorously take into account the statistical uncertainties associated with the measured fluxes (and correlations) for our discussion and analyses, allowing us to present a clearer description of net emission/sink for the different species at the various investigated sites. Nevertheless, we do not yet have sufficient measurements to provide a reliable estimate of the overall emission/sink status for the various species at the Dead Sea. The Dead Sea area includes relatively highly diverse and changing landscapes, partly due to rapid evaporation, which leads to exposure of new deposits, and our measurements indicate high variability in emission, even for the same landscape. Therefore, many more measurements are required for a reliable estimate of total emission/deposition of VHOCs in this area. We have added flux and mixing ratio ranges for all species to the abstract and give lifetimes and primary removal pathways in Sect. S1, with a reference in the Introduction (line 84). We have revised original Figs. 2 and 3 and Table 2 for easier extraction of information, as suggested in the reviewer's comment below, and have included a new figure which provides a schematic of the flux's spatial distribution in the studied area.

### ***Specific Comments***

*L46-7: You should include why CH3I and C2HCl3 are exceptions, as this is not intuitive to the reader.*

**Answer:** The text in this case has been modified to account for statistical uncertainties associated with a measurement site being a source for the tested VHOC: "Fluxes were generally positive (emission into the atmosphere), corresponding to elevated mixing ratios, but were highly variable... Taking into account statistical uncertainties, the coastal sites (particularly those where soil is mixed with salt deposits) were identified as the source for all VHOCs, but this was not statistically significant for  $CHCl_3$ . Further away from the coastal area, the bare soil sites were sources for  $CHBrCl_2$ ,  $CHBr_2Cl$ ,  $CHCl_3$ , and probably also for  $CH_2Br_2$  and  $CH_3I$ , and the agricultural sites were sources for  $CHBr_3$ ,  $CHBr_2Cl$  and  $CHBrCl_2$ ." (lines 45-58).

*L49-51: For the statement: "Correlation analysis, in agreement with recent studies, indicated common controls for the formation and emission of all the above trihalomethanes but also for  $CH_2Br_2$ .", I'm not convinced this is entirely accurate – for example, what about  $CHCl_3$ ? Also how does the correlation indicate that the factors controlling the formation and emissions are the same?*

**Answer:** Two sentences have been included to address these two points based on the revised analyses which take into account statistical uncertainties: "Correlation analysis, in agreement with recent studies, indicated common controls for the emission of  $CHBr_2Cl$  and  $CHBrCl_2$ , and likely also for  $CHBr_3$ . There were no indications for correlation of the brominated trihalomethanes with  $CHCl_3$ ." (lines 61-

64). We agree that the correlation is not necessarily indicative of similar formation controls, but we believe that it is indicative of similar emission controls.

*L55: “elevate” should be “elevated”*

**Answer:** Corrected (line 68)

*L61: When you introduce VSLs here, you should include here that this refers to compounds that have lifetimes of less than 6 months.*

**Answer:** This is now included (line 75).

*L64: replace “destruction of ozone” with “ozone destruction”*

**Answer:** Changed accordingly (line 78)

*L73: add “which”, so it reads “...C<sub>2</sub>H<sub>5</sub>Cl, which originate...”*

**Answer:** Amended (lines 87-88)

*L134-5: Bromide (Br-) and chloride (Cl-) should be introduced and the sentence should be revised to read “ with water salinity 12 times higher and a bromide to chloride ratio (Br-/Cl-) 7.5 times higher than in normal ocean waters.*

**Answer:** Amended (lines 151-153)

*L136: What do you mean by “landforms”? Formations from the residual salts left behind? In this case the use of the term “landform” invokes images of large scale topographical features, is this the case?*

*This brings in to question the use of the term landform in the title – is this really appropriate and accurate? I would say this work has been carried out on different terrains or ecosystems of the Dead Sea, but not different landforms.*

**Answer:** We have replaced the term landform with landscape (including the title) to indicate that the entire ecosystem is being addressed, and not just geological formations. It is true that some of the measurement sites represent similar landscapes, as in the case of different distances from the seawater in the same area (e.g., for COAST-TKM-SD, COAST-TKM-LD), but in most cases, they differ fundamentally in some aspect (e.g., soil mixed with deposits at the coast vs. bare soil far from the seawater vs. cultivated vegetation vs. natural vegetation) and the areas with the same characteristics are quite large (at least one to a few kilometers). We think that using "terrains" may imply different slopes, structures, etc. We replaced "landforms" on (original) line 136 with "newly exposed sea deposits" (line 154) to better describe the location.

*L143: I would revise this to make it a stronger statement, something like: “Studying the emission of VHOCs at the Dead Sea is also fundamental for understanding local surface ozone depletion events...”*

**Answer:** Thank you. We have modified the sentence accordingly (lines 161-164).

*L169-70: Regarding the Tamarix vegetation and watermelon fields, more details, such as density, proximity, size of agricultural development, etc., would be useful to the reader.*

*Also, I would refer change your referencing of watermelon fields from “vegetation” to “agriculture” in later sections of the manuscript – because this is a perturbed system different than the natural vegetation, it should be distinguished as such.*

**Answer:** More information is now included for the two sites, such as size, height, vegetation cover fraction and distance from the sea. In addition, meteorological conditions and estimated footprints are now included in the Supplementary Information (Tables S6 and S4, respectively). We refer in the revised manuscript to the watermelon field as an agricultural vegetation or agricultural field throughout the text. Note, however, that for the analyses, we refer to the natural vegetation and agricultural vegetation both as separate sites and as two vegetated sites (VEG; e.g., Tables 5 and 6).

*L198: Revise to “Lastly, WM-KLY...”*

**Answer:** Done (line 224)

*P8, Sect. 2.1.2. How many samples were collected in total, at each site, and at each corresponding height for each site? What were the meteorological conditions during the sampling?*

*In order to get better feel for the results presented, both for the ambient levels and the fluxes, knowing N is critically important. This will allow the reader better perspective on some of the interpretation presented.*

*Also, general information about the seasonal and local meteorology to provide an overview of the region would be instructive to the reader.*

**Answer:** In the revised version, sample information is specified in Table 1 and the number of samples at each site is presented in Fig. 2 (replacing original Table 2), while Table 2 (originally Table 4) and Fig. 3 present each evaluated flux individually; we specify that in two cases, flux was evaluated based on two samplings rather than three. Tables 4 and 5 (which present the correlation analyses; originally Tables 5 and 6) present the number of values used for the mixing ratio and flux correlations, respectively. We have added to the Supplement a table that summarizes the collected meteorological data during the different measurements (Table S6) and refer to it in the text (line 246). In the revised version, we include information about the climate of the Dead Sea, including evaporation rate, annual precipitation and seasonal variation in daily maximum temperature (lines 177-181).

*L209: Regarding the use of “fast” here: I personally wouldn't consider 20 minutes to be fast - I think the key point you are trying to make is that all samples were collected simultaneously and integrated over a 20 min period – please revise.*

*Also, I'm assuming “lifting of the canisters” should be “filling of canisters”*

**Answer:** Thank you. The sentence has been revised to clarify this point: "To minimize non-synchronized air sampling by the three canisters, we constructed a special sampling system that allows almost simultaneous filling of the canisters" (lines 240-241).

*L209-12: Please revise the following sentence – very awkward as written:*

*Facilitated by passive grab samplers (RESTEK Corporation, PA, U.S.), we performed each sampling within 20 minutes by pulling air into evacuated 1.9 L stainless steel canisters, resulting in an internal canister pressure higher than 600 torr.*

**Answer:** The sentence has been revised: "For each sample, air was drawn into a 1.9 L stainless-steel canister via passive grab samplers (Restek Corporation, PA, USA), resulting in a sampling duration of 20 min and internal canister pressures higher than 600 Torr." (lines 242-244).

*L215-16: Please revise: "...subjected to the analytical techniques..." – simply say they were analyzed by similar techniques described in Colman et al.*

**Answer:** Amended (lines 246-248)

*L218-21: You introduce all of the halocarbons here, but most, if not all should have been introduced previously. Please address.*

**Answer:** Done

*L223-28: Please provide some statistical/quantitative rationale for this - you can't simply disregard this point because it doesn't "agree" with the other measured mixing ratios for CH<sub>3</sub>Cl. Also, I don't feel it's appropriate to state that it may result in a "less accurate flux" – how do we know what the "accurate flux" is? There is variability in all of this work, and while this may, in fact, be a spurious data point, what measures were carried out to deduce this issue?*

*Where is this listed, in Table 2? Please specify here for the reader to address.*

**Answer:** This is now supported using Grubbs's test (Grubbs and Beck, 1972) and the text was revised according the comment (Sect. 2.1.2, lines 252-255). We now indicate this issue in Table 1 as well, and refer the reader to Sect. 2.1.2 (where this issue is described) from all relevant figures and tables.

*L229, Table 1: It would be useful to provide the total number of samples and how many per height. This should be summarized such that the reader doesn't have to try and count how many samples were collected on the individual days from the information in the table.*

**Answer:** We now specify the total number of samples for each experiment in Table 1. Note that the number of samples corresponding with each of the correlation analyses is now specified in both Tables 4 and 5 (which present the correlation analyses; originally Tables 5 and Table 6) as well as Fig. 2 (replacing original Table 2).

### **L279: Sect 2.3**

*Following suit with the canisters, how many total soil samples were collected and analyzed? This potentially could be moved to the SI because the information is only used for general properties at each site.*

**Answer:** We mention now in Table 3 that: "Analyses were performed for a single mixture of samples at each site." (lines 693-694). This was of particular importance for the watermelon field site, where the area was clearly not homogeneous. A different number of samples for each site was used for each sampled mixture. We prefer to keep the table in the main text because we use some of the information presented there in our discussion, mostly in Sect. 3.2.2, regarding the content of halides (e.g., lines 652-664) and organic matter (e.g., lines 769-780).



*L280-81: Please elaborate what you mean by this and what is the significance of this statement: "...at least 3 months following any rain event in the Dead Sea area."*

**Answer:** This is to ensure that sample composition and water content are not affected by drifts and percolation, following recent rain events in the area, as is now explained in the text: "Soil samples at each site were collected up to a depth of 5 cm during the summer, at least 3 months after any rain event in the Dead Sea area, to ensure no impact on the samples by recent drift and percolation." (lines 311-313).

*L265: In line reference should be Golder (1972)*

**Answer:** Corrected (line 297)

*L290: Quotes are not needed around "Discover"*

**Answer:** Done (line 322)

*L292-93: High Resolution does not need to be capitalized*

**Answer:** Done (line 324)

*L294: "low-limit" should be "lower limit"*

**Answer:** Amended (line 326)

*L302: What is meant by "corresponding available information."*

**Answer:** We have removed this sentence and refer first to the measured mixing ratios: "Overall, the measurements at the Dead Sea boundary layer revealed higher mixing ratios for all investigated VHOCs than their expected levels at the Mediterranean Sea and Red Sea MBL, indicating higher local emissions from the Dead Sea area" (line 333-335).

*L306: What is the "Dead Sea Works"?*

**Answer:** A short description of the Dead Sea Works has been added: "The main anthropogenic emission source in the area, apart from local transportation and a few small settlements, is the Dead Sea Works, a potash plant located to the south of most of the measurement sites (see Fig. 1)." (lines 184-186).

*L326: There were surface seawater, ambient air and direct flux measurements of CHBr<sub>3</sub> in Zhou et al., 2005 – how do these compare with the Dead Sea?*

**Answer:** Information about mixing ratios of CHBr<sub>3</sub> as well as fluxes for CH<sub>2</sub>Br<sub>2</sub> and CH<sub>2</sub>Br<sub>2</sub> based on Zhou et al. (2005) has been added on lines 428-434.

*L330: It appears that a range of values is missing after 2-60 pptv – there is simple "( - )"*

**Answer:** The range has been added (line 373).

*L335: Re C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I - while the reader can look at the figure, it would be useful to also state in the text what these gases are doing, on average.*

**Answer:** This sentence has been deleted because it is not valid when statistical uncertainties are taken into account, which is the case in the revised manuscript. We now address these species as follows: "It can be seen that for all species, at least one of the six studied areas could be classified as a net source, with somewhat less sites being statistically significant net sources for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I. Note that as explained above, C<sub>2</sub>HCl<sub>3</sub> was found to be affected by anthropogenic emission, which

could explain the relatively less frequent identified emissions for this species "(lines 419-423). We also discuss the measured fluxes of CH<sub>3</sub>I throughout Sect. 3.1, and compare them to fluxes reported in the literature: "The positive fluxes measured at BARE–MSMR were similar to the measured soil-emission fluxes of CH<sub>3</sub>I reported by Sive et al. (2007) at Duke Forest, averaging ~0.27 nmol m<sup>-2</sup> d<sup>-1</sup> (range, ~ 0.11–4.1 nmol m<sup>-2</sup> d<sup>-1</sup>)." (lines 485-487).

*L336-39: Can you please clarify these two sentences: Figure 2 doesn't show values higher than these. Either present the values or revise text.*

**Answer:** The sentence has been revised: "The flux magnitudes for CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> were greater than for most reported emissions in the MBL (e.g., CHBr<sub>3</sub>, 25.2–62.88 nmol m<sup>-2</sup> d<sup>-1</sup> for the Mauritanian upwelling (Quack et al., 2007); CH<sub>2</sub>Br<sub>2</sub>, 0.14–0.29 nmol m<sup>-2</sup> d<sup>-1</sup> for the New Hampshire coast (Zhou et al., 2008)), but were smaller than the corresponding average fluxes estimated by Butler et al. (2007) for global coastal areas (~220 and 110 nmol m<sup>-2</sup> d<sup>-1</sup>, respectively) and than the average flux from the New Hampshire coast as reported by Zhou et al. (2005) (~620 ± 1370 nmol m<sup>-2</sup> d<sup>-1</sup> and 113 ± 130 nmol m<sup>-2</sup> d<sup>-1</sup>, respectively)." (lines 428-434).

*L376: for the following, you either have one too many or one too few brackets: (e.g., ~600 nmol m<sup>-2</sup> d<sup>-1</sup>; (Deventer et al., 2018).*

**Answer:** Corrected (line 473)

*L360: For "nmol m<sup>-2</sup>-d<sup>-1</sup>" there appears to be an extra dash in between m-2 and d-1*

**Answer:** Corrected (line 456)

*L391-93: It is difficult to see this in Fig 2, and what/where are the anthropogenic emissions located? From DSW or other places? Can this be assessed by looking at something like the C<sub>2</sub>HCl<sub>3</sub>/C<sub>2</sub>Cl<sub>4</sub> ratio? It is likely that this data is available from the UCI group, but this (or other pairs of compounds) could be used to do a more thorough analysis on the impact of anthropogenic emissions at the sampling sites. For example, this brings in to light things like wastewater treatment facilities and the corresponding emissions of CHCl<sub>3</sub> and CHBr<sub>3</sub>. It would be useful to provide a more rigorous assessment of the influence of anthropogenic emissions in general - particularly for those not familiar with the region and to what extent they may be influencing this work - if minimal, that's great - just demonstrate this, as this statement affects your results - C<sub>2</sub>HCl<sub>3</sub> isn't the only gas here with anthropogenic sources.*

**Answer:** We have added more details to the Methods about potential anthropogenic emission sources in the area (lines 184-190), and a thorough analysis of potential anthropogenic emission sources in general and particularly for C<sub>2</sub>HCl<sub>3</sub> (Sect. S5). We summarize this analysis in the main text: "No association was observed between the measured mixing ratios and the air masses flowing from the direction of the Dead Sea Works (see Sect. S4 for anthropogenic impact), a potash plant located to the northwest of the TMRX–ET site and to the south of all other measurement sites (see Fig. 1) that is the main anthropogenic source in the area under investigation. Furthermore, the correlation analysis (Table S5) revealed that only C<sub>2</sub>HCl<sub>3</sub> was associated with C<sub>2</sub>Cl<sub>4</sub>, a well-known anthropogenic VHOC. The absence of any other associations suggested dominance of natural sources for the VHOCs in the studied

area." (lines 335-342). To the best of our knowledge, no wastewater facilities are located near the Dead Sea water.

The sentences have been revised: "Only COAST-EGD and COAST-TKM-SD sites were found to be statistically significant sources ( $p < 0.05$ , see Table 2) for  $C_2HCl_3$ , suggesting that the elevated mixing ratios for this species in the Dead Sea area result mostly from local anthropogenic emissions. This possibility is supported by the high correlations with  $C_2Cl_4$  (Table S5)." (lines 488-491).

*Suggestion: After looking at Figure 2, I feel as though it would be useful to have a summary flux figure (e.g., by compound) with the magnitude of the fluxes plotted by size or color on a map to enable the reader to get a better idea of the spatial variability of the flux magnitudes.*

**Answer:**

Thank you. We have produced a new figure—Fig. 4—which focuses on the spatial distribution and variation in measured net fluxes at the various site types. The figure clearly demonstrates higher emission from the coastal area, particularly for the sites which are closer to the seawater and from the natural vegetation for some of the VHOCs, which are generally higher than for the cultivated field. However, the natural vegetation site could not be classified as a statistically significant source for the investigated VHOCs, pointing to the need for additional measurements at this site (lines 555-560). We also keep Fig. 2, which is focused on the effect of season and distance from the seawater.

*L418: Revise to: "...VHOCs, except  $C_2HCl_3$ , were..."*

**Answer:** The sentence has been revised: "The results presented in Sect. 3.1 showed elevated mixing ratios and net fluxes for all investigated VHOCs, with relatively less frequent positive fluxes for  $CH_3I$ ,  $CHCl_3$  and  $C_2HCl_3$ ." (lines 547-548).

*L431-33: Regarding the statement that there isn't a difference between fluxes in the spring and winter, two things should be addressed: 1) is this statistically significant? 2) What is the seasonality of the temperature and overall meteorology for this area (i.e., local/regional transport patterns)? Being only slightly extratropical, would seasonality be expected to be an important driver?*

**Answer:** These two points have been addressed as follows: "Differences in VHOC emissions between winter and spring may arise from the generally much higher temperature, and lower precipitation during the latter; further considering the high evaporation rate in this area, the soil water content is expected to be generally lower in spring compared to winter (Sect. 2.1.1; see also Table S6). Figure 3 suggests that there were no clear differences in VHOC fluxes between spring and winter, as supported by statistical analysis, except for  $CH_3I$  and  $CH_2Br_2$  for which fluxes were higher in the spring, with moderate statistical significance ( $0.05 < p < 0.1$ )." (lines 578-584).

Seasonal variations between spring and winter in this area are relatively significant (e.g., summer mean daily maximal temperature of  $\sim 40$  °C decreasing gradually until winter, to a corresponding temperature of  $\sim 21$  °C; Sect. 2.1.1). Basically, the area is controlled by 19 main synoptic scenarios, with a dominant influence of local sea and Mediterranean breezes (Shafir and Alpert, 2011). In the manuscript, we focus directly on the meteorological parameters (which are further

summarized in Table S6 for the measurement periods), and soil water content (which was not measured for the specific measurement periods), rather than the dynamics and synoptics that control these parameters.

*L437: add comma after “properties”*

**Answer:** Done (line 587)

*L439-40: Regarding the sentence: “No clear impact of season or distance from the seawater on the mixing ratios can be discerned in this figure,...”, while I agree, it’s mostly because you can’t see the details in Figure 3.*

*Figure 3: In general, it is difficult to discern the spatial distributions and get useful information out of the vertical profiles because each panel is so small. From this figure, it is difficult to see and discern the gradients for many of the gases. I would recommend revising and either show a few key species and put the remainder that don’t show anything in the SI or revise the whole figure.*

**Answer:** We have revised the figure as suggested (Fig. 5 in the revised manuscript), by excluding information for those species that did not show any seasonal trend. This indeed enables us to present a less "busy" figure with somewhat larger panels. We include the original figure in the Supplement (Sect. S2). Note that the aim of this figure is to explore the effects of season and distance from the seawater on the measured mixing ratios and therefore, we use a similar scale for the y-axis associated with the same species in the same coastal area (e.g., COAST–TKM-SD and COAST–TKM-LD). As a result, in many cases, it is still difficult to see or discern the gradients in mixing ratios due to the substantial range. Pursuant to this comment, we now indicate in the caption of Fig. 5 that the figure uses even y-axis scaling for sites in the same coastal area (line 615). To make it clear that the figure focuses on mixing ratio differences vs. distance, we have arranged the panels differently and schematically indicate the distance from the seawater by arrows.

*L460: replace “these parameters” with “the soil composition parameters”; also change “The table records...” to “The results presented in Table 3 show...”*

**Answer:** Amended (lines 627-628)

*L462: “larger distance” should be replaced with “greater distances”*

**Answer:** Amended (lines 629-630)

*L465-66: replace “in” with “at” just before the site location abbreviation.*

**Answer:** Done (lines 633)

*L472-75: What do you mean by “underestimated value of Fe”? A lower limit of the total iron? Again, “low-limit” should be “lower limit”.*

**Answer:** Yes, we mean a lower limit of the total iron. The sentence has been changed accordingly (line 639).

*What does “while the emission rates became saturated” mean – I’m assuming that you mean “plateau”. For example, Huber et al. use the term “plateau”.*

**Answer:** Yes, the sentence has been clarified: "Note, however, that soil Fe content similar to that reported here as a low-limit value corresponds with those associated with the finding of small amounts of VHOC emissions, while the emission rates become saturated when enrichment with Fe(III) is relatively minor (Keppler et al.,

2000). Saturation at relatively low soil Fe concentrations was also reported by Huber et al. (2009)." (lines 640-643).

*L478: I would replace "merges" with "combines"*

**Answer:** Table 2 (originally Table 4) is now introduced in Sect. 3.1, to support the discussion of flux magnitude with the statistical analysis that is incorporated into the table. We have also removed the F:C parameter from the table (according to one of the following comments), such that we do not use "merges" in the revised sentence (line 408).

*L481: "samplings" should be "sample", and I would encourage revising this sentence to something like: "While the number of samples collected at each site was limited, Table 4 shows that the fluxes...."*

**Answer:** The sentence has been revised accordingly (lines 645-647; see response to next comment).

*L482: I would replace "In both" with "For the...sites,..."*

**Answer:** The sentence has been revised according to this and the previous comment: "While the number of samples collected at each site was limited, Table 2 and Fig. 4 indicate elevated positive fluxes for the SD sites, and to some extent also at COAST-EGD-MD, with respect to both statistically significant and non-statistically significant positive fluxes" (lines 645-647).

*L484: replace "in" with "at" before COAST-EGD-MD*

**Answer:** Corrected (line 646; see answer to previous comment)

*L485: A comma is needed after "winter"*

**Answer:** Corrected (line 648)

*L505: For consistency, replace VSLs with VHOC.*

**Answer:** This text has been deleted, because it is less strongly supported when the statistical uncertainties in our analyses are taken into account. We generally use VHOCs through the text instead VSLs, except for the Abstract, Introduction and twice in the Results and discussions, where we specifically refer to VSLs (lines 347 and 358).

*L506-07: Replace "during" with "at" before the site abbreviations.*

**Answer:** We have separated the sentence into two sentences and revised them: "COAST-EGD-SD-s was associated with the highest incidence of both statistically significant and non-significant positive fluxes. Fluxes at COAST-EGD-SD-w were generally lower and with a smaller incidence of positive fluxes." (lines 665-667).

*L515-19: Do you need the F:C ratio really aid in understanding these processes?*

**Answer:** The F:C ratio has been removed from the table, because we are also able to support our discussion without it, and because it makes the table easier to extract information from (see also response to the next comment).

*L544: Table 4. General comment: This is a hard table to read and extract information from - I almost feel as though presenting this graphically would be more impactful allowing the reader to see the trends rather than sifting through a lot of numbers that appear to vary greatly.*

*Because everything is bolded in the summary portion of Table 4, the rows should be explicitly labeled as to what the values are.*

**Answer:** We have removed F:C from the table and we believe that this makes it easier to extract data. Information in the summary section of the table has been changed (including information which relates to statistical significance, instead of the F:C information), and we also explicitly label the rows in the summary portion. Note that Table 2 (originally Table 4) has been moved to Sect. 3.1 to support the discussion of fluxes from the various sites with the statistical analysis, which is incorporated into the table. The table now appears on line 494.

*L553: Awkward as written, say something like: The results presented in Table 4 show that a higher...*

**Answer:** Amended (lines 698-699)

*L554: comma is needed after CHCl<sub>3</sub>*

**Answer:** The sentence has been revised according to the updated analysis which takes into account the statistical uncertainties: "Differently than previous studies, brominated VHOCs had relatively higher overall incidence of positive fluxes than chlorinated VHOCs (Table 2)." (lines 698-699).

*L555: "tends" should be "tended"*

**Answer:** The sentence has been revised, also based on the updated analysis, which takes into account the statistical uncertainties of a site as a net source for the species (lines 699-702).

*L558: I would suggest deleting the following (not needed): "suggesting both high emission and their balance to some extent by sinks for this species."*

*Because there were watermelon fields, was there any harvesting or drying and decomposing plant material in the vicinity of the sampling? This can be a source of an array of halocarbons, particularly gases like CHCl<sub>3</sub> and CHClBr<sub>2</sub>.*

**Answer:** The whole sentence has been deleted, because it is less strongly supported by the updated statistical analysis. There was no harvesting or drying during the measurement periods. Overall positive net fluxes from the agricultural field site were not elevated compared to the bare soil sites, and tended to be, in most cases, comparable to or lower than those from the natural vegetation (TMRX-ET) (see new Fig. 4).

*L563: I would replace "are in general" with "were"*

**Answer:** Amended (line 706)

*L566-70: Please revise – it is unclear what you are trying to say.*

**Answer:** We have revised the specified text for clarity: "The latter explanation may be supported by the fact that Albers et al. (2017) did not find any correlation between CHCl<sub>3</sub> emission rate and organic Cl in the soil. Furthermore, our study points to higher emission rates and incidence of VHOCs, and generally also of trihalomethanes,

closer to the seawater (COAST-EGD and COAST-TKM sites), which suggests higher sensitivity to soil halide content than OM (Sect 3.2.2)." (lines 709-714).

*L577-9: revise to something like: "...emission rates from both bare and vegetated soil sites supports the work by Albers et al. (2017) concerning the emission of trihalomethanes from the soil after trihaloacetyl hydrolysis (Table 3)."*

**Answer:** Thank you. The text has been revised accordingly (lines 721-723). Note that the natural vegetation site is not statistically significantly a source for the trihalomethanes (Table 2).

*L584: Agricultural emissions, such as from the watermelon farming, could be such a source. More details regarding the scale and influence of these operations would be useful.*

**Answer:** While emissions of both  $\text{CHBr}_3$  and  $\text{CHBr}_2\text{Cl}$  were observed at the agricultural field, even higher emission rates for these species were observed at the coastal sites, and for  $\text{CHBr}_2\text{Cl}$  also from bare soil (BARE-MSMR-2, BARE-MSD-2, BARE-MSD-3 and BARE-MSD-4; see Table 2 (originally Table 4) and new Fig. 4), where there is no agricultural activity. Based on this comment, we now include the following: "note that agriculture could potentially be a source for the emission of  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  for WM-KLY, but not for the other sites (Sect. 2.1.1)." (lines 729-731). Further, referring to the flux correlations between  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$ , we mention in Sect. 3.3 that: "Note that these correlations can potentially be attributed to agricultural emission, considering that WM-KLY, but not TMRX-ET, was identified as a statistically significant source for the three trihalomethanes" (lines 848-850).

*L589: replace "in" with "at" before the site name*

**Answer:** Amended (line 737)

*L589-91: Please revise the following – awkward as written: "No clearly more elevated positive flux of brominated compared to chlorinated trihalomethanes was observed for this site..."*

**Answer:** The sentence has been rephrased (lines 737-740).

*L600: include (Table 4) to direct the reader to this information*

**Answer:** Done (line 748)

*L601: For the statement "...indicating strong emission and deposition...", if the flux is positive, then the emissions outweigh the deposition or other loss processes - revise to clarify your point. Figure 2 counters the point of "strong deposition" for the methyl halides.*

**Answer:** The sentence has been revised based on this comment and the updated analysis that takes into account statistical uncertainties: "A relatively high incidence of negative fluxes was observed for  $\text{CH}_3\text{Br}$ , and more statistically significantly so for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{I}$ , implying high rates of both emission and deposition, at least for the latter two, in the studied area (Table 2)." (lines 746-748).

*L604-05: Cultivated watermelon fields (agricultural emissions) are different from local vegetation, please distinguish as such.*

**Answer:** "local vegetation" has been replaced with "agricultural field" (line 753).

*L644-46: please revise, reads awkwardly*

**Answer:** The text has been revised: "It should be noted, however, that the fluxes that we used for the methyl halide emission efficiencies were based on measured net flux rather than measured emission flux. This might also explain the inconsistency between the relative CH<sub>3</sub>I-emission efficiency calculated by Keppler et al. (2000) and by us" (lines 795-798).

*L662-663: How are the data grouped for Table 5? Is this simply for all sampling heights lumped together? Is there a difference when grouped by height?*

*Replace "evaluated" with "measured"*

**Answer:** Table 4 (originally Table 5) refers to lumped correlations, to avoid higher correlations due to systematic trends of mixing ratios with height. Where height was taken into account, correlations tended to be higher and more statistically significant, but this does not well represent the correlations between species. Pursuant to this comment, we have added the following to the caption of Table 4: "Correlations were calculated for mean mixing ratios at each site" (line 832). The sentence has been revised: "Table 4 presents the Pearson correlation coefficients ( $r$ ) between the measured mixing ratios of VHOCs at the Dead Sea, separately for all sites and for the terrestrial sites only, as well as separately for BARE, COAST, and the natural vegetation and agricultural field sites (VEG). For COAST,  $r$  is also presented individually for the two sites which were closest to the seawater (SD)." (lines 813-817).

*L670: Please consider revising: "...reinforce predominant contribution of VHOCs from terrestrial sources..." – I would consider this to be an overstatement.*

**Answer:** The sentence has been revised: "Correlations were in most cases either similar or smaller when we included measurements from the seawater site SEA-KDM, which may reinforce the notion that emission from the seawater does not contribute significantly to VHOC mixing ratios in the area of the Dead Sea." (lines 825-828).

*L672: The  $r^2$  values are quite low, and without being able to see the correlation plots of these gases, it is difficult to adequately assess the commonality of their sources and sinks. How do these specific  $r^2$  values translate in to common sources and sinks?*

**Answer:** In the revised version, we indicate the  $p$ -value associated with the presented correlation values. We also present the correlations individually for the different site types. This enables us to better support the correlation between CHCl<sub>3</sub> and methyl halides, at least for some of the site types (Table 4). Because  $r$  values (we use Pearson correlation coefficient ( $r$ ) rather than coefficient of determination ( $r^2$ ) in the revised version) cannot be directly translated into common sources and sinks, the short discussion about correlations according to Table 4 is followed by a discussion based on the flux analysis (Table 2) and flux correlation analysis (Table 5). In particular for the correlation between CHCl<sub>3</sub> and the methyl halides, the related discussion is as follows: "Interestingly, in agreement with Table 4, Table 5 also shows relatively high correlations between CHCl<sub>3</sub> and all methyl halides, particularly for the BARE sites (CH<sub>3</sub>I,  $r = 0.68$ ,  $p < 0.15$ ; CH<sub>3</sub>Br,  $r = 0.83$ ,  $p < 0.05$ ; CH<sub>3</sub>Cl,  $r < 0.86$ ,  $p < 0.05$ ), and SD sites (CH<sub>3</sub>I,  $r = 0.99$ ,  $p < 0.05$ ; CH<sub>3</sub>Br,  $r = 0.59$ ,  $p > 0.15$ ; CH<sub>3</sub>Cl,  $r = 0.91$ ,  $p < 0.1$ ). Remarkably, a high correlation was found for CH<sub>3</sub>I with CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> at



the SD sites ( $r = 0.99$ ,  $p < 0.05$  in both cases). Positive fluxes of the three species were observed at the SD sites in most cases, although with only moderate statistical significance for  $\text{CHCl}_3$  (Table 2). Weissflog et al. (2005) found that emission of  $\text{C}_2\text{HCl}_3$ ,  $\text{CHCl}_3$  and other chlorinated VHOCs can occur from salt lakes via the activity of halobacteria in the presence of dissolved Fe (III) and crystallized NaCl. The strong correlations of  $\text{CHCl}_3$ ,  $\text{C}_2\text{HCl}_3$  and  $\text{CH}_3\text{I}$  at the SD sites, where statistically significant fluxes were frequently measured for these species, reinforce the colocalized emission of  $\text{CHCl}_3$  and  $\text{C}_2\text{HCl}_3$  from salt lake sediments, as indicated by Weissflog et al. (2005), and suggest that  $\text{CH}_3\text{I}$  can be emitted in a similar fashion. The fact that the relative emission efficiency of  $\text{CH}_3\text{I}$  in our study was much higher than under the conditions used by Keppler et al. (2000) supports the possibility that mechanisms other than the abiotic emission pathway proposed by Keppler et al. (2000) influence the emission of  $\text{CH}_3\text{I}$  at the Dead Sea (Sect. 3.2.3)." (lines 883-898). Hence, we believe that the integrated analyses indicate a common source for  $\text{CHCl}_3$ ,  $\text{C}_2\text{HCl}_3$  and  $\text{CH}_3\text{I}$ . Note that, considering this comment, we removed the original sentence from the manuscript.

*L678: Replace "records" with something like "shows"*

**Answer:** Amended (line 838)

*L680-81: Change "For the two last, ..." to something like: "For the latter two sites,..."*

**Answer:** Amended (line 840)

*L685: Replace "demonstrates" with something like "shows" or The results in Table 6 show/illustrate...*

**Answer:** Amended (line 843)

*L692-94: Can you please expand upon the correlations being attributable to "common sinks" – what are the sinks and how is this driving the correlations?*

**Answer:** Taking into account statistical uncertainties in our revised analyses indicated that the cultivated and natural vegetation could not be classified as statistically significant as either sink or source for methyl halides. Therefore, considering also this comment and the length of the discussion in Sect. 3.3, we have removed this specific discussion.

*L740: replace "common emission" with something like "co-located emissions"*

**Answer:** Done (line 893)

*L826-27: I would recommend revising or omitting the following: "...from saline soil and salt lakes in stratospheric and tropospheric chemistry, ...", as there were no linkages made to how the compounds measured for this work play in to the local/regional/global budgets of tropospheric or stratospheric Cl, Br or I.*

**Answer:** We agree, and the text has been revised accordingly: "Overall, along with other studies, the findings presented here highlight the potentially important role of saline soil and salt lakes in VHOC emission, and call for further research on VHOC emission rates and controlling mechanisms, and implications on stratospheric and tropospheric chemistry." (lines 974-977).

## References

- Albers, C. N., Jacobsen, O. S., Flores, E. M. M., and Johnsen, A. R.: Arctic and Subarctic Natural Soils Emit Chloroform and Brominated Analogues by Alkaline Hydrolysis of Trihaloacetyl Compounds, *Environ Sci Technol*, 51, 6131-6138, 10.1021/acs.est.7b00144, 2017.
- Butler, J. H., King, D. B., Lobert, J. M., Montzka, S. A., Yvon-Lewis, S. A., Hall, B. D., Warwick, N. J., Mondeel, D. J., Aydin, M., and Elkins, J. W.: Oceanic distributions and emissions of short-lived halocarbons, *Global Biogeochem Cy*, 21, Artn Gb102310.1029/2006gb002732, 2007.
- Carpenter, L. J., Jones, C. E., Dunk, R. M., Hornsby, K. E., and Woeltjen, J.: Air-sea fluxes of biogenic bromine from the tropical and North Atlantic Ocean, *Atmos Chem Phys*, 9, 1805-1816, 2009.
- Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-Lewis, S. A.: Ozone-depleting substances (ODSs) and other gases of interest to the Montreal Protocol, Chapter 1 in *Scientific Assessment of Ozone Depletion: 2014*, Global Ozone Research and Monitoring Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014.
- Grubbs, F. E., and Beck, G.: Extension of Sample Sizes and Percentage Points for Significance Tests of Outlying Observations, *Technometrics*, 14, 847-860, Doi 10.2307/1267134, 1972.
- Huber, S. G., Kotte, K., Scholer, H. F., and Williams, J.: Natural Abiotic Formation of Trihalomethanes in Soil: Results from Laboratory Studies and Field Samples, *Environ Sci Technol*, 43, 4934-4939, 10.1021/es8032605, 2009.
- Keppler, F., Eiden, R., Niedan, V., Pracht, J., and Scholer, H. F.: Halocarbons produced by natural oxidation processes during degradation of organic matter, *Nature*, 403, 298-301, Doi 10.1038/35002055, 2000.
- Keppler, F., Eiden, R., Niedan, V., Pracht, J., and Scholer, H. F.: Halocarbons produced by natural oxidation processes during degradation of organic matter (vol 403, pg 298, 2000), *Nature*, 409, 382-385, DOI 10.1038/35053144z, 2001.
- Quack, B., Atlas, E., Petrick, G., and Wallace, D. W. R.: Bromoform and dibromomethane above the Mauritanian upwelling: Atmospheric distributions and oceanic emissions, *J Geophys Res-Atmos*, 112, Artn D0931210.1029/2006jd007614, 2007.
- Shafir, H., and Alpert, P.: Regional and local climatic effects on the Dead-Sea evaporation, *Climatic Change*, 105, 455-468, 10.1007/s10584-010-9892-8, 2011.
- Sive, B. C., Varner, R. K., Mao, H., Blake, D. R., Wingenter, O. W., and Talbot, R.: A large terrestrial source of methyl iodide, *Geophys Res Lett*, 34, Artn L1780810.1029/2007gl030528, 2007.
- Stull, R. B.: *An introduction to boundary layer meteorology*. Kluwer, Dordrecht 1988.
- Weissflog, L., Lange, C. A., Pfennigsdorff, A., Kotte, K., Elansky, N., Lisitzyna, L., Putz, E., and Krueger, G.: Sediments of salt lakes as a new source of volatile highly chlorinated C1/C2 hydrocarbons, *Geophys Res Lett*, 32, Artn L0140110.1029/2004gl020807, 2005.

Zhou, Y., Varner, R. K., Russo, R. S., Wingenter, O. W., Haase, K. B., Talbot, R., and Sive, B. C.: Coastal water source of short-lived halocarbons in New England, *J Geophys Res-Atmos*, 110, Artn D2130210.1029/2004jd005603, 2005.

Zhou, Y., Mao, H. T., Russo, R. S., Blake, D. R., Wingenter, O. W., Haase, K. B., Ambrose, J., Varner, R. K., Talbot, R., and Sive, B. C.: Bromoform and dibromomethane measurements in the seacoast region of New Hampshire, 2002-2004, *J Geophys Res-Atmos*, 113, Artn D0830510.1029/2007jd009103, 2008.

1 **Emission of volatile halogenated organic compounds**  
2 **over various ~~landforms at the~~ Dead Sea landscapes**

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33 **Abstract.** Volatile halogenated organic compounds (VHOCs), such as methyl halides ( $\text{CH}_3\text{X}$ ; X  
34 = Br, Cl and I) and very short-lived halogenated substances [VSLs; bromoform ( $\text{CHBr}_3$ ),  
35 dibromomethane ( $\text{CH}_2\text{Br}_2$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), trichloroethylene ( $\text{C}_2\text{HCl}_3$ ),  
36 chloroform ( $\text{CHCl}_3$ ) and dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ )] are well known for their significant  
37 influence on ozone concentrations and oxidation capacity of the troposphere and stratosphere,  
38 and for their key role in aerosol formation. Insufficient characterization of the sources and  
39 emission rate of VHOCs limits our ~~present~~ ability to understand and assess their impact in both  
40 the troposphere and ~~the~~ stratosphere. Over the last two decades, several natural terrestrial  
41 sources for VHOCs, including soil and vegetation, have been identified, but our knowledge  
42 ~~about of~~ emission rates from these sources and their responses to changes in ambient conditions  
43 remains limited. Here we report measurements of the mixing ratios and ~~the~~ fluxes of several  
44 chlorinated and brominated VHOCs from different ~~landforms~~ landscapes and natural and  
45 agricultural vegetated sites at the Dead Sea during different seasons. Fluxes ~~were highly variable~~  
46 ~~but~~ were generally positive (emissive emission into the atmosphere), corresponding ~~with to~~  
47 elevated mixing ratios, ~~but~~ for all of the VHOCs investigated in the four investigated site types  
48 ~~— bare soil, coastal, cultivated and natural vegetated sites — except for fluxes of  $\text{CH}_3\text{I}$  and~~  
49  $\text{C}_2\text{HCl}_3$  over the vegetated sites. were highly variable. Fluxes (and mixing ratios) for the  
50 investigated VHOCs ranged as follows:  $\text{CHBr}_3$  from  $-79$  to  $-187$   $\text{nmol m}^{-2} \text{d}^{-1}$  (1.9 to  
51  $-22.6$  pptv),  $\text{CH}_2\text{Br}_2$  from  $-55$  to  $-71$   $\text{nmol m}^{-2} \text{d}^{-1}$  (0.7 to  $-19$  pptv),  $\text{CHBr}_2\text{Cl}$  from  $-$   
52  $408$  to  $-768$   $\text{nmol m}^{-2} \text{d}^{-1}$  (0.4 to  $-11$  pptv),  $\text{CHBrCl}_2$  from  $-29$  to  $-45$   $\text{nmol m}^{-2} \text{d}^{-1}$  (0.5  
53 to  $-9.6$  pptv),  $\text{CHCl}_3$  from  $-577$  to  $-883$   $\text{nmol m}^{-2} \text{d}^{-1}$  (15 to  $-57$  pptv),  $\text{C}_2\text{HCl}_3$  from  $-$   
54  $74$  to  $-884$   $\text{nmol m}^{-2} \text{d}^{-1}$  (0.4 to  $-11$  pptv), methyl chloride ( $\text{CH}_3\text{Cl}$ ) from  $-5300$  to  
55  $-10,800$   $\text{nmol m}^{-2} \text{d}^{-1}$  (530 to  $-730$  pptv), methyl bromide ( $\text{CH}_3\text{Br}$ ) from  $-111$  to  $-118$   
56  $\text{nmol m}^{-2} \text{d}^{-1}$  (7.5 to  $-14$  pptv) and methyl iodide ( $\text{CH}_3\text{I}$ ) ~~from~~  $-25$  to  $-17$   $\text{nmol m}^{-2} \text{d}^{-1}$   
57 (0.4 to  $-2.8$  pptv). Taking into account statistical uncertainties, the coastal sites; (particularly at  
58 short distance from the sea (SD sites) sites those where soil is mixed with salt deposits) , were

59 identified as ~~the~~ source for all ~~investigated~~ VHOCs, but this was not statistically significant for  
60 ~~CHCl<sub>3</sub>, CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>2</sub>Cl, CHBrCl<sub>2</sub>, CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>Br and CH<sub>3</sub>I.~~ ~~F<sub>2</sub>~~  
61 ~~further away from the coastal area, the bare soil sites were found as a sources for CHBrCl<sub>2</sub>,~~  
62 ~~CHBr<sub>2</sub>Cl, CHCl<sub>3</sub>, and probably also for CH<sub>2</sub>Br<sub>2</sub> and CH<sub>3</sub>I,~~ ~~and the agricultural vegetated sites~~  
63 ~~were sources for CHBr<sub>3</sub>, CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub>.~~ In contrast to previous reports, we also  
64 observed emissions of brominated trihalomethanes, with net molar fluxes ordered as follows:  
65 CHBr<sub>2</sub>Cl > > CHCl<sub>3</sub> > CHBr<sub>3</sub> > CHBrCl<sub>2</sub>, and lowest positive flux incidence for CHCl<sub>3</sub> among  
66 ~~all trihalomethanes > CHCl<sub>3</sub>;~~ ~~t.~~ This finding can be explained by the ~~soil's~~ enrichment ~~of soil~~  
67 with Br. Correlation analysis, in agreement with recent studies, indicated common controls for  
68 the ~~formation and~~ emission of ~~CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub>, and likely also for CHBr<sub>3</sub>.~~ ~~all the above~~  
69 ~~trihalomethanes but also for CH<sub>2</sub>Br<sub>2</sub>.~~ ~~There are~~ ~~were~~ no indications for correlation of the  
70 ~~brominated trihalomethanes with CHCl<sub>3</sub>.~~ Also in line with previous reports, we observed  
71 elevated emissions of CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> from mixtures of soil and different salt-deposited  
72 structures; the ~~high flux~~ correlations ~~of flux with~~ ~~between these compounds and~~ methyl halides,  
73 ~~and~~ ~~(~~ particularly ~~with~~ CH<sub>3</sub>I); suggested that at least CH<sub>3</sub>I is also emitted via similar  
74 mechanisms or is subjected to similar controls. Overall, our results indicate elevated emission of  
75 VHOCs from bare soil under semi-arid conditions. Along with other recent studies, our findings  
76 point to the strong emission potential of a suite of VHOCs from saline soils and salt lakes, and  
77 call for additional studies of emission rates and mechanisms of VHOCs from saline soils and  
78 salt lakes.

79

## 80 1 Introduction

81 Volatile halogenated organic compounds (VHOCs), such as methyl halides (CH<sub>3</sub>X; X = Br, Cl  
82 and I) and very short-lived halogenated substances (VSLs; ~~lifetime <6 months~~) contribute  
83 substantially to the loading of tropospheric and lower stratospheric reactive halogen species  
84 ~~(RHS, containing Cl, Br or I and their oxides)~~ (Carpenter et al., 2014; Carpenter et al.,

2013;Derendorp et al., 2012). ~~RHS~~ Reactive halogen species, in turn, lead to ~~destruction of~~ ozone (O<sub>3</sub> destruction), changes in atmospheric oxidation capacity, and radiative forcing (Simpson et al., 2015). Depletion of O<sub>3</sub> in the stratosphere is associated with damage to biological tissues owing to an increase in transmittance of UVB radiation (Rousseaux et al., 1999). In the troposphere, O<sub>3</sub> ~~depletion~~ destruction is of great importance, given that O<sub>3</sub> is toxic to humans, plants, and animals, is a greenhouse gas, and plays a key role in the oxidation capacity of the atmosphere.

The lifetimes of VHOCs vary significantly (see summary in Table S1), which in turn affects their influence in both the troposphere and the stratosphere. Owing to their relatively short lifetimes (<6 months), the transport of VSLSS to the stratosphere occurs primarily in the tropics, where deep convection is frequent. Brominated VSLSS originate primarily from the ocean, whereas chlorinated VSLSS, except for chloroform (CHCl<sub>3</sub>) and chloroethane, originate primarily from anthropogenic sources (Carpenter et al., 2014). Methyl iodide (CH<sub>3</sub>I), having a relatively short lifetime, is also classified as a VSLSS, and contributes significantly to tropospheric O<sub>3</sub> destruction in the marine boundary layer (MBL) (Carpenter et al., 2014) and also, indirectly, to the formation of cloud condensation nuclei ~~formation~~ (O'Dowd et al., 2002). It is now well established that emission of brominated [e.g., bromoform (CHBr<sub>3</sub>), methylene bromide (CH<sub>2</sub>Br<sub>2</sub>), and dibromochloromethane (CHBr<sub>2</sub>Cl)] and iodinated (e.g., methyl iodide (CH<sub>3</sub>I)) VSLSS tends to be much larger ~~greater~~ in coastal areas than in the open ocean (Carpenter et al., 2009;Carpenter et al., 2000;Liu et al., 2011;Bondu et al., 2008;Manley and Dastoor, 1988;Quack and Wallace, 2004), since in the former they can also be emitted from macroalgae under oxidative stress at low tide (Pedersen et al., 1996). The ocean is also a major source of methyl bromide (CH<sub>3</sub>Br), and a significant (~19-%) source of methyl chloride (CH<sub>3</sub>Cl) (Carpenter et al., 2014), as they originate from phytoplankton, bacteria, and detritus.

Despite the numerous efforts made in recent years to evaluate halocarbon budgets, uncertainties still exist concerning the strengths of both their sources and their sinks. The

111 budgets of CH<sub>3</sub>Br and CH<sub>3</sub>Cl are unbalanced, with sinks outweighing sources by ~32% and  
112 ~17%, respectively (Carpenter et al., 2014). Uncertainties in the global budgets of naturally  
113 occurring VSLSSs are large, with discrepancies having a factor of ~2–3 between top-down and  
114 bottom-up emission inventories (Carpenter et al., 2014). This results largely from poor  
115 [characterization](#) of emission sources (Warwick et al., 2006;Hossaini et al., 2013;Ziska et al.,  
116 2013).

117 Studies over the past few decades have clearly demonstrated that terrestrial sources also  
118 constitute a major fraction of the atmospheric budget for both methyl halides and VSLSSs  
119 (Carpenter et al., 2014). Many terrestrial plants have been identified as sources of CH<sub>3</sub>Cl  
120 (Yokouchi et al., 2007), and the results of recent modeling indicate that about 55% of the  
121 global sources of CH<sub>3</sub>Cl originate from tropical lands (Xiao et al., 2010;Carpenter et al., 2014).  
122 It [has](#) also [been](#) suggested that natural terrestrial sources of CH<sub>3</sub>Br, especially emissions from  
123 terrestrial vegetation, must account for a large part of the missing sources (Gebhardt et al.,  
124 2008;Yassaa et al., 2009;Warwick et al., 2006;Gan et al., 1998;Yokouchi et al., 2002;Moore,  
125 2006;Rhew et al., 2001;Wishkerman et al., 2008), and emissions have been observed from  
126 peatlands, wetlands, salt marshes, shrublands, forests, and some cultivated crops (Gan et al.,  
127 1998;Varner et al., 1999;Lee-Taylor and Holland, 2000). CHCl<sub>3</sub> ~~was~~[has](#) also [been](#) found to be  
128 emitted from various terrestrial sources, including rice, soil, tundra, forest floor, and different  
129 types of microorganisms, such as fungi and termites (see Dimmer et al. (2001) and (Rhew et al.,  
130 2008)).

131 The importance of VHOC emission from soil, sediments, and salt lake deposits ~~was~~[has been](#)  
132 recently recognized (see Kotte et al. (2012), Ruecker et al. (2014), and references therein). For  
133 example, Keppler et al. (2000) revealed natural abiotic emission of CH<sub>3</sub>Br, CH<sub>3</sub>Cl, and CH<sub>3</sub>I, as  
134 well as additional chlorinated VHOCs from soil and sediments harboring an oxidant such as  
135 Fe(III), halides, ~~and~~[or](#) organic matter (OM), while Weissflog et al. (2005) found that salt lake  
136 sediments can be a source for several C1 and C2 chlorinated species, including CHCl<sub>3</sub> and



137 [trichloroethylene](#) ( $C_2HCl_3$ ), induced by halobacteria in the presence of dissolved Fe. Huber et al.  
138 (2009) identified ~~an~~-abiotic natural emission of trihalomethanes from soil, including  $CHCl_3$ ,  
139 [bromodichloromethane](#) ( $CHBrCl_2$ ), and  $CHBr_2Cl$ , induced by oxidation of OM by Fe(III) and  
140 hydrogen peroxide, while Hoekstra et al. (1998) identified natural emission of  $CHBr_3$  following  
141 enrichment of the soil by ~~KBr~~[potassium bromide](#). In addition, Carpenter et al. (2005) identified  
142  $CHBr_3$  emission from ~~a~~-peatland or another terrestrial source at Mace Head [\(inIreland\)](#). Albers  
143 et al. (2017) revealed that  $CHCl_3$ ,  $CHBrCl_2$ , and potentially also other trihalomethanes can be  
144 emitted from soils, probably induced by hydrolysis of trihaloacetyl compounds. Several other  
145 studies [have reported](#) strong emissions of  $CH_3Cl$ ,  $CH_3Br$ , and  $CH_3I$  from coastal marsh  
146 vegetation and to a lesser extent from the marsh's soil (Rhew et al., 2002;Rhew et al.,  
147 2001;Rhew et al., 2014;Wishkerman et al., 2008;Rhew et al., 2000), with significant importance  
148 on a global scale (Deventer et al., 2018;Manley et al., 2006). In addition, peatland has been  
149 indicated as an important source for  $CH_3Br$ ,  $CH_3Cl$ ,  $CH_3I$  and  $CHCl_3$  (Simmonds et al.,  
150 2010;Khan et al., 2012;Dimmer et al., 2001;Carpenter et al., 2005), and Sive et al. (2007)  
151 identified a globally significant source of  $CH_3I$  from mid-latitude vegetation and soil.

152 Accordingly, the need for improved understanding of VHOC emissions from saline  
153 environments and their potential importance on the global scale have been highlighted by recent  
154 studies (Weissflog et al., 2005;Kotte et al., 2012;Ruecker et al., 2014;Deventer et al., 2018).  
155 Moreover, [owing due](#) to global warming, saline environments are likely to become more prevalent  
156 (IPCC 2007;Ruecker et al., 2014). The present study is aimed at improving our knowledge ~~about~~  
157 [of](#) the emission of VHOCs from salt lake environments by quantifying the flux and ~~the~~-mixing  
158 ratios of methyl halides and halogenated VSLs from different sites in the area of the Dead Sea.

159 The Dead Sea is unique because it is the lowest point on the Earth's surface, about 430 m  
160 below sea level, with water salinity [12 times higher](#) and [a bromide \( \$Br^-\$ \) to chloride \( \$Cl^-\$ \) ratio](#)  
161 [\( \$Br^-/Cl^-\$ \) \( \$\[Br^-\]/\[Cl^-\]\$ \) ratio 12 and 7.5 times higher than in normal ocean waters, ~~respectively~~.  
162 Fast evaporation from the sea leads to a variety of newly exposed ~~landforms~~\[sea deposits\]\(#\).](#)

163 Despite the high salinity, emission of VHOCs via biotic processes at the Dead Sea is also  
164 potentially feasible. The unicellular green alga *Dunaliella parva* ~~was~~ has been found to be active  
165 in Dead Sea water (Oren and Shilo, 1985), while additional bacteria and fungi that ~~were~~ have  
166 been isolated from the sea could also potentially be active under the Dead Sea's extreme  
167 conditions (Oren et al., 2008; Jacob et al., 2017; Buchalo et al., 1998). Mycobiota, including  
168 fungi and biota, ~~were~~ have also been detected in the Dead Sea's hypersaline soil and coastal  
169 sand (Pen-Mouratov et al., 2010; Kis-Papo et al., 2001; Jacob et al., 2017).

170 Studying the emission of VHOCs at the Dead Sea is also fundamental for understanding  
171 local surface O<sub>3</sub>-depletion events ~~Studying the emission of VHOCs at the Dead Sea is also~~  
172 ~~interesting, in view of local sharp ozone depletion events~~ (Hebestreit et al., 1999; Tas et al.,  
173 2003; Matveev et al., 2001; Zingler and Platt, 2005; Tas et al., 2006) as well as ~~mercury~~ mercury-  
174 depletion events (Tas et al., 2012; Obrist et al., 2011) in the boundary layer at-of this area.  
175 Emissions of brominated and iodinated VHOCs can potentially lead to formation of the reactive  
176 iodine and bromine species that are responsible for these processes.

177

## 178 **2 Methods**

### 179 **2.1 Field measurements and samplings**

180 Field measurements were taken at selected sites along the Dead Sea to measure the mixing  
181 ratios and evaluate the vertical flux of VHOCs over different land-use types, seasons, and  
182 distance from the seawater, as summarized in Table 1. Soil samples from the various sites were  
183 analyzed and meteorological measurements were performed in situ, ~~as described below~~.

184

#### 185 **2.1.1 Measurement sites**

186 All measurements were taken at-in the Dead Sea area. The Dead Sea's geographical position is  
187 between 31°050' N and 31°590' N at ~~-~~35°30' E, about 430 m below sea level. It is located in a  
188 semi-arid area, with mean daily maximum temperatures for summer and winter of ~40 °C and ~

189 21 °C, respectively. The Dead Sea has low rates of freshwater inflow and precipitation (20–50  
190 mm y<sup>-1</sup>; Shafir and Alpert, 2010), while ~~and~~ ~~with a very high~~ seawater evaporation rates are  
191 high, estimated at about ~~rate of~~ 400 cm y<sup>-1</sup> (Alpert et al., 1997). As a result, the water salinity is  
192 12 times higher than ~~that of the normal~~ average salinity of ocean water. Dead Sea water contains  
193 on average 5.6 g L<sup>-1</sup> ~~Br<sup>-</sup> bromide~~ and 225 g L<sup>-1</sup> ~~Cl<sup>-</sup> chloride~~ (Br<sup>-</sup>/Cl<sup>-</sup> ~~ratio~~ ≈ 0.025) (Niemi,  
194 1997), whereas normal ocean water contains 0.065 g L<sup>-1</sup> ~~Br<sup>-</sup> bromide~~ and 19 g L<sup>-1</sup> ~~Cl<sup>-</sup> chloride~~  
195 (Br<sup>-</sup>/Cl<sup>-</sup> ~~ratio~~ ≈ 0.0034) (Sverdrup, 1942). ~~The main anthropogenic emission source in the area,~~  
196 ~~apart from local transportation and a few small settlements, is the Dead Sea Works, a potash~~  
197 ~~plant located to the south of most of the measurement sites (see Fig. 1). Agricultural fields,~~  
198 ~~which are mostly concentrated in the north near Kalya, in the south near Ein Tamar and near Ein~~  
199 ~~Gedi (see Fig. 1), are also potential sources for the emission of VHOCS in the area. To the best~~  
200 ~~of our knowledge, there are no wastewater facilities near the Dead Sea area, which could~~  
201 ~~otherwise also contribute to the emission of VHOCS such as CHCl<sub>3</sub> and CHBr<sub>3</sub>.~~

202 All measurement sites ~~were~~ nearly flat, homogeneous and ~~are~~ located either along or near  
203 the Dead Sea coast (see Fig. 1). ~~Overall, for our investigations we selected emissions from Sites~~  
204 ~~were classified according to surface cover:~~ ~~bare soil sites (BARE)~~ at Mishmar (~~MSMR;~~  
205 ~~BARE–MSMR~~) and at Massada (~~MSD;~~ ~~BARE–MSD~~); ~~coastal sites that are mixtures of soil~~  
206 ~~and salt deposits (COAST)~~ at Ein- ~~Gedi (EGD;~~ ~~COAST–EGD~~) and Tzukim (~~TKM;~~  
207 ~~COAST–TKM~~); ~~natural Tamarix vegetation at Ein Tamar (ET;~~ ~~TMRX–ET~~); ~~cultivated~~  
208 ~~irrigated watermelon~~ agricultural watermelon field at Kalya (~~KLY;~~ ~~WM–KLY~~); and ~~directly~~  
209 ~~from the~~ seawater at Kedem (~~KDM;~~ ~~SEA–KDM~~). ~~ing~~ Note that at SEA–KDM, we did not  
210 evaluate fluxes. Based on in- ~~situ~~ ~~wind~~ wind-direction measurements, the sampled air masses at  
211 SEA–KDM were transported over the seawater from the east (see Fig. 1); at least 1 h prior to  
212 sampling and during the sampling. To study the effect of distance from the seawater on emission  
213 rates, measurements at both COAST–EGD and COAST–TKM were taken at three and two  
214 different distances from the sea, respectively. The shorter, middle, and longer distances from the

215 seawater ~~are-were~~ termed, respectively, SD, MD and LD. Emission rates at both COAST-EGD  
216 and COAST-TKM could potentially be affected by ~~the~~ distance from the seashore; there are  
217 several reasons for this, including changes across the sites in soil salt and water ~~soil~~-content and  
218 changes in density of the extremely sparse vegetation cover. In addition, depending on the local  
219 wind direction at COAST-TKM-SD and COAST-EGD-SD, direct emission and uptake from  
220 the seawater can potentially affect the samplingsamples.

221 In the following, we briefly describe the different measurement sites, ~~;~~ ~~while~~ additional  
222 information about the sites and measurements is provided in Table 1. BARE-MSMR has a bare  
223 soil consisting of loess and a small fraction of drifted soil covered with small stones and  
224 extremely sparse vegetation, and is located in a valley 1.5 km to the west of the Dead Sea shore.  
225 BARE-MSD has bare Hamada soil, with small stones and loess, and is located 2.1 km to the  
226 west of the Dead Sea. COAST-EGD-SD has a dried-out bare saline soil, mixed with salty beds  
227 and rocks ~~and obtaining with~~ a small contribution of fresh-water inflow ~~at the Dead Sea shore~~.  
228 COAST-EGD-MD has a dried-out sea bed of bare saline soil, mixed with salty beds and rocks,  
229 0.3 km west of the Dead Sea shore. COAST-EGD-LD is a dried-out sea bed of loess saline bare  
230 soil, mixed with drifted soil, 0.8 km from the Dead Sea shore. COAST-TKM-SD is a wetted  
231 bare soil with salt deposits, groundwater inflow from the Dead Sea, and minor (<5%) fresh  
232 water inflow lines covered with perennial grasses found in wetlands (e.g., *Phragmites* sp.),  
233 about 0.5 km from the shore. COAST-TKM-LD is a flat rocky loess area about 1.5 km from the  
234 shore, with patchy salts and sparse mixed shallow vegetation, including mostly small *Atriplex*  
235 sp., *Tamarix* sp. and *Retama raetam*. TMRX-ET is a moderately dense *Tamarix*  
236 groveshrubland, of 4–5 m average height, ~2.25 km<sup>2</sup> and 60–70% vegetation cover fraction,  
237 with sandy soil, located 1.7 km south of the southern tip of the Dead Sea evaporation ponds (see  
238 Fig. 1). Lastly, WM-KLY is a well-irrigated and flat 700 x 350 m<sup>2</sup> cultivated watermelon  
239 agricultural field with cultivated watermelon located surrounded by a larger agricultural area of  
240 ~3 km<sup>2</sup>, and it is located 2.5 km NW-northwest of the Dead Sea shore (Fig. 1). It consisted

241 ~~of~~The watermelon crop had an ~~at~~ average height of ~0.67 m and 95–99% vegetation cover  
242 ~~fraction~~.

243

## 244 2.1.2 Field measurements and sampled air analysis

245 Air was sampled at each site by placing three different canisters at specified heights (see Table  
246 1) along a meteorological tower. The samples were used to quantify the mixing ratios of  
247 different VHOCs in the air, and their corresponding fluxes ~~were~~ calculated by applying the flux-  
248 gradient method (see (Stull 1988;Maier and Schack-Kirchner, 2014;Meredith et al., 2014)). ~~By~~  
249 ~~default, the differences in heights between the canisters increased exponentially with height,~~  
250 ~~considering the typical decrease in the vertical gradient of emitted species in the surface layer~~  
251 ~~(Stull 1988)~~. All canisters were placed high enough above the ground to ensure that all  
252 samplings ~~were~~ ~~was~~ performed within the inertial sublayer, except for the lowest canister at  
253 TMRX–ET. ~~In all cases, the sample footprint fell inside the target fetch, except for the sampling~~  
254 ~~at COAST–EGD, for which the~~ ~~sample footprint included a narrow strip of the seawater~~  
255 ~~(estimated at about 40-% of the footprint)~~. To minimize non-synchronized air sampling by the  
256 three canisters, we constructed a special ~~sampling~~ system that allows ~~an~~ ~~fast~~ ~~and~~ almost  
257 simultaneous ~~lifting~~ ~~fileeling~~ of the canisters. ~~For each sample, air was drawn into~~ ~~pulled~~ ~~a 1.9~~  
258 ~~L stainless–steel canister via~~ ~~Facilitated by~~ passive grab samplers (Restek Corporation, PA,  
259 U.S.A.), ~~we performed~~ ~~resulting in a sampling~~ ~~each sampling within~~ ~~duration of~~ 20 minutes ~~by~~  
260 ~~pulling air into evacuated 1.9 L stainless steel canisters, resulting in an~~ ~~and~~ internal canister  
261 pressures higher than 600 Torr. Meteorological parameters, including temperature and relative  
262 humidity, wind speed and direction, and global solar radiation, were all continuously measured,  
263 starting at least 30 min before air sampling was initiated, ~~and~~ ~~(–summarized in Table S6)~~. All  
264 canisters were sent to the Blake/Rowland group, University of California, Irvine ~~(UCI)~~, where  
265 they were ~~subjected~~ ~~analyzed by to the analytical~~ techniques ~~similar to those~~ described in ~~detail~~  
266 ~~in~~ Colman et al. (2001). Analyses were performed using gas chromatography combined with

267 mass spectrometry, ~~flame-flame~~-ionization detection and ~~electron-electron~~-capture detection to  
268 quantify the air mixing ratios of ~~bromoform~~ ( $\text{CHBr}_3$ ), ~~trichloroethene~~ ( $\text{C}_2\text{HCl}_3$ ), ~~methylene~~  
269 ~~bromide~~ ( $\text{CH}_2\text{Br}_2$ ), ~~dibromochloromethane~~ ( $\text{CHBr}_2\text{Cl}$ ), ~~bromodichloromethane~~ ( $\text{CHBrCl}_2$ ),  
270 ~~trichloroethene~~ ( $\text{C}_2\text{HCl}_3$ ), ~~chloroform~~ ( $\text{CHCl}_3$ ), ~~methyl iodide~~ ( $\text{CH}_3\text{I}$ ), ~~methyl bromide~~ ( $\text{CH}_3\text{Br}$ )  
271 and ~~methyl chloride~~ ( $\text{CH}_3\text{Cl}$ ). For all gases, accuracy ranged between 1-% and 10-% and  
272 analytical precision between 1-% and 5-% (see Table ~~S1S2~~). Note that the lower-height canister  
273 analysis for COAST-TKM-LD-s and the mid-height canister analysis of TMRX-ET-1 indicated  
274 an outlier mixing ratio for all VHOCS and for  $\text{CH}_3\text{Cl}$ , respectively ~~that seemed not to agree with~~  
275 ~~any other measured mixing ratios for this species~~ ( $p \ll 0.01$ ; Grubbs test; (Grubbs and Beck,  
276 1972)). We therefore excluded the lower-height COAST-TKM-LD-s measurement from all of our  
277 calculations and used only the lowest and ~~the~~ highest canisters in the flux calculation for  
278 TMRX-ET-1, ~~which may reflect less accurate flux evaluation. This potentially less accurate~~  
279 flux evaluation ~~as~~ is indicated in all relevant figures and tables.

280 **Table 1.** Summary of ~~volatile halogenated organic compounds~~ **VHOC samplings** over at the Dead Sea. ~~The table~~  
 281 ~~records~~ **Shown are** the date, time, ~~and~~ site name (and abbreviation) ~~for the sample~~, sampling height, **total number**  
 282 **of samplings for each experiment** and whether the ~~sampling sample~~ could potentially ~~be~~ **have been** influenced by  
 283 emission from the seawater and by precipitation prior to sampling.

Date dd/m/yyyy	Time ( <del>Local</del> <u>local</u> )	Site name / measurement abbreviation <sup>a</sup>	Sampling heights (m)	<b>Total samplings</b>	Seawater <sup>b</sup>	Precipitation (days before sampling) <sup>c</sup>
20/4/2016	08:45–08:55	BARE-MSMR / BARE-MSMR-1	2.5, 4.5, 7.0	<u>3</u>	–	>3 months
21/4/2016	08:45–08:55	WM-KLY / WM-KLY-1	1.0, 2.0, 4.0	<u>3</u>	–	>3 months
<u>02/5/2016</u>	08:45–08:55	TMRX-ET / TMRX-ET-1 <sup>*</sup>	4.5, 5.5, 7.5	<u>3*</u>	–	>3 months
<u>03/5/2016</u>	08:45–08:55	WM-KLY / WM-KLY-2	<u>1.0, 2.0, 4.0</u>	<u>3</u>	–	>3 months
25/5/2016	08:30–08:40	BARE-MSD / BARE-MSD-1	1.25, 2.5, 5	<u>3</u>	–	1–2
26/5/2016	08:30–08:40	BARE-MSD / BARE-MSD-2	1.25, 2.5, 5	<u>3</u>	–	2–3
30/5/2016	12:00–12:10	<del>WM</del> TMRX-ET / TMRX-ET-2	4.5, 5.5, 7.5	<u>3</u>	–	>3 months
31/5/2016	12:00–12:10	BARE-MSMR / BARE-MSMR-2	2.5, 4.5, 7	<u>3</u>	–	>3 months
11/7/2016	12:00–12:20	BARE-MSD / BARE-MSD-3	1.25, 2.5, 5	<u>3</u>	–	>3 months
11/7/2016	18:00–18:20	BARE-MSD / BARE-MSD-4	1.25, 2.5, 5	<u>3</u>	–	>3 months
21/2/2017	11:20–11:40	COAST-TKM-SD / COAST-TKM-SD-w	1, 2.5, 6.5	<u>3</u>	+/-	5
22/2/2017	11:00–11:20	COAST-TKM-LD / COAST-TKM-LD-w	1.5, 3, 7	<u>3</u>	–	6
28/2/2017	11:20–11:40	COAST-EGD-SD / COAST-EGD-SD-w	1, 2.5, 6.5	<u>3</u>	+	0
<u>01/3/2017</u>	11:07–11:27	COAST-EGD-MD / COAST-EGD-MD-w	1, 2.5, 6.5	<u>3</u>	+/-	>3 months
<u>02/3/2017</u>	11:00–11:20	COAST-EGD-LD / COAST-EGD-LD-w	1, 2.5, 6.5	<u>3</u>	–	>3 months
<u>02/3/2017</u>	12:55–13:15	SEA-KDM / SEA-KDM-w	1	<u>1</u>	+	>3 months
25/4/2017	11:30–11:50	COAS-EGD-SD / COAST-EGD-SD-s	1, 2.5, 6.5	<u>3</u>	+	>3 months
26/4/2017	11:00–11:20	COAST-EGD-MD / COAST-EGD-MD-s	1, 2.5, 6.5	<u>3</u>	+/-	>3 months
27/4/2017	11:00–11:20	COAST-EGD-LD / COAST-EGD-LD-s	1, 2.5, 6.5	<u>3</u>	–	>3 months
<u>03/5/2017</u>	12:10–12:30	COAST-TKM-SD / COAST-TKM-SD-s	1, 2.5, 6.5	<u>3</u>	–	>3 months
<u>04/5/2017</u>	10:30–10:50	COAST-TKM-LD / COAST-TKM-LD-s	1.5, 3, 7	<u>3**</u>	–	>3 months
<u>04/5/2017</u>	12:30–12:50	SEA-KDM / SEA-KDM-s	1	<u>1</u>	+	>3 months

284  
 285 <sup>a</sup> The suffixes "s" and "w" refer to ~~samplings~~ **samples taken** during ~~the~~ spring and winter, respectively. <sup>b</sup>"SD", MD",  
 286 and <sup>c</sup>"LD" refer to relatively short, medium, and long distance from the coastline, respectively (see Sect. 2.1).

287 <sup>b</sup> "+", "-" and "+/-" respectively indicate that the samplings could be were, could not be, or may be influenced by  
288 emission from the seawater, respectively.

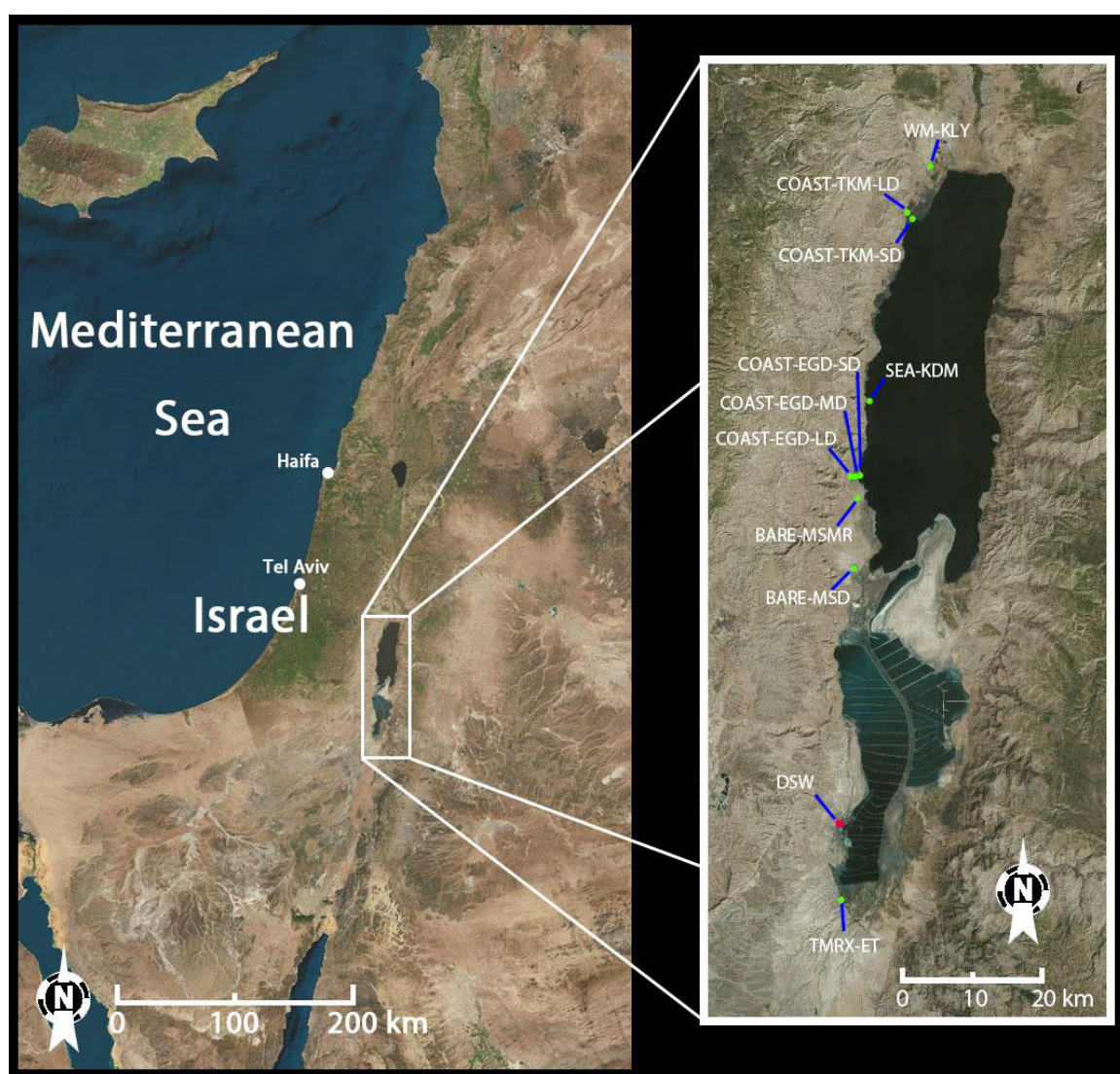
289 <sup>c</sup> Values indicate the number of days before sampling during-on which precipitation occurred.

290 Additional abbreviations: MSD, Masada; MSM<sup>SR</sup>, Mishmar; KLY, Kalya; ET, Ein-Tamar; KDM, Kedem; EGD,  
291 Ein-Gedi; BARE, bare soil site; COAST, coastal soil-salt mixture site; WM, agricultural cultivated watermelon  
292 site; TMRX, natural *Tamarix* site; SEA, sampling near the seawater (see Sect. 2.1.1).

293 \*Samples exclude one CH<sub>3</sub>Cl measurement in TMRX-ET-1 (see Sect. 2.1.2).

294 \*\* Samples exclude one measurement for all VHOCs (see Sect. 2.1.2).

295



296  
297 **Fig-ure 1.** Location and satellite image of the Dead Sea measurement sites (see Sect. 2.1.2) and Dead Sea Works  
298 (DSW). Left: location of the Dead Sea. Right: zoom-in ef-on the area of the measurement sites.

299

300



301 **2.2 Vertical flux evaluation**

302 The vertical flux,  $F_c$ , of a species  $c$ , was evaluated according to the gradient approach using the  
303 vertical gradient of  $c$ ,  $\frac{\partial c}{\partial z}$ , and a constant,  $K_c$ :

$$F_c \equiv -K_c \frac{\partial C}{\partial z} \quad (1)$$

304  $K_c$  represents the rate of turbulent exchange in Eq. 1 and was evaluated on the basis of the  
305 Monin–Obukhov similarity theory (MOST) described by Lenschow (1995):

$$K_{C(z)} = u_* K Z \phi_c(\zeta) \quad (2)$$

307 where  $u_*$  is the friction velocity,  $K$  is the Von Kármán constant,  $Z$  is the measurement height  
308 and  $\phi_c$  is a universal function of the dimensionless parameter  $\zeta$ . According to MOST, vertical  
309 fluxes in the surface layer can be evaluated on the basis of the dimensionless length parameter,  
310  $\zeta$ , according to

$$\zeta = (z - d)/L \quad (3)$$

312 where  $z$ ,  $d$  and  $L$  are the vertical coordinate, zero displacement, and the Monin–Obukhov length,  
313 respectively (Schmugge and André, 1991).

314 We relied on the commonly used assumption that  $\phi_c$  is similar to  $\phi_h$  for chemical species  
315 with a relatively long lifetime (Dearellano et al., 1995), and calculated  $\phi_h$  using the following  
316 equation for the relationship between  $\phi_h$  and  $\zeta$ , which was found to be valid for  $0.004 \leq z/L \leq$   
317  $4$  (Dyer and Bradley, 1982; Yang et al., 2001):

$$\phi_h = (1 - 14\zeta)^{-1/2} \quad (4)$$

319 We derived  $L$  from the Pasquill and Gifford stability class (Pasquill and Smith, 1971) and  
320 roughness length ( $z_0$ ) according to Golder (1972).  $z_0$  was evaluated based on the specific surface  
321 characteristics at each site using information provided by the WMO (2008). The stability class

322 was evaluated using the in-~~situ~~-~~situ~~-measured solar radiation and wind speed (Gifford,  
323 2000;Pasquill and Smith, 1971).  $u_*$  was derived from the logarithmic wind profile according to  
324 MOST, using the following equation:

$$325 \quad u(z) = \frac{u_*}{k} \ln\left(\frac{z-d}{z_0}\right) \quad (5)$$

326 where  $u(z)$  is the wind speed at height  $z$ , and  $\psi_m$  is a correction for diabatic effect on momentum  
327 transport. Using the measured  $u$  at a height of 10 m, we calculated the wind speed at each  
328 measurement height according to Gualtieri and Secci (2011):

$$329 \quad u_2 = u_1 \frac{\ln(z_2/z_0) - \psi_m(z_2/L)}{\ln(z_1/z_0) - \psi_m(z_1/L)} \quad (6)$$

330 where  $\psi_m$  is calculated using:

$$331 \quad \Psi_m(Z/L) = 2\ln(1 + X/2) + \ln(1 + X^2/2) - 2\arctan(X) + \pi/2 \quad (7)$$

332 and

$$X = (1 - 15 \left(\frac{Z}{L}\right)^{1/4}) \quad (8)$$

333

### 334 2.3 Soil analyses

335 Soil samples at each site were collected up to a depth of 5 cm during the summer, at least 3  
336 months following-after any rain event in the Dead Sea area, to ensure no impact on the samples  
337 by recent drift and percolation. The samples were analyzed for bromineBr, chlorineCl, iodineI,  
338 organic-matterOM, moisture and Fe in the soil, as well as for soil pH-of-the-soil. Prior to halide  
339 quantification, extractions for each sample were prepared using HNO<sub>3</sub> (BCE, 1990). Total Br  
340 and I were quantified using inductively coupled plasma mass spectrometry (ICP-MS). Total Cl  
341 was quantified by potentiometric titration against AgNO<sub>3</sub>.

342 To quantify Fe in the soil, microwave-assisted digestion with reverse aqua regia was used,  
343 and Fe concentration was determined by inductively coupled plasma optical emission  
344 spectrometry (ICP-OES). A batch of each sample (~300 mg of dry soil) was digested in reverse  
345 aqua regia (HNO<sub>3</sub> (65-%) :- HCl (30-%); 3:1 mixture, v/v). Digestion was allowed to proceed in

346 quartz vessels using a "Discover" sample digestion system at high temperature and pressure  
347 (CEM Corporation, NC, USA). The vessels were cooled and the volume was ~~made up~~brought to  
348 20 mL with deionized water. Element concentrations were measured in clear solutions using  
349 ~~High-high-r~~Resolution dual-view ICP-OES PlasmaQuant PQ 9000 Elite (Analytik Jena,  
350 Germany). The reported values represent the lower-limit, because the samples were not  
351 completely dissolved. Soil water content and OM were determined by weight loss under dry  
352 combustion at 105 °C and 400 °C, respectively. Soil pH was measured in 1:1 (v/v) soil-to-water  
353 extracts with a model 420 pH-meter (Thermo Orion, ~~Waltham,~~ MA, USA).

354

355

### 356 **3 Results and discussion**

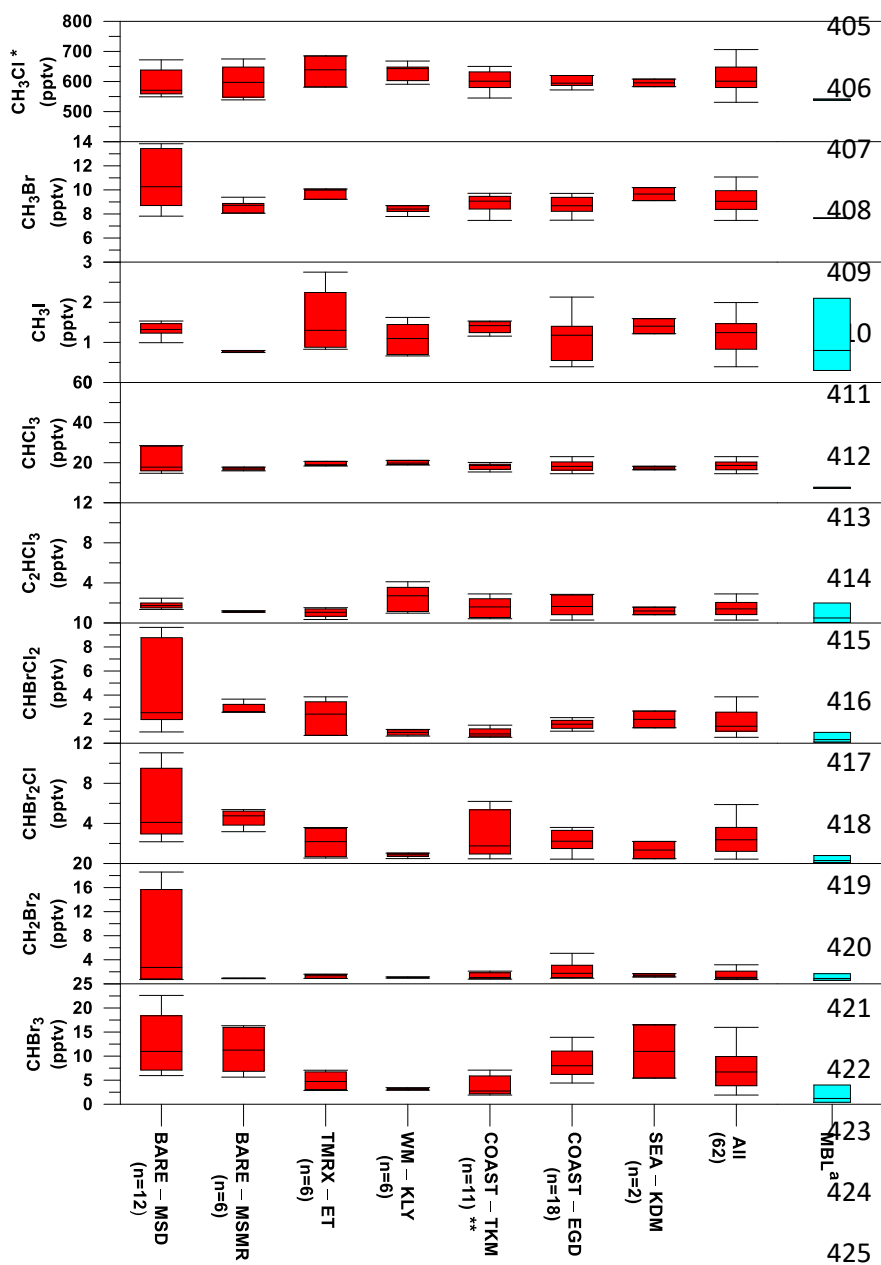
#### 357 **3.1 VHOC flux and mixing ratio**

358 ~~We compared the measured mixing ratios and fluxes with corresponding available~~  
359 ~~information.~~Overall, the measurements at the Dead Sea boundary layer revealed higher mixing  
360 ratios for all investigated VHOCs than their expected levels at the Mediterranean Sea and Red  
361 Sea MBL, indicating higher local emissions from the Dead Sea area. No association was  
362 observed between the measured mixing ratios and the air masses flowing from the direction of  
363 the Dead Sea Works (see Sect. S455 for anthropogenic impact), a potash plant which is located  
364 to the north-west of the TMRX-ET site and to the south of all other measurement sites (see Fig.  
365 1), ~~and that~~ is the main anthropogenic source in the area under investigation. Furthermore, the  
366 correlation analysis (Table S5) revealed that only C<sub>2</sub>HCl<sub>3</sub> was associated with C<sub>2</sub>Cl<sub>4</sub>, a well-  
367 known anthropogenic VHOC. The absence of any other associations suggested dominance of  
368 natural sources for the VHOCs in the studied area. The measured mixing ratios for the different  
369 species at the measurement sites are summarized and compared with mixing ratios from the  
370 MBL in Table S3 and in Fig. 2. ~~presents a comparison between measured mixing ratios at the~~  
371 ~~different measurement sites and reported values for the global MBL.~~ The ~~values~~figure indicates

372 that median mixing ratios measured at the Dead Sea were generally higher than the  
373 corresponding mixing ratios in the MBL. Our calculations suggest that the mixing ratios at the  
374 Dead Sea are higher by factors of 1.2–8.0 for brominated and chlorinated VSLs and ~1.5, 1.3  
375 and 1.1 for CH<sub>3</sub>I, CH<sub>3</sub>Br and CH<sub>3</sub>Cl, respectively. It should be noted, however, that while Fig. 2  
376 implies elevated VHOCS emission from the Dead Sea, comparison of mean or median mixing  
377 ratios of VHOCS for the Dead Sea with those for the MBL is not straightforward, considering  
378 that VHOCS mixing ratios in the MBL are sensitive to several factors, including season and  
379 latitude. Moreover, the measurement height can play a significant role in affecting the mixing  
380 ratios, due to decreasing mixing ratios with height over areas where local emissions occurs.  
381 Hence, we also compared the measured fluxes and mixing ratios with their corresponding values  
382 measured in coastal areas, where the highest mixing ratios in the MBL were generally measured  
383 due to stronger emissions. The measured mixing ratios and fluxes at the Dead Sea were  
384 generally in most cases also comparable to or higher than in coastal areas.

385 Owing to their large contribution to stratospheric Br, CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> are the most  
386 extensively studied VSLs in the MBL (Hossaini et al., 2010). The mixing ratios of CHBr<sub>3</sub> and  
387 CH<sub>2</sub>Br<sub>2</sub> that we measured at the Dead Sea ranged from 1.9 to 22.6 pptv and from 0.7 to 18.6  
388 pptv, respectively, ~~which are~~ higher than most of their reported mixing ratios in coastal areas  
389 where the highest mixing ratios have typically been measured. For example, Carpenter et al.  
390 (2009) reported elevated mixing ratios for CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> along the eastern Atlantic coast  
391 ranging from 1.9 to 4.9 and from 0.9 to 1.4 ppt, respectively, and Nadzir et al. (2014) reported  
392 mixing ratios of 0.82–5.25 pptv and 0.90–1.92 ppt for CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub>, respectively, for  
393 several tropical coastal areas, including the Strait of Malacca, the South China Sea and the Sulu-  
394 -Sulawesi Seas. Somewhat higher mixing ratios for CHBr<sub>3</sub> have been measured in only a few  
395 locations, including some at-in coastal areas near New Hampshire (Zhou et al., 2008), San  
396 Cristobal Island (Yokouchi et al., 2005; O'Brien et al., 2009), Cape Verde (O'Brien et al., 2009),  
397 Borneo (Pyle et al., 2011), ~~and~~ Cape Point (Kuyper et al., 2018; Butler et al., 2007), and at the

398 [Atmospheric Observing Station at Thompson Farm in New Hampshire, USA \(TF\) during the](#)  
 399 [summer](#) (Zhou et al., 2005), whereas the range (and average) concentrations at those locations  
 400 were 0.2–37.9 pptv (5.6–6.3), 4.2–43.6 pptv (14.2), 2.0–43.7 pptv (4.3–13.5), 0.2–60 pptv  
 401 (1.3–1.7), and 4.4–64.6 pptv (24.8) and 0.6–37.9 pptv (2.6–5.9), respectively. For CH<sub>2</sub>Br<sub>2</sub>, the  
 402 corresponding mixing ratios were reported as 1.3–2.3 pptv, 0.5–4.1 pptv, 0.7–8.8 pptv and 0.4–  
 403 4.2 pptv in New Hampshire, San Cristobal Island, and Cape Verde, and TF, respectively, which  
 404 are comparable with the mixing ratios measured at the Dead Sea.



426

427

428  
429 **Figure 2.** Comparison of VHOC mixing ratios (in pptv) measured at the Dead Sea with their corresponding values  
430 at the marine boundary layer (MBL). For the Dead Sea sites, boxes indicate median, upper, and lower quartiles, and  
431 bars show minimum and maximum VHOC mixing ratios (see Table 1 for site abbreviations; "n" specifies the  
432 number of samples for each site). For the MBL, boxes indicate the median, minimum and maximum mixing ratios  
433 reported by Carpenter et al. (2014).<sup>a</sup> -Values for CH<sub>3</sub>Cl and CH<sub>3</sub>Br represent mean and range for 2012 based on  
434 flask measurements by the US National Oceanic and Atmospheric Administration (NOAA)  
435 (<http://www.esrl.noaa.gov/gmd/dv/site/>) and in situ measurements by the Advanced Global Atmospheric Gases  
436 Experiment (AGAGE) (<http://agage.eas.gatech.edu/>), which were performed at ground stations, not in all cases  
437 representing the MBL. \*Related CH<sub>3</sub>Cl measurement excludes one sample at TMRX-ET-1 (see Sect. 2.1.2).  
438 \*\*Related measurements exclude one measurement sample for all VHOCs (see Sect. 2.1.2).

440 Table 2 presents the measured fluxes of all VHOCs studied, alongside the corresponding  
441 statistical significance for a specific species' emission or depletion to a specific site. Note that  
442 considering the similar characteristics of the two SD sites, and of the two BARE sites, we  
443 assumed a common emission source from the two sites, in both cases, in evaluating the  
444 statistical significance for these sites being a net source or net sink for the studied species.  
445 Considering the small number of measurements at each site, the table classifies the statistical  
446 significance of the fluxes' negative or positive values at a specific site into four different  
447 categories. While  $p$ -values  $< -0.05$  are used here to indicate statistical significance,  $p$ -values of  
448  $< 0.1$  and  $< 0.15$  are also indicated when present.

449 Figure 3 presents the measured fluxes of all VHOCs studied, individually for statistically  
450 significant and non-significant fluxes emitted or depleted to a specific site. Non-significant  
451 fluxes are marked with black and gray for  $0.05 < p < 0.1$  and  $p > 0.1$ , respectively. On average,  
452 the net fluxes of all measured species, except C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I, were positive at most of the  
453 investigated sites. It can be seen that for all species, at least one of the six studied areas, could be  
454 classified as a net source, with somewhat less sites being statistically significant a net sources  
455 for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I. Note that as explained above, C<sub>2</sub>HCl<sub>3</sub> was found to be affected by

456 anthropogenic emission, which could explain the relatively less frequent identified emissions for  
457 this species. Figure 3 clearly demonstrates that the COAST sites, and particularly the SD sites,  
458 are associated with the highest number of VHOCS with positive flux. These sites were also  
459 found as a source for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I. Figure 3 does not indicate elevated VHOCS  
460 emissions from the vegetated sites, (WM-KLY and TMRX-ET), compared to the BARE  
461 sites, BARE-MSD and BARE-MSMR.

462 ~~puces are used here to ,puces of and also indicated when present~~The flux magnitudes for  
463 CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> were ~~higher greater~~ than for most reported emissions ~~at-in~~ the MBL ~~((e.g.,~~  
464 ~~CHBr<sub>3</sub>, 25.2–62.88 nmol m<sup>-2</sup> d<sup>-1</sup> for the Mauritanian upwelling (Quack et al., 2007); CH<sub>2</sub>Br<sub>2</sub>,~~  
465 ~~0.14–0.29 nmol m<sup>-2</sup> d<sup>-1</sup> for the New Hampshire coast (Zhou et al., 2008)),~~ but ~~in most cases~~  
466 were smaller than the corresponding average fluxes estimated by Butler et al. (2007) for global  
467 coastal areas (~~~220 and 110 nmol m<sup>-2</sup> d<sup>-1</sup>~~), respectively) ~~and from than the average flux from~~  
468 ~~the New Hampshire coast as reported by Zhou et al. (2005) (~620 ± 1370 nmol m<sup>-2</sup> d<sup>-1</sup> and~~  
469 ~~113 ± 130 nmol m<sup>-2</sup> d<sup>-1</sup>, respectively).~~ ~~In some cases, however, the fluxes of both species~~  
470 ~~were higher than these values.~~

471 Relatively high positive CHCl<sub>3</sub> fluxes were measured for ~~CHCl<sub>3</sub> emission rates were~~  
472 ~~positive for most measurements and particularly high for including~~ BARE-MSMR (247 nmol  
473 m<sup>-2</sup> d<sup>-1</sup>), TMRX-ET-2 (213 nmol m<sup>-2</sup> d<sup>-1</sup>) and for ~~COAST-EGD-SD-s (883 nmol m<sup>-2</sup> d<sup>-1</sup>),~~  
474 ~~and although the two latter two sites were not identified as a net source for CHCl<sub>3</sub> (Table 2).~~  
475 BARE-MSMR-1 (247 nmol m<sup>-2</sup> d<sup>-1</sup>) (see Yi et al., 2018). For comparison, the emission from  
476 BARE-MSMR-1 ~~is was~~ similar to the maximum emission found for tundra peat by Rhew et al.  
477 (2008), ~~while whereas~~ the averaged emissions from COAST-EGD-SD-s and TMRX-ET-2 ~~are~~  
478 ~~were~~ higher than those from temperate peatlands (~~~496 nmol m<sup>-2</sup> d<sup>-1</sup>~~ as measured by Dimmer  
479 et al. (2001)). Whereas emissions ~~during for~~ COAST-EGD-SD-s and TMRX-ET-2 might have  
480 been affected by ~~vegetation-seawater~~ and ~~vegetation-seawater~~, respectively, the emission ~~from~~  
481 for BARE-MSMR can be completely attributed to soil. The latter emission flux in

482 BARE-MSMR ~~is was~~ higher than the maximum emission rate in arctic and subarctic soils  
483 ( $\sim 115 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) reported by Albers et al. (2017).

484 ~~Average calculated fluxes for the a~~All investigated site types, except offor the natural  
485 vegetation (TMRX-ET), were identified as net sources for ~~additional brominated VSLs,~~  
486 ~~CHBr<sub>2</sub>Cl<sub>7</sub> and CHBrCl<sub>2</sub> were positive for all sites except for CHBr<sub>2</sub>Cl at COAST-TKM (Fig.~~  
487 3). The mixing ratios of CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub> were higher by factors of  $\sim 4$ – $14$  and  $\sim 5$ – $11$ ,  
488 respectively, than the average reported values for the MBL<sub>2</sub> and were also higher than the  
489 ~~measured~~ mixing ratios measured in nearby coastal areas, except for the extremely high  
490 CHBr<sub>2</sub>Cl mixing ratios attributed to emittedssion from a rock pool at Gran Canaria (ranging  
491 from 19 to 130 ppt; (Ekdahl et al., 1998)). For example, Brinckmann et al. (2012) found mean  
492 mixing ratios for CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub> in coastal areas at of the Sylt Islands (North Sea) of up  
493 to 0.2 and 0.1 ppt, respectively, while Nadzir et al. (2014) found CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub> mixing  
494 ratios of 0.07–0.15 ppt and 0.15–0.22 ppt, respectively, in the tropics. The measured CHBr<sub>2</sub>Cl  
495 fluxes ~~that we obtained~~ for CHBr<sub>2</sub>Cl at the Dead Sea ~~are were~~ also higher than the reported  
496 values of 0.8 (range; -1.2–10.8)  $\text{nmol m}^{-2} \text{ d}^{-1}$  at coastal areas sampled during the Gulf of  
497 Mexico and East Coast Carbon cruise (GOMECC), (Liu et al., 2011). Typically, the net  
498 CHBrCl<sub>2</sub> net-flux at the Dead Sea ~~is was~~ significantly higher than corresponding fluxes from  
499 arctic and subarctic soils, as recently reported by Albers et al. (2017), ranging from ~~(see Fig.~~  
500 2)0.03–5.27 nmol m<sup>-2</sup> d<sup>-1</sup>.

501 COAST-TKM and COAST-EGD-SD were found asto be the only net source sites for  
502 CH<sub>3</sub>Cl~~The CH<sub>3</sub>Cl flux at the Dead Sea was positive for only half of the measurements, while a~~  
503 ~~net positive flux for all measurements was obtained only at COAST-TKM.~~ The highest positive  
504 fluxes were measured at COAST-EGD-SD and COAST-TKM-SD, with maximum net fluxes  
505 of  $\sim 10,800$  and  $4900 \text{ nmol m}^{-2} \text{ d}^{-1}$ , respectively. These fluxes are comparable in magnitude to  
506 those reported for several terrestrial sources, such as tropical forests ( $\sim 4520 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) by  
507 Gebhardt et al. (2008) or by Yokouchi et al. (2002), and for other tropical or subtropical



508 vegetation (Yokouchi et al., 2007), and they are higher than emissions from dryland ecosystems,  
509 including shortgrass steppe or shrublands (Rhew et al., 2001). In some cases, the measured  
510 fluxes were higher than average emissions from salt marshes (e.g.,  $\sim 7300 \text{ nmol m}^{-2} \text{ d}^{-1}$ ;  
511 (Deventer et al., 2018)), but significantly smaller than the maximum fluxes from salt marshes  
512 (e.g.,  $570,000 \text{ nmol m}^{-2} \text{ d}^{-1}$ ; (Rhew et al., 2000)).

513 Both COAST-TKM and COAST-EGD sites were identified as net sources, and with less  
514 statistical significance ( $p < 0.1$ ) also BARE-MSMR, for  $\text{CH}_3\text{Br}$  (Table 2). In contrast to  $\text{CH}_3\text{Cl}$ ,  
515 emissions of  $\text{CH}_3\text{Br}$  at the Dead Sea were significantly lower than the average reported  
516 emissions from marshes (e.g.,  $\sim 600 \text{ nmol m}^{-2} \text{ d}^{-1}$ ; (Deventer et al., 2018)). The fluxes  
517 measured at the Dead Sea were also lower than the reported emission from a coastal beach in a  
518 Japanese archipelago island ( $\sim 53,000 \text{ nmol m}^{-2} \text{ d}^{-1}$ ), but higher, in most cases, than in other  
519 dryland ecosystems (see Rhew et al. (2001)).

520 ~~The net flux of  $\text{CH}_3\text{I}$  measured at the Dead Sea was negative in 60 % of the~~  
521 ~~measurements~~ Similar to  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , for  $\text{CH}_3\text{I}$ , COAST-TKM and COAST-EGD, and  
522 particularly the SD sites, were identified as net sources (Table 2). BARE-MSMR was also  
523 identified as a net source for  $\text{CH}_3\text{I}$ . Positive measured net fluxes of this compound were in most  
524 cases comparable to other reported fluxes over soil and vegetation. For example, Sive et al.  
525 (2007) reported a  $\text{CH}_3\text{I}$  flux of  $\sim 18.7 \text{ nmol m}^{-2} \text{ d}^{-1}$  over soil and vegetation at TF, and a  
526 somewhat lower emission ( $\sim 12.6 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) in Duke Forest, NC, USA. While the elevated  
527 flux during at COAST-EGD-SD-s ( $17.0 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) could potentially have been affected by  
528 flow of the sampled air over the seawater, the positive net fluxes in at BARE-MSMR (1.00 and  
529  $4.42 \text{ nmol m}^{-2} \text{ d}^{-1}$ ) indicate significant emission from bare soil at the Dead Sea. The emission  
530 rates positive fluxes that were measured in at BARE-MSMR are were similar to the measured  
531 soil-emission fluxes of  $\text{CH}_3\text{I}$  reported by Sive et al. (2007) at Duke Forest, averaging  $\sim 0.27$   
532  $\text{nmol m}^{-2} \text{ d}^{-1}$  (range,  $\sim 0.11\text{--}4.1 \text{ nmol m}^{-2} \text{ d}^{-1}$ ).

533 ~~Most of the sites were~~ Only COAST–EGD and COAST-TKM-SD sites were found, on  
534 average, to be a sink to be statistically significant sources ( $p < 0.05$ , see Table 2) being a source  
535 for  $C_2HCl_3$ , which may suggesting that the elevated mixing ratios for this species in the Dead  
536 Sea area ~~mostly~~ results mostly from local anthropogenic emissions. ~~–This possibility is~~  
537 supported by the high correlations with  $C_2Cl_4$  (Table S5). –or emission from a more distant  
538 natural source such as the Mediterranean or Red Sea. The former possibility is supported by high  
539 correlation with  $C_2Cl_4$  (Sect. S4). Emissions from a more distant natural source, such as the  
540 Mediterranean– Sea or Red Sea, are unlikely given their large distance away (~1690 km and  
541 ~91600 km, respectively).  
542 Considering, however, the large distance of the Red Sea (~160km) and the Mediterranean Sea  
543 (~90km) from the Dead Sea, it is unlikely that emission from these sources lead to significant  
544 sink of  $C_2HCl_3$  or any other VHOc at the Dead Sea.

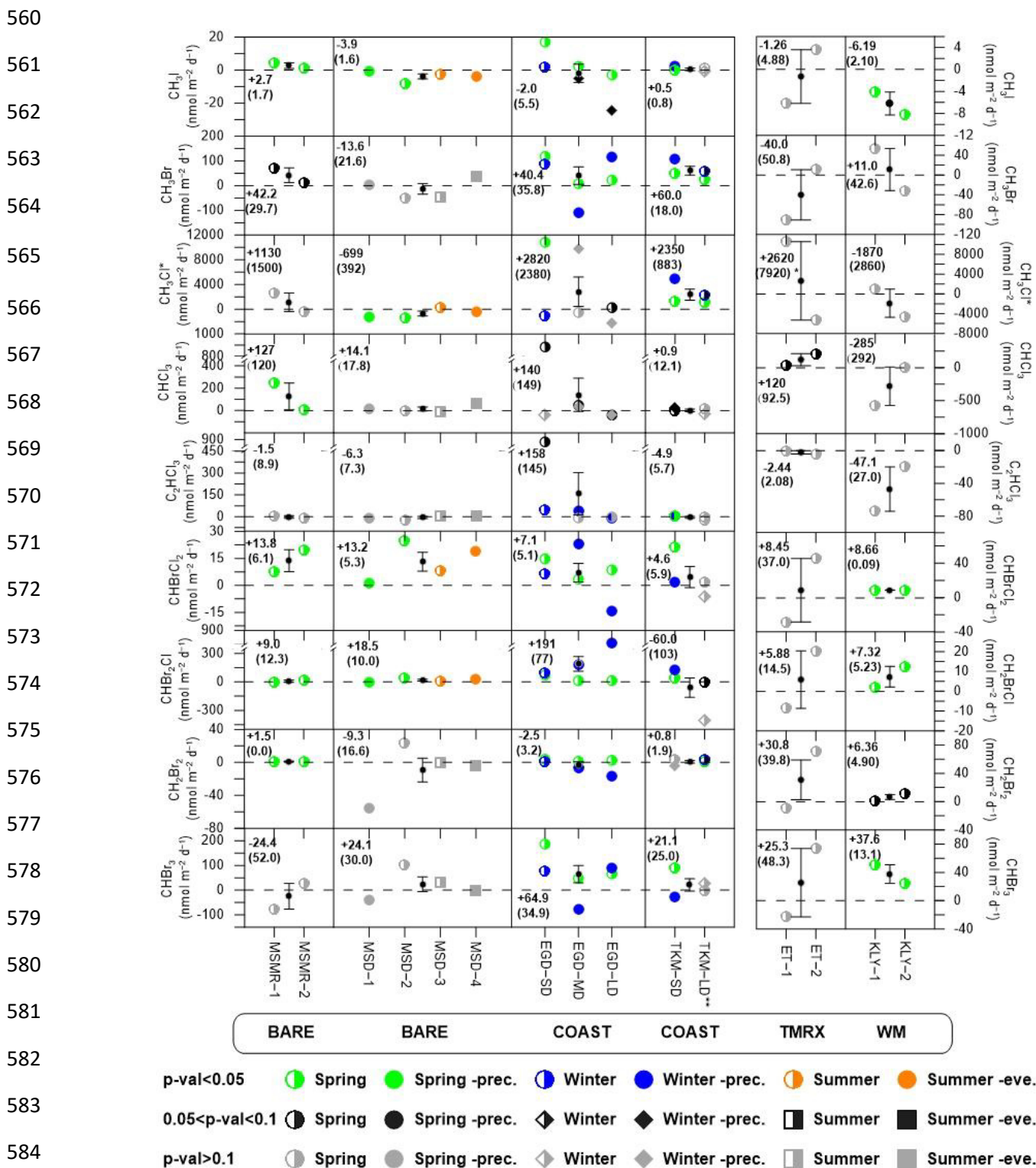
545 **Table 42.** VHOC fluxes for the different measurement sites and its correspondence with mixing ratios. Shown are  
546 the measured flux ( $\text{nmol m}^{-2} \text{d}^{-1}$ ); obtained for the different measurements. Values in bold and in parentheses  
547 indicate that the related measurement site is a significant ( $p < 0.05$ ) or non-significant ( $p > 0.15$ ) net source or sink  
548 for the specific VHOC based on one-sample t-test. Additional categories are defined below. These calculations  
549 assume COAST-EGD-SD and COAST-TKM-SD as the same source (see Section 2.1.2). Also shown are the  
550 average flux (mean) and average positive flux (mean positive) for all species, as well as the percentage of incidence  
551 of positive flux (X) out of total measured fluxes, individually for each site and each VHOC (See Table 1 for  
552 abbreviations of the different measurement sites). All presented values, including mean, mean positive and X  
553 include only fluxes associated with  $p < 0.05$  (bolded; S) and values associated with  $p \geq 0.05$  (presented in  
554 parentheses; NS), based on one-sample t-test.

Species	CH <sub>2</sub> Br <sub>2</sub>	CHBr <sub>3</sub>	CHBr <sub>2</sub> Cl	CHBrCl <sub>2</sub>	CHCl <sub>3</sub>	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>3</sub> Cl	CH <sub>3</sub> Br	CH <sub>3</sub> I	X (%)	
BARE-MSMR-1	<b>1.43</b>	(-76.5)	<b>-3.27</b>	<b>7.68</b>	<b>247</b>	(7.33)	(2629)	<b>71.9<sup>b9a</sup></b>	<b>4.42</b>	<b>33</b> (78)	
BARE-MSMR-2	<b>1.51</b>	(27.6)	<b>21.3</b>	<b>19.9</b>	<b>6.51</b>	(-10.4)	(-378)	<b>12.6<sup>b6a</sup></b>	<b>1.00</b>	<b>44</b> (78)	
BARE-MSD-1	(-55.4)	(-37.7)	<b>-3.58</b>	<b>1.32</b>	(12.1)	<b>-11.0<sup>e0b</sup></b>	<b>-1266</b>	(5.26)	<b>-0.73</b>	<b>11</b> (33)	
BARE-MSD-2	(23.5)	(103)	<b>41.8</b>	<b>24.5</b>	(-6.02)	<b>-24.8<sup>e8b</sup></b>	<b>-1368</b>	(-50.3)	<b>-8.14</b>	<b>22</b> (44)	
BARE-MSD-3	(-0.60)	(32)	<b>8.69</b>	<b>7.92</b>	(-14.6)	<b>4.32<sup>e32b</sup></b>	<b>311</b>	(-47.9)	<b>-2.95</b>	<b>22</b> (56)	
BARE-MSD-4	(-4.61)	(-1.41)	<b>26.96</b>	<b>19.1</b>	(64.7)	<b>6.39<sup>e39b</sup></b>	<b>-472</b>	(38.44)	<b>-3.58</b>	<b>22</b> (56)	
COAST-EGD-SD-w	<b>0.85</b>	<b>78.1</b>	<b>90.0</b>	<b>6.63</b>	(-42.8)	<b>47.3</b>	<b>-1040</b>	<b>88.4</b>	<b>1.45</b>	<b>78</b> (78)	
COAST-EGD-MD-w	<b>-6.53</b>	<b>-79.0</b>	<b>187</b>	<b>23.1</b>	(38.5)	<b>37.5</b>	(9719)	<b>-111</b>	<b>-5.46<sup>b16a</sup></b>	<b>33</b> (56)	
COAST-EGD-LD-w	<b>-16.7</b>	<b>88.7</b>	<b>768</b>	<b>-14.2</b>	(-43.7)	<b>-8.97</b>	(-2281)	<b>116</b>	<b>-24.5<sup>b5a</sup></b>	<b>33</b> (33)	
COAST-EGD-SD-s	<b>3.71</b>	<b>187</b>	<b>72.3</b>	<b>14.8</b>	883 <sup>b</sup>	<b>884<sup>b884a</sup></b>	<b>10817</b>	<b>118</b>	<b>17.0</b>	<b>78</b> (100)	
COAST-EGD-MD-s	<b>1.35</b>	<b>48.6</b>	<b>13.4</b>	<b>3.42</b>	<b>46.4<sup>b4a</sup></b>	<b>-8.39<sup>e39b</sup></b>	(-530)	<b>8.10</b>	<b>2.27</b>	<b>67</b> (78)	
COAST-EGD-LD-s	<b>2.52</b>	<b>66.0</b>	<b>13.8</b>	<b>8.68</b>	<b>-40.8<sup>b8a</sup></b>	<b>-2.03<sup>e03b</sup></b>	<b>261<sup>b261a</sup></b>	<b>22.3</b>	<b>-2.96</b>	<b>56</b> (67)	
COAST-TKM-SD-w	<b>-4.45<sup>e15b</sup></b>	<b>-28.1</b>	<b>123</b>	<b>1.62</b>	<b>22.8<sup>b8a</sup></b>	<b>0.89</b>	<b>4895</b>	<b>110</b>	<b>2.42</b>	<b>67</b> (78)	
COAST-TKM-LD-w	<b>2.95</b>	(28.5)	(-408)	(-6.2)	(-32.9)	<b>-22.0<sup>e0b</sup></b>	<b>2200</b>	<b>57.3</b>	(-1.03)	<b>33</b> (44)	
COAST-TKM-SD-s	<b>3.80<sup>e80b</sup></b>	<b>87.7</b>	<b>42.7</b>	<b>21.4</b>	<b>0.99<sup>b99a</sup></b>	<b>2.00</b>	<b>1210</b>	<b>49.3</b>	<b>-0.38</b>	<b>67</b> (89)	
COAST-TKM-LD-s*	<b>0.56</b>	(-3.83)	<b>2.07<sup>b07a</sup></b>	(1.67)	(12.6)	<b>-0.34<sup>e31b</sup></b>	<b>1100</b>	<b>23.6</b>	(0.97)	<b>33</b> (78)	
TMRX-ET-1**	(-8.93)	(-23.0)	(-8.64)	(-28.5)	<b>27.6<sup>b6a</sup></b>	<b>-0.36<sup>e36b</sup></b>	(10500*)	(-90.8)	(-6.14)	<b>0</b> (11)	
TMRX-ET-2	(70.6)	(73.7)	(20.4)	(45.4)	<b>213<sup>b213a</sup></b>	<b>-4.53<sup>e53b</sup></b>	(-5300)	(10.9)	(3.61)	<b>0</b> (78)	
WM-KLY-1	<b>1.45<sup>b45a</sup></b>	<b>50.7</b>	<b>2.09</b>	<b>8.57</b>	(-577)	<b>-74.4<sup>e1b</sup></b>	(983)	(53.5)	<b>-4.01</b>	<b>33</b> (56)	
WM-KLY-2	<b>11.3<sup>b3a</sup></b>	<b>24.5</b>	<b>12.6</b>	<b>8.76</b>	(6.31)	<b>-20.0<sup>e0b</sup></b>	(-4730)	(-31.6)	<b>-8.29</b>	<b>33</b> (67)	
Mean	S NS	<b>-0.84</b> (1.43)	<b>52.4</b> (32.3)	<b>88.5</b> (51.1)	<b>10.2</b> (8.78)	<b>70.9</b> (41.2)	<b>-2.2</b> (40.1)	<b>1640</b> (1360)	<b>48.2</b> (22.7)	<b>-2.75</b> (-1.74)	
Mean positive	S NS	<b>1.86</b> (9.66)	<b>78.9</b> (68.9)	<b>102</b> (90.4)	<b>11.8</b> (13.2)	<b>127</b> (122)	<b>21.9</b> (124)	<b>3400</b> (4060)	<b>65.9</b> (52.4)	<b>6.17</b> (4.14)	
X (%)	S NS	<b>40</b> (65)	<b>40</b> (65)	<b>70</b> (80)	<b>75</b> (85)	<b>10</b> (65)	<b>20</b> (40)	<b>30</b> (55)	<b>45</b> (75)	<b>20</b> (40)	

555 <sup>a</sup>  $0.05 < p < 0.1$  for a measurement site as net source or sink for a specific species.  
 556 <sup>b</sup>  $0.1 < p < 0.15$  for a measurement site as net source or sink for a specific species; S and NS indicate  $p < 0.05$  and  
 557  $p > 0.05$ , respectively.

558 \* Flux calculation excludes one measurement for all VHOCs (see Sect. 2.1.2).

559 \*\* Flux calculation excludes one  $\text{CH}_2\text{Cl}$  sample (see Sect. 2.1.2).



585 **Figure 3.** ~~VHOCs fluxes at the different measurement sites. Fluxes associated with  $p$ -values  $< 0.05$  are marked by~~  
586 ~~colored circles to indicate measurements during spring, winter, and summer, with full-colored circles indicating~~  
587 ~~measurements up to 3 days after a rain event in spring (Spring-prec.), up to 6 days after a rain event in winter~~  
588 ~~(Winter-prec.) and in the evening in summer (Summer-eve). Gray and black shapes indicate fluxes associated with~~  
589 ~~no clear statistical significance ( $p > 0.1$  and  $0.05 < p < 0.1$ , respectively). At the center of each graph, the small~~  
590 ~~black circles and error bars represent the average and standard error of the mean (SEM), respectively, for each~~  
591 ~~measurement site. Dashed lines represent zero flux. In each box, the numbers indicate the mean flux and SEM (in~~  
592 ~~parentheses) for each site and species. Additional information is provided about measurement conditions (Tables 1,~~  
593 ~~and S6), measurement abbreviations (Table 1) and statistical analysis (Table 2). \*Calculation of  $\text{CH}_3\text{Cl}$  flux mean~~  
594 ~~and SEM excludes one sample at TMRX-ET-1 (see Sect. 2.1.2). \*\*Calculation of mean flux and SEM excludes~~  
595 ~~one sampling canister at COAST-TKM-LD (see Sect. 2.1.2).~~

596 ~~**23. VHOCs fluxes at the different measurement sites.** Fluxes are marked by circles to individually indicate~~  
597 ~~measurements during spring, winter, summer, up to 3 days after a rain event in spring ("Spring-prec."), up to 6 days~~  
598 ~~after a rain event in winter ("Winter-prec.") and in summer during evening ("Summer-eve"); for more information~~  
599 ~~about measurement conditions see Table 1. Black filled circles and error bars respectively represent the average and~~  
600 ~~standard error of the mean (SEM) for each measurement site. Dashed lines represent zero flux. Mean flux value and~~  
601 ~~standard deviation (SD; in parenthesis) are shown for each site and species. See Table 1 for measurement sites and~~  
602 ~~measurement abbreviations. \* Calculation of mean flux and SD excludes one  $\text{CH}_3\text{Cl}$  measurement in TMRX-ET-1~~  
603 ~~(see Sect. 2.1.2).~~

604

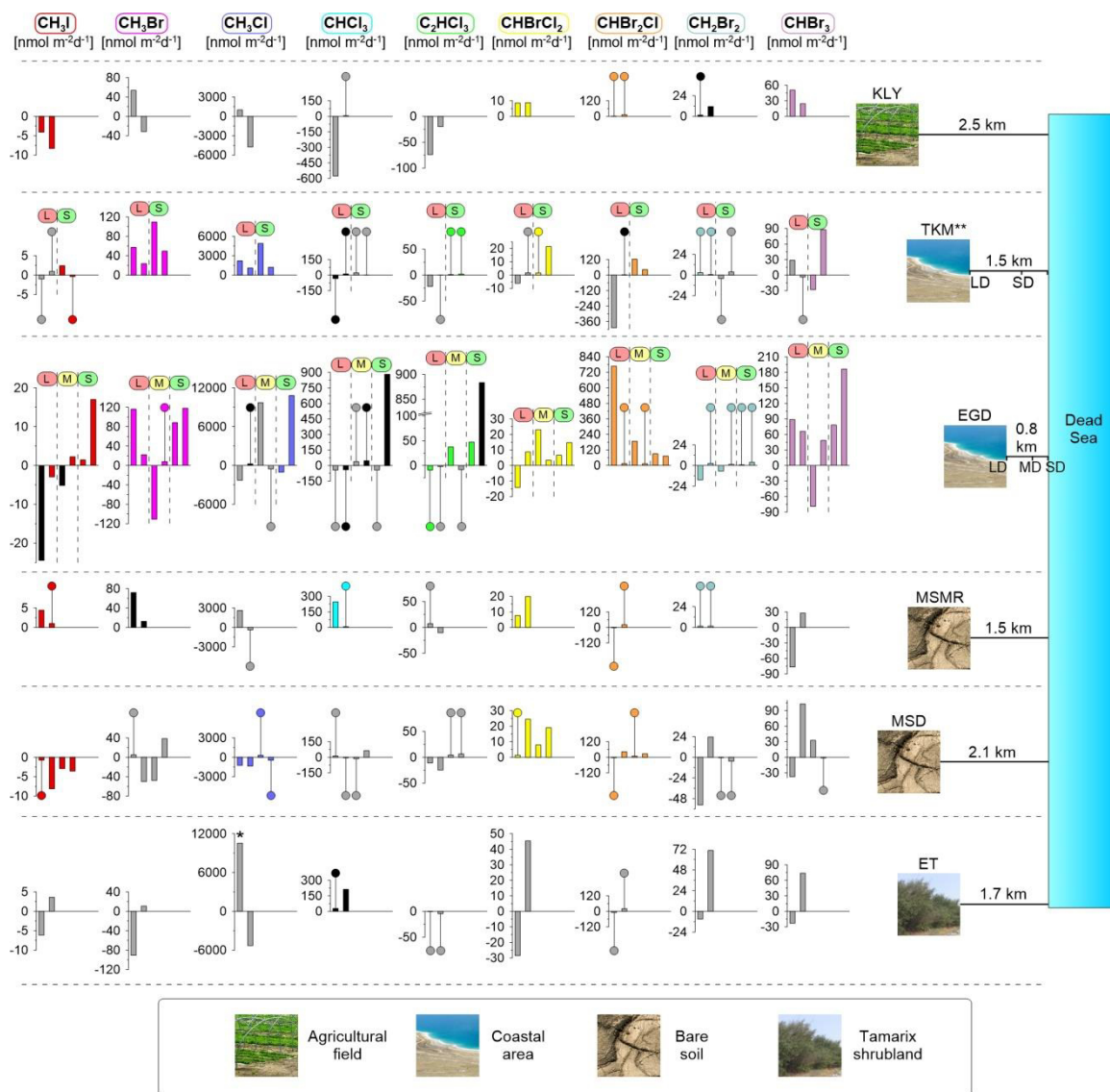
## 605 **3.2 Factors controlling the VHOC flux of VHOCs**

### 606 **3.2.1 Seasonal, meteorological and spatial effects**

607 The results presented in Sect. 3.1 ~~record showed~~ elevated mixing ratios and net fluxes for all  
608 investigated VHOCs, with relatively less frequent positive fluxes for  $\text{CH}_3\text{I}$ ,  $\text{CHCl}_3$  and  $\text{C}_2\text{HCl}_3$ .  
609 ~~For All~~ of the investigated VHOCs, ~~a except  $\text{C}_2\text{HCl}_3$  were associated with a positive flux was~~  
610 ~~measured positive average net flux from~~ for at least one of the two bare soil sites,  
611 BARE-MSMR and BARE-MSD, ~~which are located a few kilometers from the Dead Sea water.~~  
612 ~~For several VHOCs ( $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$  and  $\text{CHCl}_3$ ), at least one of these sites was~~  
613 ~~identified as a significant net source ( $p < 0.05$ , (Fig. 2 Table 2)). Additional measurements are~~  
614 ~~required to determine whether the other VHOCs are also emitted from these bare soil sites. Note~~

615 ~~that~~ and for all VHOCS, except C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>Cl, ~~all~~ measured mixing ratios were highest  
616 over at least one of these bare soil sites (Table S32). ~~These findings suggest that a significant~~  
617 ~~emission for all of the investigated VHOCS occurred from bare soil located within at least a few~~  
618 ~~kilometers from the Dead Sea water.~~ Figure 4 further provides the spatial distribution of the  
619 investigated VHOCS at the various sites. Elevated positive fluxes are seen at the coastal sites,  
620 with a general tendency toward higher positive net fluxes closer to the seashore. Figure 4 also  
621 demonstrates relatively high positive fluxes for the natural vegetation in TMRX—ET, higher  
622 than for WM—KLY. However, additional measurements are required to decipher whether this  
623 site can be classified as a statistically significant source for VHOCS (see Table 2).

624 No clear impact of meteorological conditions on the measured net flux rates or mixing ratios  
625 was observed. We could not identify any clear association between flux magnitude and any  
626 parameter, including solar radiation intensity, measurement time, temperature, and daytime  
627 relative humidity.



628

629 **Figure 4.** Bar graphs of VHOc fluxes from the different site types, organized by relative orientation to the Dead  
 630 Sea and with visual indicators of surface cover type. Colored bars represent measured fluxes associated with  $p$ -  
 631 values  $< 0.05$ . Gray and black bars indicate fluxes associated with no clear statistical significance (black for  $0.05 < p$   
 632  $< 0.1$  and gray for  $p > 0.1$ ). Circles with drop lines are used to mark fluxes with relatively low values. Different  
 633 colors refer to different VHOcs as indicated at the top of the figure. The different site types are indicated in the  
 634 legend. S, M and L indicate short, medium and long distance of the measurement site from the seawater for the  
 635 coastal sites (SD, MD and LD, respectively; see Sect. 2.1.1). See Table 1 for measurement sites and measurement  
 636 abbreviations. \*-CH<sub>3</sub>Cl flux calculation excludes one sample in TMRX-ET-1 (see Sect. 2.1.2). \*\*-\*Flux calculation  
 637 excludes one sampling canister in COAST-TKM-LD (see Sect. 2.1.2).  
 638 Bar graphs of VHOc fluxes from the different site types, organized by relative orientation to the Dead Sea  
 639 and with visual indicators of surface cover type.

640 Our findings on the effects of season and distance from the sea on the measured fluxes are  
641 presented in Fig. 23, which shows the measured fluxes for spring and winter and for different  
642 distances from the sea at COAST-EGD and COAST-TKM. Differences in VHOCs emissions  
643 between winter and spring may arise from the generally much higher temperature, and lower  
644 precipitation during the latter; further considering the high evaporation rate in this area, the soil  
645 water content is expected to be generally lower in spring compared to winter (Sect. 2.1.1; see  
646 also Table S6). Figure 3- suggests that there were no clear differences in VHOC fluxes between  
647 spring and winter, as supported by statistical analysis, except for CH<sub>3</sub>I and CH<sub>2</sub>Br<sub>2</sub> for which  
648 fluxes were higher in the spring, with moderate statistical significance ( $0.05 < p < 0.1$ ).~~It can be~~  
649 ~~seen from the figure that whereas for most compounds there were no clear differences in fluxes~~  
650 ~~between spring and winter, the measured fluxes for CH<sub>3</sub>I, CHBrCl<sub>2</sub> and CH<sub>2</sub>Br<sub>2</sub> were generally~~  
651 ~~higher in the spring.~~

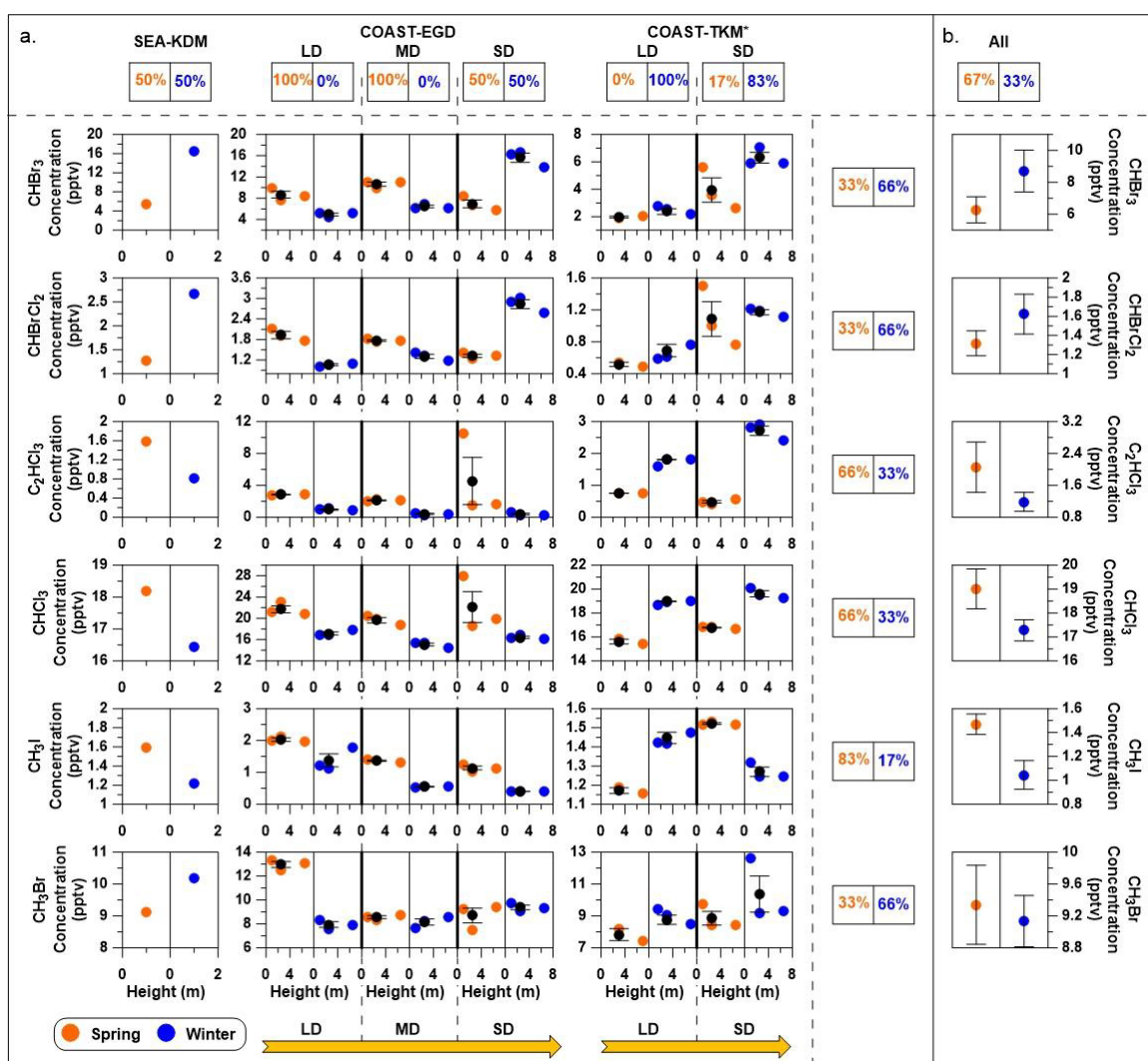
652 -No clear impact of distance from the seawater on the measured net fluxes could be detected,  
653 including in cases where a significant fraction of the footprint included the seawater, such as  
654 ~~during for COAST-TKM-SD-w and, to a lesser extent, during COAST-EGD-SD-w and~~  
655 ~~COAST-EGD-SD-s. However, owing to variations in soil properties, the emissions near the~~  
656 ~~seawater tended to be more frequent and more intense (see Sects. 3.2.2, 3.2.3).~~

657 Figure 3-5 compares the mixing ratios of the measured VHOCs at different distances from  
658 the seawater, individually for winter and spring. Note that differences in sampling heights at  
659 different sites can lead to a biased comparison between mixing ratios at different sites;  
660 nevertheless, in most cases, differences across measurement sites were larger than across  
661 vertical heights. -No clear impact of season or distance from the seawater on the mixing ratios  
662 can be discerned in this figure, also ~~for based on~~ the sampling over SEA-KDM which directly  
663 ~~represents~~ air masses over the seawater (Sect. 2.1.1). Nevertheless, further investigation, using  
664 direct flux measurements over the Dead Sea water, is needed to study the potential emission of  
665 VHOCs from this water body. While no clear impact of season on mixing ratios was observed,



666 for most sites, differences between two measurement sets resulted in consistent differences in  
 667 mixing ratios, such that one measurement set resulted in higher mixing ratios for all or most  
 668 species than the other. This suggests that other factors play a significant role in emission rates of  
 669 all or most VHOCs in the studied area. Only the CH<sub>3</sub>I results indicated moderate statistical  
 670 significance ( $0.05 < p < 0.1$ ) for higher mixing ratios in the spring vs. winter, in agreement with  
 671 seasonal trends for its flux, as discussed above.

672



673 **Figure 35.** Seasonal and spatial influences on measured mixing ratios of VHOCs for coastal sites only. (a)

674 Measured VHOC mixing ratios are presented vs. vertical height above surface level, separately for winter (blue)  
 675 and spring (orange). Black filled circles and error bars represent average and SEM, respectively. LD, MD and SD  
 676 indicate long, medium and short distance from the seawater, respectively, while SEA-KDM is located at the  
 677 seawater (see Sect. 2.1.1). Values above and to the right of the figure indicate the percentages of higher average  
 678 mixing ratios in the (left box) or winter (right box), individually for each site (SEA-KDM, COAST-TKM)

679 ~~and EGD sites) and for each specific species, respectively. (b) For each species-, the average mixing ratios over all~~  
680 ~~sites (SEA\_KDM, COAST\_EGD and COAST\_TKM) are presented (All), and the corresponding percentage of~~  
681 ~~higher average mixing ratios in spring and in winter are also presented. See Table 1 for measurement site~~  
682 ~~abbreviations. Species with no observed difference between seasons were excluded (see Fig. S1 for complete~~  
683 ~~information); y axes for sites in the same coastal area (COAST\_TKM or COAST\_EGD) are evenly scaled.~~  
684 ~~\*Measurements exclude one sampling canister at COAST\_TKM-LD (see Sect. 2.1.2).~~  
685 ~~Seasonal and spatial influences on measured mixing ratios of VHOCs for coastal sites only.~~ Measured VHOC  
686 mixing ratios are presented vs. vertical height above surface level, separately for winter (blue) and spring (orange).  
687 Black filled circles and error bars represent the average and SEM, respectively. Values above and to the right of the  
688 figure indicate the percentage of time during which average mixing ratios were higher during spring (left box) or  
689 during winter (right box), individually for TKM, EGD and SEA\_KDM sites, and for all of these sites together  
690 (All), for all sites and all species, respectively (see Table 1 for measurement site abbreviations).

691

### 692 **3.2.2 Impact of specific site characteristics and ambient conditions**

693 The formation of VHOCs requires a chemical interaction between [OM](#) and halides, induced by  
694 biogeochemical, biochemical, or macrobiotic processes (Kotte et al., 2012; Breider and Albers,  
695 2015). Despite the extreme salinity, biotic activity was detected in [both](#) the water and the soil of  
696 the Dead Sea (see Sect. 1), demonstrating that biotic activity can potentially contribute to  
697 VHOC emission in this area. Previous studies on emission of VHOCs from soil and sediments  
698 revealed that [OM](#) content and type, halide ion concentrations, pH, and the presence of an  
699 oxidizing agent (most frequently referred to [as](#) Fe-(III)) also play important roles in the emission  
700 rate of VHOCs (see (Kotte et al., 2012)).

701 Table 3 provides a basic representation of ~~the soil composition parameters~~ [these parameters](#).  
702 [The results presented in Table 3 show](#) ~~The table records~~ substantial enrichment of Cl and Br in  
703 the sites closest to the seawater (COAST\_EGD-SD and COAST\_TKM-SD) and lower  
704 concentrations at ~~larger~~ [greater](#) distances from the seawater. For comparison, both Br and Cl  
705 concentrations [were generally](#) much higher than those reported by Kotte et al. (2012) for various  
706 saline soils and sediments (0.12–0.32 g kg<sup>-1</sup> and 6.1–120 g kg<sup>-1</sup>, respectively), but ~~are~~ lower [for](#)  
707 [Br in at](#) BARE-MSMR and BARE-MSD ~~for Br~~ and [for both Cl and Br at WM-KLY](#) ~~for both~~

708 ~~Cl and Br in WM=KLY~~. No enrichment of I in the soil samples was observed (e.g., see Keppler  
709 et al. (2000);Kotte et al. (2012)). The OM content of the samples ~~is-was~~ generally higher than  
710 would be expected in desert soil. For comparison, forest floors typically contain 1–5-% OM  
711 (Osman, 2013). Detection of VHOC emissions from the soil ~~was-is~~, in some cases, ~~-~~associated  
712 with higher soil OM (e.g., Albers et al., 2017; Keppler et al., 2000) and in some cases with lower  
713 soil OM (e.g., Kotte et al., 2012; Hubber et al., 2009) than ~~that~~ reported here. Table 3 provides  
714 only an ~~lower limit of the total -underestimated value of~~ Fe, rather than Fe-(III), in the samples.  
715 Note, however, that ~~similar~~ soil Fe content ~~similar as to that~~ reported here as a low-limit value  
716 ~~corresponded-corresponds~~ with ~~those associated with~~ the finding of small amounts of VHOCs  
717 emissions, while the emission rates ~~became-become~~ saturated when enrichment with Fe-(III)  
718 ~~was-is~~ relatively minor (Keppler et al., 2000). Saturation at relatively low soil Fe concentrations  
719 was also reported by Huber et al. (2009). Hence, variations in Fe across different sites may  
720 ~~result-play a minor role~~ in ~~different-affecting~~ emission rates.

721 ~~Table 4 merges the mixing ratios, fluxes, and the ratio between flux and corresponding~~  
722 ~~mixing ratio (F:C) during all measurement periods, for all investigated VHOCs. F:C is used to~~  
723 ~~study the potential contribution of each site to the VHOC mixing ratios measured at that site.~~  
724 ~~While the number of samples collected at each site was limited, The number of samplings at~~  
725 ~~each site was limited, but~~ Table 2 ~~and Fig. 4~~ indicates ~~elevated positive fluxes that the fluxes~~  
726 ~~measured at some of the sites were relatively high. Iforn both COAST=TKM and COAST=EGD~~  
727 ~~sites we observed relatively high frequencies of elevated fluxes, particularly from the SD sites,~~  
728 and to some extent also ~~in-at the~~ COAST=EGD-MD, ~~with respect to both statistically significant~~  
729 ~~and non-statistically significant positive fluxes~~. Moreover, for both COAST=EGD and  
730 COAST=TKM, during both spring and winter, the occurrence of positive fluxes was correlated  
731 with proximity to seawater (i.e., COAST=EGD-SD > COAST=EGD-MD > COAST=EGD-LD,  
732 and COAST=TKM-SD > COAST=TKM-LD). ~~2~~ All of these ~~COAST~~ sites contain mixtures of  
733 soil and salt-deposited structures (see Sect. 2.1.1), and Table 3 indicates that soil concentrations

734 of both Br and Cl correlated with proximity to seawater at both COAST-EGD and  
735 COAST-TKM. The concentration of I in the soil showed a similar trend only at the  
736 COAST-TKM sites (see Table 3). ~~This~~ The association between the magnitude and incidence of  
737 the positive net flux ~~magnitude and incidence~~ and ~~the~~ soil halide concentrations points to an  
738 increase in VHOC emission with salinity, even under the hypersaline conditions of the Dead Sea  
739 area. This interpretation is supported by the fact that whereas for COAST-TKM-SD<sub>2</sub> both soil  
740 water and OM content were relatively high, for COAST-EGD-SD<sub>2</sub> no other measured  
741 parameter which could limit the emission of VHOCs, except for the ~~halides~~ soil halide  
742 concentration, was ~~clearly~~ higher than for both COAST-EGD-MD and COAST-EGD-LD  
743 (Table 3). The ~~generally~~ fact that higher emission rates for COAST-TKM tended to be similar  
744 or lower in terms of incidence and magnitude, compared to COAST-EGD ~~than~~ for  
745 COAST-TKM (Table 2) ~~may~~ suggests, in view of the apparently lower Fe content for  
746 COAST-EGD ~~the latter~~ (Table 3), that the emission of VHOCs from these sites ~~was~~ is not  
747 significantly limited by the availability of Fe-(III) in the soil.

748 ~~Our measurements revealed no clear contribution of vegetation to the emission fluxes or the~~  
749 ~~mixing ratios (Fig. 2 and Table 2), but it should be emphasized that our ability to define their~~  
750 ~~role in VHOC emission and uptake in this study was limited. Table 4 indicates relatively high~~  
751 ~~positive net fluxes for several species in one out of the two measurements at each of the~~  
752 ~~vegetated sites TMRX-ET and WM-KLY. Particularly for TMRX-ET 2, emissions were high~~  
753 ~~for all of the investigated VSLS except C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>Cl (Fig. 2, Table 4).~~

754 ~~Whereas during~~ COAST-EGD-SD-s was associated with the all highest incidence of both  
755 statistically significant and non-significant positive fluxes. ~~measured emission fluxes were~~  
756 ~~positive and high,~~ emissions Fluxes at COAST-EGD-SD-w were generally lower and with a  
757 smaller incidence of ~~and were negative for CH<sub>3</sub>Cl~~ positive fluxes ~~and CHCl<sub>3</sub>~~. Based on the wind  
758 direction, in both cases, the sampling footprint included both the seawater and a narrow strip of  
759 bare soil mixed with salty beds (estimated at about 40-60% of the footprint); very close to the

760 seawater. The main notable difference between the two measurement days ~~is~~ was that  
761 precipitation occurred just before the COAST-EGD-SD-w measurement, ~~while~~ whereas there  
762 was no precipitation event for several weeks prior to the COAST-EGD-SD-s measurement  
763 (Table 1). ~~Note that the much higher fluxes during COAST-EGD-SD-s than during~~  
764 ~~COAST-EGD-SD-w did not result in a proportional increase in F:C (e.g., for C<sub>2</sub>HCl<sub>3</sub>), and for~~  
765 ~~some species the F:C for COAST-EGD-SD-s was even lower than for COAST-EGD-SD-w~~  
766 ~~(e.g., for CHBr<sub>3</sub> and CH<sub>3</sub>Br). This decoupling between fluxes and mixing ratios may be~~  
767 ~~attributable to the fact that flux and concentrations can have very different footprints, such that~~  
768 ~~under a widespread rain event the mixing ratios at COAST-EGD-SD might be less directly~~  
769 ~~affected by the local changes in the net fluxes.~~

770 ~~A less widespread and more spatially limited r~~R~~ain events~~ also occurred ~1.5 and ~2.5 days  
771 before BARE-MSD-1 and BARE-MSD-2 measurements, respectively. ~~It is notable~~Note that  
772 the emission fluxes for BARE-MSD-1 ~~are~~ were lower and more negative for most of the  
773 species than those for BARE-MSD-3 or BARE-MSD-4. ~~Also~~In addition, the occurrence of  
774 positive net fluxes tended to ~~increase~~ according to the order BARE-MSD-1 < BARE-MSD-2  
775 < BARE-MSD-3 ~~< BARE-MSD-4~~ (see Table 2). ~~This~~ The analyses for both COAST-EGD  
776 and BARE-MSD ~~suggests~~ that increased soil water content caused by rain events can decrease  
777 the emission rates or enhance soil-uptake rates of certain VHOCs. ~~Furthermore, the local rain~~  
778 ~~event in BARE-MSD may be a major reason for the generally more frequent and higher net~~  
779 ~~fluxes in BARE-MSMR than in BARE-MSD, and the fact that unlike in the case of~~  
780 ~~COAST-EGD-SD measurements, the low flux values for BARE-MSD-1 are accompanied, in~~  
781 ~~most cases, by proportionally low F:C values (Table 4). Interestingly, ~2.5 days after the rain~~  
782 ~~event the measured fluxes at BARE-MSD-2 were higher for all brominated VSLs but negative~~  
783 ~~for all other VHOCs, which may indicate the involvement of microbial activity in the emission~~  
784 ~~processes.~~

785 ~~The~~ A reduction in net flux rates following rain events did not occur for all species, and  
786 ~~there was not clearly consistency consistent, in this aspect,~~ across the ~~two sites~~ BARE-MSD  
787 and COAST-EGD-SD sites. Thus, further research on the effects of rain on the various VHOCs  
788 and ambient conditions is required. Nevertheless, the analyses clearly demonstrate that strong  
789 emission rates do not depend on rain occurrence, in agreement with findings by Kotte et al.  
790 (2012). The lower emission fluxes following the rain event may be attributable to the low  
791 infiltration rate of VHOCs through into the soil, or by to salt dilution and washout, or both.

792 Our measurements suggested elevated contribution of natural vegetation to some of the  
793 investigated VHOCs (Fig. 4), but with no statistical significance for this site being a source of  
794 any of the investigated VHOCs (Table 2). This might reflect the fact that only a few  
795 measurements are available for this site. No clear contribution of the agricultural vegetation to  
796 the emission fluxes was found in this study.

797 **Table 3.** Soil properties, ~~OM,~~ soil water content (SWC), I, Br, Cl and Fe ~~fraction of dry weight fraction and soil~~  
 798 pH. ~~Analyses were performed for a single mixture of samples at each site.~~ See Table 1 for measurement site  
 799 abbreviations.

<u>Site</u>	<u>pH</u>	<u>OM</u> <u>(%)</u>	<u>SWC</u> <u>(%)</u>	<u>I</u> <u>mg kg soil dw<sup>-1</sup></u>	<u>Br</u> <u>µg kg soil dw<sup>-1</sup></u>	<u>Cl</u> <u>µg kg soil dw<sup>-1</sup></u>	<u>Fe</u> <u>mg kg soil dw<sup>-1</sup></u>
<u>BARE=MSMR</u>	<u>7.46</u>	<u>1.96</u>	<u>1.90</u>	<u>2.24</u>	<u>0.007</u>	<u>6.70</u>	<u>≥20800</u>
<u>BARE=MSD</u>	<u>7.41</u>	<u>3.61</u>	<u>3.61</u>	<u>2.79</u>	<u>0.027</u>	<u>41.2</u>	<u>≥7450</u>
<u>COAST=EGD-SD</u>	<u>7.61</u>	<u>2.28</u>	<u>1.79</u>	<u>0.24</u>	<u>1.47</u>	<u>202</u>	<u>≥1120</u>
<u>COAST=EGD-MD</u>	<u>7.93</u>	<u>0.35</u>	<u>0.35</u>	<u>0.57</u>	<u>0.293</u>	<u>37.4</u>	<u>≥3140</u>
<u>COAST=EGD-LD</u>	<u>7.70</u>	<u>3.67</u>	<u>2.58</u>	<u>1.03</u>	<u>0.008</u>	<u>26.1</u>	<u>≥5950</u>
<u>COAST=TKM-SD</u>	<u>7.43</u>	<u>24.1</u>	<u>33.7</u>	<u>3.19</u>	<u>3.93</u>	<u>169</u>	<u>≥12500</u>
<u>COAST=TKM-LD</u>	<u>7.80</u>	<u>3.40</u>	<u>1.64</u>	<u>1.14</u>	<u>0.186</u>	<u>19.5</u>	<u>≥10600</u>
<u>TMRX=ET</u>	<u>7.88</u>	<u>3.14</u>	<u>2.97</u>	<u>2.69</u>	<u>0.474</u>	<u>85.2</u>	<u>≥10100</u>
<u>WM=KLY</u>	<u>7.64</u>	<u>4.10</u>	<u>1.40</u>	<u>1.69</u>	<u>0.013</u>	<u>1.12</u>	<u>≥7680</u>

800  
801  
802

\* Calculation of flux excludes one CH<sub>3</sub>Cl measurement in TMRX=ET 1 (see Sect. 2.1.2).

803

### 804 3.2.3 Factors controlling the flux of specific VHOCS

805

806 Trihalomethanes: ~~In contrast?~~ Differently than previous studies, B brominated VHOCS had The  
 807 results presented in Table 2 show that Table 4 indicates a relatively higher overall incidence of  
 808 positive fluxes measured in brominated than in chlorinated VHOCS (Table 2), except for  
 809 CHCl<sub>3</sub> for which the net flux is positive for 65 % of the measurements. The net flux of the  
 810 brominated trihalomethanes also tends to be higher than the more chlorinated trihalomethanes  
 811 (CHBr<sub>2</sub>Cl > CHBr<sub>3</sub> > CHBrCl<sub>2</sub> > CHCl<sub>3</sub>; see Table 4). The overall average net flux of the  
 812 trihalomethanes decreased according to CHBr<sub>2</sub>Cl > CHCl<sub>3</sub> > CHBr<sub>3</sub> > CHBrCl<sub>2</sub>, while CHCl<sub>3</sub>  
 813 showed the lowest incidence of positive and highest mean positive fluxes among all  
 814 trihalomethanes. When averaging over the positive fluxes only, CHCl<sub>3</sub> exhibits the second

815 ~~highest flux of all investigated VHOCs ( $175 \text{ nmol m}^{-2} \text{ s}^{-1}$ ), suggesting both high emission and~~  
816 ~~their balance to some extent by sinks for this species.~~

817 Natural emission of trihalomethanes from soil has been shown to occur without microbial  
818 activity ~~involvement~~, induced via oxidation of ~~organic matter~~ OM by an electron acceptor such  
819 as Fe(III) (Huber et al., 2009) or via hydrolysis of trihaloacetyl compounds (Albers et al., 2017).  
820 The soils studied by Albers et al. (2017) ~~are in general~~ were significantly richer in OM than the  
821 soils at the Dead Sea, except for COAST-TKM-SD. Hence, the apparently higher emission  
822 from the Dead Sea soil may indicate either a different mechanism leading to the release of  
823 trihalomethanes from the soil or only a weak dependency on availability of soil OM ~~in the soil~~.  
824 The latter ~~possibility~~ explanation may be supported by the fact that Albers et al. (2017) did not  
825 find any correlation between ~~chloroform~~  $\text{CHCl}_3$  emission rate and organic ~~chlorine~~ Cl in the  
826 soil. Furthermore, our study points to higher emission rates and incidence of VHOCs, and  
827 generally also of trihalomethanes, closer to the seawater, and by the association found in the  
828 present study between soil halide content and VHOC flux for (COAST-EGD and  
829 COAST-TKM sites), which suggests higher sensitivity to soil halide content than OM (Sect  
830 3.2.2).

831 While trihalomethane formation via OM oxidation ~~was has been~~ reported to occur more  
832 rapidly at low pH, and specifically at  $\text{pH} \leq \sim 3.5$  (Huber et al., 2009; Ruecker et al., 2014), its  
833 formation via hydrolysis of trihaloacetyl is expected to occur more rapidly at the relatively high  
834 pH of  $\geq 7$  (Hoekstra et al., 1998; Albers et al., 2017). Yet, according to Ruecker et al. (2014), in  
835 hypersaline sediments, the formation of VHOCs via OM oxidation involving Fe(III) can occur  
836 at  $\text{pH} > 8$  for biotic processes. Therefore, given the relatively high pH ( $\sim 7.4$ – $7.9$ ; Table 3) at  
837 these SD sites, as well as the sites, our present findings of BARE and WM-KLY sites, the high  
838 trihalomethane-emission rates from both bare and agricultural field sites support the work by  
839 Albers et al. (2017) concerning the emission of trihalomethanes from the soil following  
840 trihaloacetyl hydrolysis. ~~emission rates from bare and from vegetated soil sites support the~~



841 ~~evidence supplied by Albers et al. (2017) concerning the emission of trihalomethanes from the~~  
842 ~~soil after trihaloacetyl hydrolysis (Table 3).~~

843 ~~\_\_\_\_\_~~ Albers et al. (2017) ~~demonstrated~~ showed that their proposed mechanism supports the  
844 emission of  $\text{CHCl}_3$  and  $\text{CHBrCl}_2$  from soil, and suggested that additional halomethanes with a  
845 higher number of Br atoms can be expected to be emitted via this mechanism, but at much lower  
846 rates. Hence, the higher-elevated net fluxes for  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  at the Dead Sea (Table 2)  
847 could occur either because of the markedly higher composition of different-Br halides in the  
848 Dead Sea soil (see Table 3) or because another mechanism is also playing a role in the emission-  
849 ; note that agriculture could potentially be a source for the emission of  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  for  
850 WM-KLY, but not for the other sites (Sect. 2.1.1). ~~The finding of~~ Hoekstra et al. (1998)  
851 finding that ~~bromine-Br~~ Br enrichment mainly enhances the emission of  $\text{CHBr}_3$  and  $\text{CHBr}_2\text{Cl}$ ,  
852 rather than that of  $\text{CHBrCl}_2$ , supports the former possibility, namely, relatively elevated  
853 emission of  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  due to -higher Br content in the soil. While both Cl and Br soil  
854 contents are relatively high for both COAST SD sites and COAST-EGD-MD, where emission  
855 of brominated trihalomethanes was higher than that of chlorinated trihalomethanes (see Table  
856 42), a remarkably high Br/Cl value (1:43) relative to other sites was found ~~in-at~~ COAST-TKM-  
857 SD. ~~No clearly~~ Table 2 does not indicate a clear difference in the flux magnitude of more  
858 elevated-positive flux of the brominated compared to chlorinated trihalomethanes ~~-was-observed~~  
859 for this site, suggesting that the main reason for the relatively elevated brominated  
860 trihaloethanes at the SD sites and COAST-EGD-MD is the high Br content rather than the  
861 Br/Cl ratio.

862 ~~\_\_\_\_\_~~ The relatively elevated net flux of brominated trihalomethanes from ~~the soil~~ BARE and  
863 ~~vegetated sites~~ WM-KLY indicates that relatively high rates of emission of these species can  
864 also occur from soils that are much less rich in Br than the SD sites and COAST-EGD-MD sites  
865 (see Tables 32, 43). Yet, the emission rates of  $\text{CHBrCl}_2$  at the Dead Sea were generally higher

866 than those observed by Albers et al. (2017), probably reflecting the higher soil chlorine-Cl soil  
867 content at the Dead Sea.

868 Methyl halides: A relatively high incidence of negative fluxes was observed for  
869 Similarly to  $\text{CHCl}_3$ , the methyl halides  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$ , and more statistically  
870 significantly so for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{I}$ , exhibit relatively large differences between their average  
871 overall measured fluxes and the average positive flux, implying high rates of both emission and  
872 deposition, at least for the latter two, in the studied area (Table 2). The average positive flux of  
873  $\text{CH}_3\text{Cl}$  is was the highest of all the VHOCs investigated, indicating strong emission and  
874 deposition for this species at the Dead Sea. Several studies have indicated that soil tends to act  
875 as a sink for  $\text{CH}_3\text{Cl}$  (Rhew et al., 2003). The relatively high positive net fluxes of  $\text{CH}_3\text{Cl}$  and  
876  $\text{CH}_3\text{Br}$  at WM-KLY-1 (983 and 53.5  $\text{nmol m}^{-2} \text{d}^{-1}$ , respectively) may point to emission of this  
877 species from the local vegetation agricultural field, in agreement with previous studies (Sect. 1),  
878 and potentially caused by a microbial- or fungal-induced emission (Moore et al., 2005; Watling  
879 and Harper, 1998), but this should be further investigated considering the lack of statistical  
880 significance.

881 A pPositive net fluxes for  $\text{CH}_3\text{I}$  was observed at least once at each of the vegetated soils, bare  
882 soils, or soils mixed with salt deposit mixtures (Table 4), but the fluxes we observed were not  
883 significantly higher than those obtained in previous studies (Sect. 3.1), a finding that might be  
884 attributable attributed to the small concentrations of I in the soil relative to those of the other  
885 halides. At Duke Forest, Sive et al. (2007) observed a soil-emission  $\text{CH}_3\text{I}$  flux of  $\sim 0.27 \text{ nmol}$   
886  $\text{m}^{-2} \text{d}^{-1}$  on average (ranging from  $\sim 0.11$  to  $0.31 \text{ nmol m}^{-2} \text{d}^{-1}$ ) under precipitation conditions  
887 in June, and higher emission rates ( $0.8$  and  $4.1 \text{ nmol m}^{-2} \text{d}^{-1}$ ) under warmer and dryer  
888 conditions in September. In agreement with those findings, although generally in general our  
889 analyses did not indicate clear seasonal effects, we found that in all cases, the net  $\text{CH}_3\text{I}$  fluxes  
890 were higher in spring than in winter, except for COAST-TKM-SD (Fig. 23). Also, in 83% of  
891 the measurements the  $\text{CH}_3\text{I}$  mixing ratios were higher in spring than in winter As discussed in

892 Sect. 3.2.1, the mixing ratios of CH<sub>3</sub>I also tended to be higher in magnitude in spring compared  
893 to winter, with moderate statistical significance ( $0.05 < p < 0.1$  in both cases)-(Figs. 3, 35).

894 Relatively high fluxes of CH<sub>3</sub>Cl and CH<sub>3</sub>Br, and to a lesser extent of CH<sub>3</sub>I, were observed at  
895 the COAST-TKM and COAST-EGD sites, particularly from the sites closest to the seawater  
896 (Fig. 4). According to Keppler et al. (2000), the presence of Fe(III), OM and halide ions ~~are is~~  
897 basically sufficient to result in emission of methyl halides from both soil and sediments by a  
898 natural abiotic process (Sect. 1). The strong emission of methyl halide from the COAST-TKM  
899 and COAST-EGD sites indicates that these species can be emitted at high rates from saline soil  
900 that is not rich in OM. The strongest emissions occurred from COAST-TKM-SD and,  
901 ~~COAST-EGD-SD and to some extent from COAST-EGD-MD,~~ which may pointin, g to  
902 aindicate high sensitivity of methyl halide emission to soil OM and/or halide content (see Table  
903 3). ~~However, t~~The fact that the emission of methyl halides, particularly CH<sub>3</sub>Br and CH<sub>3</sub>Cl, from  
904 COAST-TKM-SD, where soil OM is substantially higher than at all other investigated sites, is  
905 werewas not higher similar to or lower than the emission from COAST-EGD-SD-s and  
906 ~~COAST-EGD-MD~~may indicate that emission of methyl halides was not sensitive to soil OM in  
907 our study. Note that the lower fluxes for EGD-SD-w compared to EGD-SD-s can be associated  
908 to a prior rain event for the former (Sect. 3.2.2).

909 In controlled experiments to study ~~of~~ emissions of the three methyl halides from soil ~~by~~  
910 ~~controlled experiments~~, Keppler et al. (2000) found a decrease in the efficiency of methyl halide  
911 emission according to CH<sub>3</sub>I > CH<sub>3</sub>Br > CH<sub>3</sub>Cl (10:1.5:1; mole fractions). We estimated the  
912 emission efficiencies of the different methyl halides based on the ratio between their fluxes and  
913 the concentrations of halide in the soil. To maintain consistency with the calculations of Keppler  
914 et al. (2000), our calculation was also based on mole fractions, and took into account only  
915 positive fluxes, on the assumption that they are closer in magnitude to emission. This  
916 corresponded with measured soil halide concentration proportions for Cl:Br:I ~~as of~~  
917 384872.4E5:4451.5E3:1, and the evaluated emission efficiency proportions were

918 ~~57.7~~15:~~1.564~~:1 for CH<sub>3</sub>I, CH<sub>3</sub>Br and CH<sub>3</sub>Cl, respectively, in case that when two outliers were  
919 excluded from the calculations. These calculations ~~verify~~ confirmed ~~an~~ the increasing efficiency  
920 of methyl halide emission ~~such that following~~: CH<sub>3</sub>Cl < CH<sub>3</sub>Br < CH<sub>3</sub>I, in agreement with  
921 Keppler et al. (2000), suggesting. ~~These findings suggest~~ that at least the methylation and  
922 emission of CH<sub>3</sub>Br and CH<sub>3</sub>Cl in our study were controlled by abiotic mechanisms similar to  
923 those reported by Keppler et al. (2000). The apparently higher relative efficiency of CH<sub>3</sub>I  
924 emission may ~~point to indicate~~ emissions of CH<sub>3</sub>I via other mechanisms in the studied area, as  
925 discussed in Sect. 3.3. It should be noted, however, that the fluxes that we based ~~used for the~~  
926 methyl halide emission efficiencies were based on measured net flux rather than measured  
927 emission flux. ~~our calculations on positive flux and not emission flux, This~~ ~~which~~ might also be  
928 ~~a reason for explain~~ the inconsistency between the relative CH<sub>3</sub>I-emission efficiency ~~of CH<sub>3</sub>I~~  
929 calculated by Keppler et al. (2000) and by us.

930 ~~C<sub>2</sub>HCl<sub>3</sub>~~: ~~C<sub>2</sub>HCl<sub>3</sub> is associated with~~ ~~had~~ ~~the second lowest incidence of positive fluxes,~~  
931 with statistically significant ( $p < 0.05$ ) positive fluxes only from the COAST SD sites and  
932 COAST-EGD-MD (Table 2). ~~Only COAST-EGD~~ ~~was found to be, on average, a source for~~  
933 C<sub>2</sub>HCl<sub>3</sub>, ~~mostly derived from strong emissions from COAST-EGD SD (see, e.g., Fig. 2)~~.  
934 COAST-EGD SD is a These sites are mixtures of salt beds and deposits with salty soil and  
935 therefore, the elevated emissions of C<sub>2</sub>HCl<sub>3</sub> at these sites appear to support previous evidence  
936 for the emission of this gas by halobacteria from salt lakes, as reported by Weissflog et al.  
937 (2005). Additional chlorinated VHOCs, including CHCl<sub>3</sub> and CH<sub>3</sub>Cl, also demonstrated  
938 increased emission from this site, in line with the findings of Weissflog et al. (2005). Note that  
939 the net measured fluxes for most of the VHOCs investigated at the COAST-EGD-SD-w site  
940 were smaller than those at COAST-EGD-SD-s, as discussed in Sect. 3.2.2.

941 CH<sub>2</sub>Br<sub>2</sub>: CH<sub>2</sub>Br<sub>2</sub> showed positive fluxes from all site types, with a positive average net  
942 flux from most sites (see Fig. 23), but its fluxes over the vegetated and agricultural sites were  
943 not statistically significant. ~~The highest fluxes were observed over TMRX-ET (TMRX-ET-2)~~

944 ~~and over bare soil (BARE-MSD 2).~~ Correlation of CH<sub>2</sub>Br<sub>2</sub> with trihalomethanes will be  
945 discussed in Sect. 3.3.

946

### 947 3.3 Flux and mixing ratio correlations between VHOCS

948 Table ~~5-4~~ presents the Pearson correlation coefficients (r) between the ~~evaluated-measured~~  
949 mixing ratios of VHOCS at the Dead Sea, separately for all sites and for the terrestrial sites only,  
950 as well as separately for BARE, COAST, and the natural vegetation and agricultural field sites  
951 (VEG). For COAST, r is also presented individually for the two sites which were closest to the  
952 seawater (SD). The correlations' significance levels are also indicated. In most cases, the  
953 correlations between species over ~~the-all~~ terrestrial sites were low (~~r<sup>2</sup> < 0.1~~), but were  
954 substantially higher for the brominated trihalomethanes [~~CHBr<sub>3</sub>-CHBrCl<sub>2</sub> (r<sup>2</sup> = 0.6279),~~  
955 ~~CHBr<sub>2</sub>Cl-CHBrCl<sub>2</sub> (r<sup>2</sup> = 0.7587), and CHBr<sub>2</sub>Cl-CHBr<sub>3</sub> (r<sup>2</sup> = 0.7285)]], supporting a common  
956 source mechanism for these species. High correlations between these three trihalomethanes can  
957 be attributed to high correlations at the BARE and VEG sites. Relatively high correlations ~~\_-~~were  
958 also obtained, although to a lesser extent, between methyl halides, particularly between CH<sub>3</sub>Cl  
959 and CH<sub>3</sub>Br (~~r<sup>2</sup> = 0.575~~), which can be attributed to correlations at the COAST sites,  
960 particularly the SD sites. For COAST, and particularly for SD, a high correlation was observed  
961 between C<sub>2</sub>HCl<sub>3</sub> and CHCl<sub>3</sub>. Correlations were in most cases either similar or smaller; when we  
962 included measurements from the seawater site SEA-KDM, which may reinforce the notion  
963 predominant-that emission from the seawater does not contribute significantly to contribution-of  
964 VHOCS from terrestrial sources mixing ratios in the area of the Dead Sea.~~

965 ~~Table 5 shows relatively high correlations of CHCl<sub>3</sub> with all the methyl halides CH<sub>3</sub>Cl, CH<sub>3</sub>Br~~  
966 ~~and CH<sub>3</sub>I (with r<sup>2</sup> ranging from 0.19 to 0.28), suggesting common emission sources and/or sinks~~  
967 ~~for these species.~~

968 **Table 54.** Correlations between the mixing ratios of VHOCs. Shown is the Pearson correlation coefficient ( $r$ )  
 969 coefficient of determination ( $r^2$ ) between each VHOC pair for the measured mixing ratio, when calculated over all  
 970 sites excluding SEA-KDM (NO-KDM), all sites (ALL), bare soil sites (BARE), coastal sites (COAST), short  
 971 distance from the sea at the coastal sites (SD) and the vegetated sites (VEG). Correlations were calculated for mean  
 972 mixing ratios at each site. The  $p$ -value for  $r$  being significantly different from zero is indicated based on one-  
 973 sample t-test, in four categories: value in bold,  $p < 0.05$ ; value in parentheses,  $p > 0.15$ ; <sup>a</sup> $p < 0.1$ ; <sup>b</sup> $p < 0.15$ .

		CHBrCl <sub>2</sub>	CHBr <sub>3</sub>	CHBr <sub>2</sub> Cl	CHCl <sub>3</sub>	CH <sub>2</sub> Br <sub>2</sub>	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>3</sub> Cl	CH <sub>3</sub> Br
CH <sub>3</sub> I	NO-KDM (n=20)	(-0.23)	(-0.15)	(-0.15)	<b>0.45</b>	(0.12)	(0.17)	(0.31)	0.36
	ALL (n=22)	(-0.23)	(-0.15)	(-0.15)	<b>0.45</b>	(0.10)	(0.16)	(0.31)	<b>0.36<sup>b</sup>0.36<sup>a</sup></b>
	BARE (n = 6)	<b>0.76<sup>e</sup>0.76<sup>b</sup></b>	<b>0.90<sup>b</sup>0.90<sup>a</sup></b>	<b>0.84<sup>b</sup>0.84<sup>a</sup></b>	(0.32)	(-0.12)	(0.18)	(0.38)	(0.34)
COAST (n = 10) <sup>*</sup>	SD (n = 4)	<b>0.78</b>	(0.39)	(0.57)	(0.42)	(0.24)	(0.29)	<b>0.86</b>	(0.55)
	VEG (n = 4)	<b>-0.95</b>	(0.21)	(0.14)	(-0.23)	(-0.06)	(-0.41)	(0.60)	(0.63)
	ALL-NO-KDM	(-0.49)	(-0.45)	(-0.51)	<b>0.86<sup>e</sup>0.86<sup>b</sup></b>	(0.79)	(-0.11)	<b>0.85<sup>e</sup>b</b>	(0.62)
CH <sub>3</sub> Br	ALL	(0.19)	0.37 <sup>b</sup>	(0.26)	<b>0.43</b>	<b>0.52</b>	(0.19)	<b>0.75</b>	
	BARE (n = 6)	(0.18)	0.38 <sup>b</sup>	(0.25)	<b>0.42</b>	<b>0.51</b>	(0.17)	<b>0.75</b>	
	COAST (n = 10) <sup>*</sup>	(0.00)	(0.01)	(-0.05)	(0.49)	<b>0.98</b>	(0.08)	(0.38)	
COAST (n = 10) <sup>*</sup>	SD (n = 4)	(0.22)	(0.60)	(0.46)	(0.54)	(0.32)	(0.39)	<b>0.86</b>	
	VEG (n = 4)	(-0.58)	<b>0.88<sup>b</sup>0.88<sup>a</sup></b>	(0.77)	(0.56)	(0.41)	(0.41)	<b>0.99</b>	
	ALL-NO-KDM	(0.27)	(0.30)	(0.22)	(0.76)	<b>0.93<sup>b</sup>0.93<sup>a</sup></b>	(-0.73)	(0.78)	
CH <sub>3</sub> Cl <sup>a,**</sup>	ALL	(0.04)	(0.21)	(0.13)	<b>0.53</b>	(0.08)	(0.12)		
	BARE (n = 6)	(0.00)	(0.04)	(0.02)	<b>0.28</b>	0.01	0.12		
	COAST (n = 10) <sup>*</sup>	(0.39)	(0.71)	(0.53)	(0.70)	(0.29)	(0.18)		
COAST (n = 10) <sup>*</sup>	SD (n = 4)	(0.39)	(0.50)	(0.45)	(0.36)	(0.21)	(0.29)		
	VEG (n = 4)	(-0.51)	<b>0.94<sup>b</sup>0.91<sup>a</sup></b>	(0.71)	(0.63)	(0.30)	(0.47)		
	ALL-NO-KDM	(-0.39)	(-0.35)	(-0.44)	<b>1.00</b>	<b>0.95</b>	(-0.59)		
C <sub>2</sub> HCl <sub>3</sub>	ALL	(0.11)	(0.18)	(0.16)	(0.26)	(-0.01)			
	BARE (n = 6)	(0.12)	(0.09)	(0.17)	0.27	0.00			
	COAST (n = 10) <sup>*</sup>	(0.78)	(0.56)	(0.75)	(0.63)	(-0.12)			
COAST (n = 10) <sup>*</sup>	SD (n = 4)	(0.39)	(0.50)	(0.38)	<b>0.93</b>	(0.24)			
	VEG (n = 4)	(0.50)	(0.79)	(0.56)	<b>0.98</b>	(0.26)			
	ALL-NO-KDM	(-0.30)	(-0.32)	(-0.25)	(-0.56)	(-0.70)			
CH <sub>2</sub> Br <sub>2</sub>	ALL	(0.06)	(0.23)	(0.12)	(0.17)				
	BARE (n = 6)	(0.07)	(0.20)	(0.12)	(0.17)				
	COAST (n = 10) <sup>*</sup>	(-0.19)	(-0.13)	(-0.24)	(0.32)				
COAST (n = 10) <sup>*</sup>	SD (n = 4)	(0.67)	(0.77)	(0.52)	(0.42)				
	VEG (n = 4)	(-0.18)	(0.41)	<b>0.87<sup>e</sup>0.87<sup>b</sup></b>	(0.26)				
	ALL-NO-KDM	(-0.10)	(-0.06)	(-0.15)	<b>0.95</b>				
CHCl <sub>3</sub>	ALL	0.35 <sup>b</sup>	(0.27)	(0.24)					
	BARE (n = 6)	(0.35)	(0.21)	(0.24)					
	COAST (n = 10) <sup>*</sup>	<b>0.84<sup>b</sup>0.84<sup>a</sup></b>	<b>0.77<sup>b</sup>e</b>	<b>0.84<sup>b</sup>0.84<sup>a</sup></b>					
COAST (n = 10) <sup>*</sup>	SD (n = 4)	(0.51)	(0.59)	(0.57)					
	VEG (n = 4)	(0.34)	<b>0.89<sup>b</sup>0.89<sup>a</sup></b>	(0.63)					
	ALL-NO-KDM	(-0.41)	(-0.38)	(-0.46)					
CHBr <sub>2</sub> Cl	ALL	<b>0.87</b>	<b>0.85</b>						
	BARE (n = 6)	<b>0.87</b>	<b>0.75</b>						
	COAST (n = 10) <sup>*</sup>	<b>0.97</b>	<b>0.90</b>						
COAST (n = 10) <sup>*</sup>	SD (n = 4)	(0.17)	(0.39)						
	VEG (n = 4)	(-0.25)	(0.81)						
	ALL-NO-KDM	<b>1.00</b>	<b>1.00</b>						
CHBr <sub>3</sub>	ALL	<b>0.79</b>							
	BARE (n = 6)	<b>0.69</b>							
	COAST (n = 10) <sup>*</sup>	<b>0.76<sup>e</sup>0.76<sup>b</sup></b>							
COAST (n = 10) <sup>*</sup>	SD (n = 4)	<b>0.78<sup>b</sup>0.78<sup>a</sup></b>							
	VEG (n = 4)	(-0.13)							
	ALL-NO-KDM	(0.76)							

974 <sup>a</sup>Correlations for CH<sub>3</sub>Cl over VEG sites were excluded one CH<sub>3</sub>Cl measurement in TMRX-ET-1 (see Sect. 2.1.2).

975 \* Correlation calculation for COAST-TKM-LD excluded one sampling canister (see Sect. 2.1.2).

976 \*\* Correlation calculation for CH<sub>3</sub>Cl excluded one sample for TMRX-ET-1 (see Sect. 2.1.2).

977 Table 6-5 ~~records shows~~ the correlations between the measured VHOc fluxes, separately for  
978 all sites, ~~bare soil~~ BARE sites, ~~vegetated sites (VEG) sites~~, TMRX-ET sites and WM-KLY  
979 sites, as well as for ~~the sites closer to the seawater, including all~~ COAST-TKM and  
980 COAST-EGD sites. For the ~~two last~~ latter two sites, correlations are also presented separately  
981 for the ~~two SD sites closest to the seawater (COAST-TKM-SD and COAST-EGD-SD)~~. Note  
982 that the table compares net flux rather than emission flux, and therefore the reported correlations  
983 are expected to be affected by both sinks and sources for the different VHOcs.

984 The results in Table 6-5 ~~demonstrates show~~ moderate to high positive correlations in most  
985 cases when all sites are included in the calculation, whereas in ~~general many cases,~~ the  
986 correlations were significantly higher when calculated for sites of the same type, suggesting  
987 common emission mechanisms or controls. ~~In most cases correlations for the vegetated sites~~  
988 ~~were higher than the overall correlations for all sites. The relatively high correlations in the~~  
989 ~~vegetated sites may be in line with previous studies indicating high emissions from vegetation at~~  
990 ~~marsh coasts (Rhew et al., 2002; Deventer et al., 2018), but positive fluxes for methyl halides~~  
991 ~~were obtained only in a few cases at the vegetated sites, and not in all cases for all methyl~~  
992 ~~halides simultaneously. Hence, it appears that the correlations between methyl halides at the~~  
993 ~~vegetated sites are more likely to be attributable to common sinks. The fairly elevated~~  
994 ~~correlations between methyl halide fluxes at the SD sites, together with the fact that, in most~~  
995 ~~cases, fluxes of the three methyl halides from these sites were positive and high, suggests that~~  
996 ~~these sites have a common source or sources for methyl halides.~~

997 High correlations were obtained for VEG ~~for~~ between  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  ( $r \geq$   
998  $0.94$ ;  $p < 0.05$ ), except for the correlation between  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBr}_3$  ( $r = 0.82$ ;  $p > 0.15$ ).  
999 Note that these correlations can potentially be attributed to agricultural emission, considering  
1000 that WM-KLY, but not TMRX-ET, was identified as a statistically significant source for the  
1001 three trihalomethanes. trihalomethanes in the vegetated sites ( $r \geq 0.82$ ), except for  $\text{CHCl}_3$ , whose  
1002 correlations with other trihalomethanes were lower. At the BARE sites, high positive

1003 correlations between the fluxes of the three brominated trihalomethanes were observed which  
1004 were all associated with  $p$ -values  $<0.05$ , except for a lower correlation between  $\text{CHBr}_3$  and  
1005  $\text{CHBrCl}_2$  ( $r = 0.72$ ;  $p < 0.1$ ). Furthermore, high correlations between the mixing ratios of the  
1006 three trihalomethanes were obtained for these two sites, although relatively low statistical  
1007 significance was obtained for the correlation between  $\text{CHBr}_3$  and  $\text{CHBrCl}_2$  at these sites (see  
1008 Table 54). This further supports the notion that the three brominated trihalomethanes can be  
1009 emitted via similar mechanisms or controls. Moderately low  $p$ -values for the correlations  
1010 between  $\text{CH}_2\text{Br}_2$  and both  $\text{CH}_2\text{Br}_2\text{Cl}$  ( $p < -0.15$ ) and  $\text{CHBrCl}_2$  ( $p < 0.1$ ) at these sites further  
1011 suggests common controls for  $\text{CH}_2\text{Br}_2$ , and the brominated trihalomethanes (see Table 5).  
1012 ~~Correlation of  $\text{CHCl}_3$  with the brominated trihalometahanes are generally either insignificant or~~  
1013 ~~negative.~~

1014 ~~We also observed high correlations of  $\text{CH}_2\text{Br}_2$  with all trihalomethanes, particularly for the~~  
1015 ~~vegetated sites ( $r \geq 0.77$ ), and somewhat lower correlations with  $\text{CHCl}_3$  ( $r = 0.55$ ).  $\text{CH}_2\text{Br}_2$  also~~  
1016 ~~showed high correlations with  $\text{CHBrCl}_2$  ( $r = 0.90$ ) and  $\text{CHBr}_3$  ( $r = 0.88$ ) at the SD sites,~~  
1017 ~~suggesting a common emission mechanism for  $\text{CH}_2\text{Br}_2$  and the other trihalomethanes.~~

1018 Correlation of  $\text{CH}_2\text{Br}_2$  with  $\text{CHBr}_2\text{Cl}$  at the SD sites was strongly negative ( $r = -0.93$ ;  $p <$   
1019  $0.1$ ), similar to the negative correlation between  $\text{CHBr}_2\text{Cl}$  and the other brominated  
1020 trihalomethanes,  $\text{CHBrCl}_2$  ( $r = -0.98$ ;  $p < 0.05$ ) and  $\text{CHBr}_3$  ( $r = -0.65$ ;  $p > 0.15$ ), at these sites.  
1021 This, together with the fact that the measured fluxes of these three species were generally  
1022 positive over the SD sites, suggest competitive emission between  $\text{CHBr}_2\text{Cl}$  and ~~both~~  $\text{CHBrCl}_2$   
1023 and potentially also  $\text{CHBr}_3$ , at least at the SD sites. This is supported by the analysis in Sects.  
1024 3.2.2 and 3.2.3, which ~~have~~ demonstrated that the halide content of the soil appears to play a  
1025 major role in controlling the emission rates of VHOCs under the studied conditions. High  
1026 ~~positive correlation between all four brominated species was observed for the bare soil sites as~~  
1027 ~~well as for the vegetated sites (see Table 6), further supporting the notion that  $\text{CHBr}_2\text{Cl}$  too can~~



1028 ~~be emitted via mechanisms similar to those of the other two brominated trihalomethanes and~~  
1029 ~~CH<sub>2</sub>Br<sub>2</sub>.~~

1030 Table ~~6-5~~ also indicates overall low correlations between CHCl<sub>3</sub> and all of the brominated  
1031 trihalomethanes, mostly resulting from negative correlations at the ~~bare soil~~BARE sites. There  
1032 anticorrelation of CHCl<sub>3</sub> with trihalomethanes increased in the order CHBrCl<sub>2</sub> < CHBr<sub>2</sub>Cl <  
1033 CHBr<sub>3</sub>. The incidence of the chlorinated ~~was also a higher incidence of positive fluxes at the~~  
1034 ~~bare soil sites for the~~ trihalomethanes (CHCl<sub>3</sub> and CHBrCl<sub>2</sub>), compared to the less chlorinated,  
1035 ones (CHBr<sub>3</sub> and CHBr<sub>2</sub>Cl) also tended to be higher at the BARE sites compared to the other  
1036 sites (Table 42). Hence, the negative correlation between CHCl<sub>3</sub> and the brominated  
1037 trihalomethanes at the bare soil sites may indicate competitive emission between the more  
1038 chlorinated and ~~the~~ more brominated trihalomethanes. The situation at the ~~bare~~BARE soil sites  
1039 resembles previous reports of ~~the~~ predominant emission of CHCl<sub>3</sub> at the expense of the more  
1040 brominated species (e.g., (Albers et al., 2017; Huber et al., 2009)), particularly CHBr<sub>3</sub> and  
1041 CHBr<sub>2</sub>Cl. ~~This, and was~~ expected, given the higher Cl/Br ratio at these sites (see Table 3). We  
1042 should emphasize that even at the ~~bare soil~~BARE sites, we observed relatively high positive  
1043 fluxes of brominated trihalomethanes, particularly CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub>, which would not  
1044 generally be expected (Albers et al., 2017), and can be attributed to the relatively high bromine  
1045 Br enrichment ~~of in~~ the soil.

1046 Interestingly, in agreement with Table 54, Table ~~6-5~~ also shows relatively high correlations  
1047 between CHCl<sub>3</sub> and all methyl halides, ~~particularly for~~ the BARE sites (CH<sub>3</sub>I, r = 0.68, p <  
1048 0.15; CH<sub>3</sub>Br, r = 0.83, p < 0.05; CH<sub>3</sub>Cl, r < 0.86, p < 0.05), -and (r ≥ 0.68) and at the SD sites  
1049 (CH<sub>3</sub>I, r ≥ = 0.5999, p < 0.05; CH<sub>3</sub>Br, r = 0.59, p > 0.15; CH<sub>3</sub>Cl, r = 0.91, p < 0.1). ~~We also~~  
1050 ~~found high correlations for the SD sites between C<sub>2</sub>HCl<sub>3</sub> and all methyl halides (r ≥ 0.59).~~  
1051 Remarkably, a high correlation was found ~~correlations were obtained between CH<sub>3</sub>I and the~~  
1052 ~~brominated trihalomethanes and CH<sub>2</sub>Br<sub>2</sub> at the vegetated sites (r ≥ 0.57), and for CH<sub>3</sub>I with~~  
1053 CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> at the SD sites (r = 0.99, p < 0.05 in both cases). ~~In most cases the flux of~~

1054 ~~CH<sub>3</sub>I was negative at the vegetated sites; therefore, it is not clear whether the strong correlations~~  
1055 ~~between CH<sub>3</sub>I and the brominated trihalomethanes at these sites point to common sources or~~  
1056 ~~sinks. In contrast, p~~Positive fluxes of ~~both CH<sub>3</sub>I and the brominated trihalomethanes and~~  
1057 ~~CH<sub>2</sub>Br<sub>2</sub>~~the three species were observed at the SD sites in most cases, although with only  
1058 moderate statistical significance for ~~C<sub>2</sub>HCl<sub>3</sub> and CHCl<sub>3</sub> (Table 2), pointing to a common source~~  
1059 ~~of these species at the SD sites.~~ Weissflog et al. (2005) found that emission of C<sub>2</sub>HCl<sub>3</sub>, CHCl<sub>3</sub>  
1060 and other chlorinated VHOCs can occur from salt lakes via the activity of halobacteria in the  
1061 presence of dissolved Fe<sub>2</sub>(III) and crystallized NaCl. The strong correlations of CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub>  
1062 and CH<sub>3</sub>I (~~r = -0.99 in all cases~~)at the SD sites, where statistically significant fluxes were  
1063 frequently measured for these species, reinforce the ~~common co-located~~emissions of CHCl<sub>3</sub>  
1064 and C<sub>2</sub>HCl<sub>3</sub> from salt lake sediments, as indicated by Weissflog et al. (2005), and ~~may also~~  
1065 ~~indicate~~suggest that CH<sub>3</sub>I can be emitted in a similar fashion. The fact that the relative emission  
1066 efficiency of CH<sub>3</sub>I in our study was much ~~more efficient~~higher than under the conditions used  
1067 by Keppler et al. (2000) supports the possibility that mechanisms other than the abiotic emission  
1068 pathway proposed by Keppler et al. (2000) influence the emission of CH<sub>3</sub>I at the Dead Sea  
1069 (Sect. 3.2.3).

1070 ~~The relatively high correlations between fluxes of CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> and the other methyl~~  
1071 ~~halides, CH<sub>3</sub>Br and CH<sub>3</sub>Cl, for Bare and SD, may suggest that these methyl halides are also~~  
1072 ~~emitted, via similar mechanisms, from the salt deposits.~~

1073 **Table 65.** Correlations between the measured net fluxes of VHOCs. The table records the Pearson  
 1074 correlation coefficient (r) for the measured net flux between each VHOC pair, calculated over all sites except  
 1075 SEA-KDM (All), bare soil sites (BARE), coastal sites (COAST), short distance from the sea at the coastal sites  
 1076 (SD) and the vegetated sites (VEG). The p-value for r being significantly different from zero is indicated based on  
 1077 t-test, in four categories: by default, bolded,  $p < 0.05$ ; value in parentheses,  $p > 0.15$ ; <sup>a</sup> $p < 0.1$ ; <sup>b</sup> $p < 0.15$ .

		CHBrCl <sub>2</sub>	CHBr <sub>3</sub>	CHBr <sub>2</sub> Cl	CHCl <sub>3</sub>	CH <sub>2</sub> Br <sub>2</sub>	C <sub>2</sub> HCl <sub>3</sub>	CH <sub>3</sub> Cl	CH <sub>3</sub> Br
CH <sub>3</sub> I	All (n = 20)	0.34 <sup>b</sup> <sub>e</sub>	(0.13)	<b>-0.56</b>	<b>0.59</b>	(0.19)	<b>0.59</b>	<b>0.45</b>	(0.23)
	BARE (n = 6)	(-0.54)	<b>-0.85</b>	<b>-0.78</b>	0.68 <sup>e</sup> 68 <sup>b</sup>	(-0.32)	(0.54)	0.73 <sup>b</sup> 73 <sup>a</sup>	0.77 <sup>b</sup> 77 <sup>a</sup>
	COAST (n = 10)*	0.50 <sup>e</sup> 50 <sup>b</sup>	(0.26)	<b>-0.64</b>	<b>0.66</b>	<b>0.81</b>	<b>0.63</b>	0.54 <sup>b</sup>	(0.08)
	SD (n = 4)	(0.13)	(0.72)	(-0.05)	0.99	(0.35)	<b>0.99</b>	0.90 <sup>b</sup>	(0.69)
	VEG (n = 4)	(0.76)	(0.72)	(0.57)	(0.31)	0.88 <sup>eb</sup>	(0.16)	(0.11)	<b>0.45</b>
CH <sub>3</sub> Br	All (n = 20)	(-0.08)	0.39 <sup>b</sup> 39 <sup>a</sup>	(0.22)	(0.20)	(-0.06)	0.33 <sup>c</sup>	(0.30)	
	BARE (n = 6)	(-0.22)	<b>-0.83</b>	(-0.45)	<b>0.83</b>	(-0.21)	(0.57)	(0.61)	
	COAST (n = 10)*		<b>0.65</b>	(0.19)	(0.29)	(-0.04)	(0.33)	(-0.24)	
	SD (n = 4)	0.51 <sup>b</sup> 51 <sup>a</sup>	(0.07)	(0.69)	(0.59)	(-0.40)	(0.59)	(0.69)	
	VEG (n = 4)	(0.67)	0.87 <sup>e</sup> 87 <sup>b</sup>	(0.47)	(-0.57)	(0.36)	(-0.76)	<b>0.94</b>	
CH <sub>3</sub> Cl**	All (n = 19)	(0.27)	(0.05)	(0.00)	-0.37 <sup>b</sup>	(-0.15)	<b>0.54</b>		
	BARE (n = 6)	(-0.33)	(-0.63)	(-0.54)	<b>0.86</b>	(0.21)	0.74 <sup>e</sup> 74 <sup>b</sup>		
	COAST (n = 10)*	0.58 <sup>b</sup> 58 <sup>a</sup>	(-0.09)	(-0.16)	<b>0.69</b>	(0.14)	<b>0.66</b>		
	SD (n = 4)	(0.07)	(0.45)	(0.08)	0.94 <sup>b</sup> 94 <sup>a</sup>	(0.12)	0.86 <sup>e</sup> 86 <sup>b</sup>		
	VEG (n = 3)	(0.45)	(0.68)	(0.31)	(-0.75)	(0.06)	(-0.91)		
C <sub>2</sub> HCl <sub>3</sub>	All (n = 20)	(0.10)	<b>0.53</b>	(0.05)	<b>0.83</b>	(0.02)			
	Bare (n = 6)	(-0.41)	-0.66 <sup>e</sup> 66 <sup>b</sup>	(-0.52)	(0.56)	(-0.10)			
	COAST (n = 10)*	(0.30)	<b>0.65</b>	(-0.01)	<b>0.99</b>	(0.26)			
	SD (n = 4)	(0.26)	(0.81)	(-0.19)	<b>0.99</b>	(0.48)			
	VEG (n = 4)	(-0.05)	(-0.34)	(0.12)	<b>0.96</b>	(0.33)			
CH <sub>2</sub> Br <sub>2</sub>	All (n = 20)	<b>0.62</b>	0.36 <sup>e</sup> 36 <sup>b</sup>	(-0.17)	(0.15)				
	BARE (n = 6)	0.77 <sup>b</sup> 77 <sup>a</sup>	(0.58)	0.68 <sup>c</sup>	(0.08)				
	COAST (n = 10)*	(0.45)	(0.26)	<b>-0.85</b>	(0.27)				
	SD (n = 4)	0.90 <sup>b</sup> 90 <sup>a</sup>	0.88 <sup>c</sup>	-0.93 <sup>b</sup> 93 <sup>a</sup>	(0.45)				
	VEG (n = 4)	0.94 <sup>b</sup> 94 <sup>a</sup>	0.77 <sup>b</sup>	0.87 <sup>e</sup> 87 <sup>b</sup>	(0.55)				
CHCl <sub>3</sub>	All (n = 20)	(0.01)	(0.30)	(0.01)					
	BARE (n = 6)	(-0.25)	-0.74 <sup>b</sup> 74 <sup>a</sup>	(-0.46)					
	COAST (n = 10)*	(0.31)	0.60 <sup>b</sup> 60 <sup>a</sup>	(-0.04)					
	SD (n = 4)	(0.27)	(0.77)	(-0.18)					
	VEG (n = 4)	(0.22)	(-0.09)	(0.40)					
CHBr <sub>2</sub> Cl	All (n = 20)	(-0.11)	(0.16)						
	Bare (n = 6)	<b>0.95</b>	<b>0.86</b>						
	COAST (n = 10)*	(-0.22)	(0.11)						
	SD (n = 4)	<b>-0.98</b>	(-0.65)						
	VEG (n = 4)	<b>0.94</b>	(0.82)						
CHBr <sub>3</sub>	All (n = 20)	(0.22)							
	BARE (n = 6)	0.72 <sup>b</sup> 72 <sup>a</sup>							
	COAST (n = 10)*	(-0.04)							
	SD (n = 4)	(0.65)							
	VEG (n = 4)	<b>0.95</b>							

1078 <sup>a</sup> - Correlations for CH<sub>3</sub>Cl over VEG sites were excluded one CH<sub>3</sub>Cl measurement in at TMRX-ET-1 (see Sect.  
 1079 2.1.2).

1080 <sup>\*</sup> - Correlations calculations for COAST-TKM-LD excluded one sampling canister (see Sect. 2.1.2).

1081 <sup>\*\*</sup> - Correlation calculation for CH<sub>3</sub>Cl excluded one sample for TMRX-ET-1 (see Sect. 2.1.2).

1082

1083 **Summary**

1084 The results of this study demonstrate high emission rates of the investigated ~~methyl halides as~~  
1085 ~~well as of brominated and chlorinated VSL~~VHOCs in the Dead Sea region, corresponding with  
1086 mixing ratios which, in most cases, are significantly higher than typical values in the MBL.  
1087 Overall, our measurements indicate a generally higher elevated incidence (~~in 65–85 % of~~  
1088 ~~measurements~~) of positive fluxes of brominated ~~than of vs.~~ chlorinated VHOCs, ~~except for~~  
1089 ~~CHCl<sub>3</sub>, for which the incidence of positive net fluxes was also relatively high (65 % of~~  
1090 ~~measurements)~~ compared to previous studies. The high incidence of the former can be attributed  
1091 primarily to the relatively large amount of Br in the soil, rather than the Br/Cl ratio. We did not  
1092 detect any clear effect of meteorological parameters, emission from the seawater, or season,  
1093 other than — in agreement with Sive et al. (2007) — ~~an~~ apparently higher emission of CH<sub>3</sub>I  
1094 during in spring ~~than during vs.~~ winter. Three of the investigated site types – bare soil, coast and  
1095 agricultural field – were identified as statistically significant ( $p < 0.05$ ) sources for at least  
1096 parts of the investigated VHOCs. The fluxes, in general, were highly variable, showing  
1097 changes between sampling periods, even for a specific species at a specific site. Accordingly,  
1098 ~~taking into account statistical uncertainties, in fewer cases the~~ Only a few ~~The~~ coastal sites,  
1099 particularly at a short distance from the sea (SD sites) where soil is mixed with salt deposits,  
1100 were found as a sources for all of the investigated VHOCs, for which some of the measurements  
1101 indicated positive net flux, as but not statistically significantly for CHCl<sub>3</sub>, which were  
1102 ambiguous Further from the coastal area, the bare soil sites were found as a sources for  
1103 CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl, CHCl<sub>3</sub>, and apparently also for CH<sub>2</sub>Br<sub>2</sub> and CH<sub>3</sub>I, and the agricultural  
1104 vegetation site was a source for CHBr<sub>3</sub>, CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub>. Our measurements reinforce  
1105 reports of -CHCl<sub>3</sub> and CHBrCl<sub>2</sub> emission from bare soil, but indicate that such emission can also  
1106 occur also under relatively low soil organic content. To the best of our knowledge, we report  
1107 here for the first time strong emission of CHBr<sub>2</sub>Cl and emission of CH<sub>2</sub>Br<sub>2</sub> from hypersaline  
1108 bare soil, four investigated site types, the cultivated and natural vegetated, the bare soil and the

1109 ~~coastal sites, are identified as potential net sources for all VHOCs investigated, except for the~~  
1110 ~~emission of CH<sub>3</sub>I and C<sub>2</sub>HCl<sub>3</sub> from the vegetated sites. Hence, this study reveals strong emission~~  
1111 ~~of VHOCs over~~ at least a few kilometers from the Dead Sea. We could not identify the  
1112 contribution of either natural or agricultural vegetation to the emission of the investigated  
1113 VHOCs.es of .... The fluxes, in general, were highly variable, showing changes between  
1114 ~~sampling periods even for a specific species at a specific site.~~

1115 ~~The Emissions were~~ highest emissions from the SD sites; were associated with maximum  
1116 ~~salinity is maximal~~, and ~~which~~ clearly showed an increased incidence of positive flux with  
1117 ~~decreasing distance~~proximity to from the seawater, pointing to the sensitivity of VHOC  
1118 emission rates to salinity, even ~~at the hypersaline coastal area of the Dead Sea.~~under hypersaline  
1119 conditions. The measurements did not indicate either increased or reduced emissions of VHOCs  
1120 from the seawater itself. Emission of VHOCs has been shown to occur from dry soil under  
1121 semi-arid conditions during the summer, in agreement with the finding from other geographical  
1122 locations that soil water does not seem to be a limiting factor in VHOC emission (Kotte et al.,  
1123 2012). Rain events appeared ed to attenuate the emission rates of VHOCs at the Dead Sea.  
1124 Measurements at a bare soil site suggested a decrease in VHOC emission rates for 1–3 days  
1125 after a rain event, ~~while the gradual increase in VHOC emission more than three days after the~~  
1126 ~~rain event suggests that these VHOC emissions are, at least partially, biotic induced.~~

1127 ~~Trihalomethanes, including CHCl<sub>3</sub>, CHBr<sub>2</sub>Cl, CHBr<sub>3</sub> and particularly CHBrCl<sub>2</sub>, are~~  
1128 ~~associated with the highest number of sites at which their flux was, on average, positive, while~~  
1129 ~~CHBr<sub>3</sub>, CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub> showed relatively high incidence of positive fluxes, with values~~  
1130 ~~of 65 %, 80 % and 85 %, respectively. This finding, together with the relatively high~~  
1131 ~~correlations observed between~~ Both flux and mixing ratios correlation analyseis pointed to  
1132 common formation and emission mechanisms for CHBr<sub>2</sub>Cl and CHBrCl<sub>2</sub>, in line with previous  
1133 studies, for at least at the agricultural watermelon cultivation field and bare soil sites. These  
1134 analyses further strongly suggest common formation and emission mechanisms for CHBr<sub>3</sub> with

1135 ~~these two trihalomethanes. brominated trihalomethanes, points to common formation and~~  
1136 ~~emission mechanisms of in line with previous studies. Our analyses further suggest emission of~~  
1137 ~~CH<sub>2</sub>Br<sub>2</sub> via mechanisms that are common to the trihalomethanes. Correlation of the brominated~~  
1138 ~~trihalomethanes with CHCl<sub>3</sub> was lower.~~ Whereas Albers et al. (2017) suggested that CHBr<sub>3</sub> and  
1139 CHBr<sub>2</sub>Cl are emitted from soil only in relatively small amounts compared to CHCl<sub>3</sub>, our results  
1140 ~~point to~~ indicated their higher emission via common mechanisms with the other trihalomethanes.  
1141 The overall average net flux of the trihalomethanes decreased according to CHBr<sub>2</sub>Cl > CHCl<sub>3</sub> >  
1142 CHBr<sub>3</sub> > CHBrCl<sub>2</sub> > CHCl<sub>3</sub>, while CHCl<sub>3</sub> showed the lowest incidence of positive fluxes among  
1143 all trihalomethanes. The enhanced emission of brominated trihalomethanes probably reflects ~~the~~  
1144 enrichment of the Dead Sea soil with Br, in line with findings by ~~Hoekstra et al. (1998),~~  
1145 Hoekstra et al. (1998). ~~who identified a higher natural emission of CHBr<sub>3</sub> and CHBr<sub>2</sub>Cl rather~~  
1146 ~~than of CHBrCl<sub>2</sub> from the soil, following the soil's enrichment with KBr.~~

1147 We identified the SD-coastal sites as a probable source for all methyl halides, whereas  
1148 neither agricultural field nor natural vegetated-vegetation sites appear were identified as either  
1149 net sink or a net source more likely to act as a net sink for these species, except for the  
1150 agricultural field being a net sink for CH<sub>3</sub>I. Comparing the proportion of Br and Cl in the soil  
1151 ~~for the various sites with proportions of measured positive flux of CH<sub>3</sub>Br and CH<sub>3</sub>Cl are in line~~  
1152 ~~with reports by Keppler et al. (2001) about emission of methyl halides via abiotic oxidation of~~  
1153 ~~organic matter in the soil. Similar calculations in our study~~ Our analysis demonstrated, however,  
1154 much higher efficiencies of CH<sub>3</sub>I emission than of CH<sub>3</sub>Br and CH<sub>3</sub>Cl emissions as a function of  
1155 halides in the soil, than compared to those reported by Keppler et al. (2000), pointing to  
1156 emission of CH<sub>3</sub>I via other mechanisms. The strong correlation between both fluxes and mixing  
1157 ratios of CH<sub>3</sub>I, CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub>, ~~high correlation of CH<sub>3</sub>I emission with that of CHCl<sub>3</sub> and~~  
1158 ~~C<sub>2</sub>HCl<sub>3</sub>,~~ particularly at the SD sites, strongly suggests that, the coastal area of the Dead Sea acts  
1159 as an emission source for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I via similar mechanisms, although these sites  
1160 were associated with only moderate statistical significance ( $p < 0.1$ ) as a net source for CHCl<sub>3</sub>.

1161 The emission of CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> from these sites is in line with findings by  
1162 Weissflog et al. (2005), of emission of various chlorinated VHOCs, including CHCl<sub>3</sub>  
1163 and C<sub>2</sub>HCl<sub>3</sub>, from salt lake sediments, ~~suggests that the Dead Sea, particularly the SD, sites~~  
1164 ~~probably act as an emission source for CHCl<sub>3</sub>, C<sub>2</sub>HCl<sub>3</sub> and CH<sub>3</sub>I via similar mechanisms.~~  
1165 Weissflog et al. (2005) reported that the emission of chlorinated VHOCs in their study was  
1166 induced by microbial activity. Keppler et al. (2000) reported the involvement of an abiotic  
1167 process in the formation of alkyl from soil and sediments, and the observed correlation between  
1168 methyl halides and between CH<sub>3</sub>I and both CHCl<sub>3</sub> and C<sub>2</sub>HCl<sub>3</sub> may indicate that the two  
1169 processes occur simultaneously in the coastal area of the Dead Sea. ~~Further research will be~~  
1170 ~~needed to decipher the relative importance of each process in soil and salt sediments, including~~  
1171 ~~more direct emission measurements from a better defined landform, e.g., by using flux~~  
1172 ~~chambers.~~

1173 Of all the VHOCs investigated in our study, CHBr<sub>3</sub> showed the  
1174 highest enrichment with respect to MBL mixing ratios. Owing to the relatively short  
1175 tropospheric lifetime of CHBr<sub>3</sub>, its photolysis contributes significantly to reactive bromine  
1176 formation in the MBL. However, although relatively high, the elevated CHBr<sub>3</sub> fluxes and  
1177 mixing ratios that we measured at the Dead Sea, cannot be directly related to  
1178 the high mixing ratios of reactive bromine species that were found at the Dead Sea (e.g., see  
1179 Matveev et al. (2001) and Tas et al. (2005)) via its photolysis, which are frequently associated  
1180 with BrO > 100 ppt (e.g., see Matveev et al. (2001) and Tas et al. (2005)). Similarly, if CH<sub>3</sub>I  
1181 photolysis is the only source of reactive iodine-I species, the measured fluxes and elevated  
1182 mixing ratios of CH<sub>3</sub>I are not high enough to account for the high IO<sub>2</sub> iodine monoxide(?) in this  
1183 area. Given their relatively fast photolysis, however, CH<sub>3</sub>I and CHBr<sub>3</sub>, as well as CH<sub>2</sub>Br<sub>2</sub>, may  
1184 well have roles to play in the initiation of reactive bromine and iodine formation in this area.

1185 Overall, along with other studies, the findings presented here highlight the potentially  
1186 important role of ~~important role played by emission of VHOCs from~~ saline soil and salt lakes in

1187 VHOC emission, and call for further research on VHOC emission rates and controlling  
1188 mechanisms, and implications on stratospheric and tropospheric chemistry, ~~and call for further~~  
1189 ~~research on VHOC emission rates and controlling mechanisms.~~

1190

1191 **Data availability.** Data are available upon request from the corresponding author Eran Tas  
1192 (eran.tas@mail.huji.ac.il).

1193

1194 **Author contribution:** ET, AG ~~RR~~ and ~~AW~~ ~~RR~~ designed the experiments. MS, GL and QL  
1195 carried out the field measurements ~~out~~ and DB carried out the sampled air ~~analysis~~analyses. GL  
1196 contributed ~~in to~~ designing and constructing a special mechanism for the simultaneous lifting  
1197 and dropping of sampling canisters. Data curation and formal analysis were performed by ET  
1198 and MS with support from RR. ET and MS ~~and ET~~ prepared the manuscript with contributions  
1199 from all co-authors. ~~AW?~~

1200

1201 **Competing interests.** The authors declare that they have no conflict of interest.

1202

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### 1208 **References**

- 1209 Albers, C. N., Jacobsen, O. S., Flores, E. M. M., and Johnsen, A. R.: Arctic and Subarctic Natural Soils Emit  
1210 Chloroform and Brominated Analogues by Alkaline Hydrolysis of Trihaloacetyl Compounds, *Environ Sci*  
1211 *Technol*, 51, 6131-6138, 10.1021/acs.est.7b00144, 2017.
- 1212 Alpert, P., Shafir, H., and Issahary, D.: Recent changes in the climate at the dead sea - A preliminary study,  
1213 *Climatic Change*, 37, 513-537, Doi 10.1023/A:1005330908974, 1997.
- 1214 Bondu, S., Cocquempot, B., Deslandes, E., and Morin, P.: Effects of salt and light stress on the release of  
1215 volatile halogenated organic compounds by *Solieria chordalis*: a laboratory incubation study, *Botanica*  
1216 *Marina*, 51, 485-492, 10.1515/Bot.2008.056, 2008.



1217 Breider, F., and Albers, C. N.: Formation mechanisms of trichloromethyl-containing compounds in the  
1218 terrestrial environment: A critical review, *Chemosphere*, 119, 145-154,  
1219 10.1016/j.chemosphere.2014.05.080, 2015.

1220 Brinckmann, S., Engel, A., Bonisch, H., Quack, B., and Atlas, E.: Short-lived brominated hydrocarbons -  
1221 observations in the source regions and the tropical tropopause layer, *Atmos Chem Phys*, 12, 1213-1228,  
1222 10.5194/acp-12-1213-2012, 2012.

1223 Buchalo, A. S., Nevo, E., Wasser, S. P., Oren, A., and Molitoris, H. P.: Fungal life in the extremely  
1224 hypersaline water of the Dead Sea: first records, *P Roy Soc B-Biol Sci*, 265, 1461-1465, DOI  
1225 10.1098/rspb.1998.0458, 1998.

1226 Butler, J. H., King, D. B., Lobert, J. M., Montzka, S. A., Yvon-Lewis, S. A., Hall, B. D., Warwick, N. J., Mondeel,  
1227 D. J., Aydin, M., and Elkins, J. W.: Oceanic distributions and emissions of short-lived halocarbons, *Global*  
1228 *Biogeochem Cy*, 21, Artn Gb102310.1029/2006gb002732, 2007.

1229 Carpenter, L. J., Green, T. J., Mills, G. P., Bauguitte, S., Penkett, S. A., Zanis, P., Schuepbach, E.,  
1230 Schmidbauer, N., Monks, P. S., and Zellweger, C.: Oxidized nitrogen and ozone production efficiencies in  
1231 the springtime free troposphere over the Alps, *J Geophys Res-Atmos*, 105, 14547-14559, Doi  
1232 10.1029/2000jd900002, 2000.

1233 Carpenter, L. J., Wevill, D. J., O'Doherty, S., Spain, G., and Simmonds, P. G.: Atmospheric bromoform at  
1234 Mace Head, Ireland: seasonality and evidence for a peatland source, *Atmos Chem Phys*, 5, 2927-2934,  
1235 DOI 10.5194/acp-5-2927-2005, 2005.

1236 Carpenter, L. J., Jones, C. E., Dunk, R. M., Hornsby, K. E., and Woeltjen, J.: Air-sea fluxes of biogenic  
1237 bromine from the tropical and North Atlantic Ocean, *Atmos Chem Phys*, 9, 1805-1816, 2009.

1238 Carpenter, L. J., MacDonald, S. M., Shaw, M. D., Kumar, R., Saunders, R. W., Parthipan, R., Wilson, J., and  
1239 Plane, J. M. C.: Atmospheric iodine levels influenced by sea surface emissions of inorganic iodine,  
1240 *Nature Geoscience*, 6, 108-111, 10.1038/Ngeo1687, 2013.

1241 Carpenter, L. J., Reimann, S., Burkholder, J. B., Clerbaux, C., Hall, B. D., Hossaini, R., Laube, J. C., and Yvon-  
1242 Lewis, S. A.: Ozone-depleting substances (ODSs) and other gases of interest to the Montreal Protocol,  
1243 Chapter 1 in *Scientific Assessment of Ozone Depletion: 2014*, Global Ozone Research and Monitoring  
1244 Project – Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014.

1245 Colman, J. J., Swanson, A. L., Meinardi, S., Sive, B. C., Blake, D. R., and Rowland, F. S.: Description of the  
1246 analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-  
1247 Tropics A and B, *Analytical Chemistry*, 73, 3723-3731, DOI 10.1021/ac010027g, 2001.

1248 Dearrellano, J. V. G., Duynkerke, P. G., and Zeller, K. F.: Atmospheric Surface-Layer Similarity Theory  
1249 Applied to Chemically Reactive Species, *J Geophys Res-Atmos*, 100, 1397-1408, Doi 10.1029/94jd02434,  
1250 1995.

1251 Derendorp, L., Wishkerman, A., Keppler, F., McRoberts, C., Holzinger, R., and Rockmann, T.: Methyl  
1252 chloride emissions from halophyte leaf litter: Dependence on temperature and chloride content,  
1253 *Chemosphere*, 87, 483-489, 10.1016/j.chemosphere.2011.12.035, 2012.

1254 Deventer, M. J., Jiao, Y., Knox, S. H., Anderson, F., Ferner, M. C., Lewis, J. A., and Rhew, R. C.: Ecosystem-  
1255 Scale Measurements of Methyl Halide Fluxes From a Brackish Tidal Marsh Invaded With Perennial  
1256 Pepperweed (*Lepidium latifolium*), *J Geophys Res-Atmos-Biogeosciences*, 10.1029/2018JG004536,  
1257 2018.

1258 Dimmer, C. H., Simmonds, P. G., Nickless, G., and Bassford, M. R.: Biogenic fluxes of halomethanes from  
1259 Irish peatland ecosystems, *Atmos Environ*, 35, 321-330, Doi 10.1016/S1352-2310(00)00151-5, 2001.

1260 Dyer, A. J., and Bradley, E. F.: An Alternative Analysis of Flux-Gradient Relationships at the 1976 Itce,  
1261 *Bound-Lay Meteorol*, 22, 3-19, Doi 10.1007/Bf00128053, 1982.

1262 Ekdahl, A., Pedersen, M., and Abrahamsson, K.: A study of the diurnal variation of biogenic volatile  
1263 halocarbons, *Mar Chem*, 63, 1-8, Doi 10.1016/S0304-4203(98)00047-4, 1998.

1264 Gan, J., Yates, S. R., Ohr, H. D., and Sims, J. J.: Production of methyl bromide by terrestrial higher plants,  
1265 *Geophys Res Lett*, 25, 3595-3598, Doi 10.1029/98gl52697, 1998.

1266 Gebhardt, S., Colomb, A., Hofmann, R., Williams, J., and Lelieveld, J.: Halogenated organic species over the  
1267 tropical South American rainforest, *Atmos Chem Phys*, 8, 3185-3197, 2008.

- 1268 Gifford, F. A.: Turbulent diffusion typing schemes: A review," under (R. L. Schoup, Ed.) "Consequences of  
1269 Effluent Release, Nucl. Safety 17 (I), 6846,1976.
- 1270 EPA, United States Environmental Protection Agency Meteorological Monitoring Guidance for Regulatory  
1271 Modeling Applications, 2000.
- 1272 Golder, D.: Relations among stability parameters in the surface layer ;3(1):47–58., Boundary-Layer  
1273 Meteorol, 31, 47-58, 1972.
- 1274 Grubbs, F. E., and Beck, G.: Extension of Sample Sizes and Percentage Points for Significance Tests of  
1275 Outlying Observations, Technometrics, 14, 847-&, Doi 10.2307/1267134, 1972.
- 1276 Gualtieri, G., and Secci, S.: Comparing methods to calculate atmospheric stability-dependent wind speed  
1277 profiles: A case study on coastal location, Renew Energ, 36, 2189-2204, 10.1016/j.renene.2011.01.023,  
1278 2011.
- 1279 Hebestreit, K., Stutz, J., Rosen, D., Matveiv, V., Peleg, M., Luria, M., and Platt, U.: DOAS measurements of  
1280 tropospheric bromine oxide in mid-latitudes, Science, 283, 55-57, DOI 10.1126/science.283.5398.55,  
1281 1999.
- 1282 Hoekstra, E. J., De Leer, E. W. B., and Brinkman, U. A. T.: Natural formation of chloroform and brominated  
1283 trihalomethanes in soil, Environ Sci Technol, 32, 3724-3729, DOI 10.1021/es980127c, 1998.
- 1284 Hossaini, R., Chipperfield, M. P., Monge-Sanz, B. M., Richards, N. A. D., Atlas, E., and Blake, D. R.:  
1285 Bromoform and dibromomethane in the tropics: a 3-D model study of chemistry and transport, Atmos  
1286 Chem Phys, 10, 719-735, 10.5194/acp-10-719-2010, 2010.
- 1287 Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, E., Quack, B., Kruger, K.,  
1288 Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bonisch, H., Keber, T., Oram, D., Mills, G., Ordonez, C., Saiz-  
1289 Lopez, A., Warwick, N., Liang, Q., Feng, W., Moore, E., Miller, B. R., Marecal, V., Richards, N. A. D., Dorf,  
1290 M., and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos Chem  
1291 Phys, 13, 11819-11838, 10.5194/acp-13-11819-2013, 2013.
- 1292 Huber, S. G., Kotte, K., Scholer, H. F., and Williams, J.: Natural Abiotic Formation of Trihalomethanes in  
1293 Soil: Results from Laboratory Studies and Field Samples, Environ Sci Technol, 43, 4934-4939,  
1294 10.1021/es8032605, 2009.
- 1295 IPCC (Ed.) Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental  
1296 Panel on Climate Change. , Cambridge University Press, Cambridge, United Kingdom and New York, NY,  
1297 USA, 2007.
- 1298 Jacob, J. H., Hussein, E. I., Shakhathreh, M. A. K., and Cornelison, C. T.: Microbial community analysis of the  
1299 hypersaline water of the Dead Sea using high-throughput amplicon sequencing, Microbiologyopen, 6,  
1300 ARTN e50010.1002/mbo3.500, 2017.
- 1301 Keppler, F., Eiden, R., Niedan, V., Pracht, J., and Scholer, H. F.: Halocarbons produced by natural oxidation  
1302 processes during degradation of organic matter, Nature, 403, 298-301, Doi 10.1038/35002055, 2000.
- 1303 Keppler, F., Eiden, R., Niedan, V., Pracht, J., and Scholer, H. F.: Halocarbons produced by natural oxidation  
1304 processes during degradation of organic matter (vol 403, pg 298, 2000), Nature, 409, 382-+, DOI  
1305 10.1038/35053144z, 2001.
- 1306 Khan, M. A. H., Whelan, M. E., and Rhew, R. C.: Effects of temperature and soil moisture on methyl halide  
1307 and chloroform fluxes from drained peatland pasture soils, J Environ Monitor, 14, 241-249,  
1308 10.1039/c1em10639b, 2012.
- 1309 Kis-Papo, T., Grishkan, I., Oren, A., Wasser, S. P., and Nevo, E.: Spatiotemporal diversity of filamentous  
1310 fungi in the hypersaline Dead Sea, Mycol Res, 105, 749-756, Doi 10.1017/S0953756201004129, 2001.
- 1311 Kotte, K., Low, F., Huber, S. G., Krause, T., Mulder, I., and Scholer, H. F.: Organohalogen emissions from  
1312 saline environments - spatial extrapolation using remote sensing as most promising tool,  
1313 Biogeosciences, 9, 1225-1235, 10.5194/bg-9-1225-2012, 2012.
- 1314 Kuyper, B., Palmer, C. J., Labuschagne, C., and Reason, C. J. C.: Atmospheric bromoform at Cape Point,  
1315 South Africa: an initial fixed-point data set on the African continent, Atmos Chem Phys, 18, 5785-5797,  
1316 10.5194/acp-18-5785-2018, 2018.
- 1317 Lee-Taylor, J. M., and Holland, E. A.: Litter decomposition as a potential natural source of methyl bromide,  
1318 J Geophys Res-Atmos, 105, 8857-8864, Doi 10.1029/1999jd901112, 2000.

- 1319 Lenschow, D. H.: Micrometeorological techniques for measuring biosphere-atmosphere trace gas  
 1320 exchange. *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, P.A. Matson and R.C. Hariss,  
 1321 Eds., *Methods in Ecology*, Blackwell Science, Oxford, 126-163., 1995.
- 1322 Liu, Y. N., Yvon-Lewis, S. A., Hu, L., Salisbury, J. E., and O'Hern, J. E.: CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>, and CHClBr<sub>2</sub> in U.S.  
 1323 coastal waters during the Gulf of Mexico and East Coast Carbon cruise, *J Geophys Res-Oceans*, 116, Artn  
 1324 C1000410.1029/2010jc006729, 2011.
- 1325 Maier, M., and Schack-Kirchner, H.: Using the gradient method to determine soil gas flux: A review,  
 1326 *Agricultural and Forest Meteorology*, 192, 78-95, 10.1016/j.agrformet.2014.03.006, 2014.
- 1327 Manley, S. L., and Dastoor, M. N.: Methyl-Iodide (Ch<sub>3</sub>i) Production by Kelp and Associated Microbes,  
 1328 *Marine Biology*, 98, 477-482, Doi 10.1007/Bf00391538, 1988.
- 1329 Manley, S. L., Wang, N. Y., Walser, M. L., and Cicerone, R. J.: Coastal salt marshes as global methyl halide  
 1330 sources from determinations of intrinsic production by marsh plants, *Global Biogeochem Cy*, 20, Artn  
 1331 Gb301510.1029/2005gb002578, 2006.
- 1332 Matveev, V., Peleg, M., Rosen, D., Tov-Alper, D. S., Hebestreit, K., Stutz, J., Platt, U., Blake, D., and Luria,  
 1333 M.: Bromine oxide - ozone interaction over the Dead Sea, *J Geophys Res-Atmos*, 106, 10375-10387, Doi  
 1334 10.1029/2000jd900611, 2001.
- 1335 Meredith, L. K., Commane, R., Munger, J. W., Dunn, A., Tang, J., Wofsy, S. C., and Prinn, R. G.: Ecosystem  
 1336 fluxes of hydrogen: a comparison of flux-gradient methods, *Atmospheric Measurement Techniques*, 7,  
 1337 2787-2805, 10.5194/amt-7-2787-2014, 2014.
- 1338 Moore, R. M., Gut, A., and Andreae, M. O.: A pilot study of methyl chloride emissions from tropical  
 1339 woodrot fungi, *Chemosphere*, 58, 221-225, 10.1016/j.chemosphere.2004.03.011, 2005.
- 1340 Moore, R. M.: Methyl halide production and loss rates in sea water from field incubation experiments,  
 1341 *Mar Chem*, 101, 213-219, 10.1016/j.marchem.2006.03.003, 2006.
- 1342 Nadzir, M. S. M., Phang, S. M., Abas, M. R., Rahman, N. A., Abu Samah, A., Sturges, W. T., Oram, D. E.,  
 1343 Mills, G. P., Leedham, E. C., Pyle, J. A., Harris, N. R. P., Robinson, A. D., Ashfold, M. J., Mead, M. I., Latif,  
 1344 M. T., Khan, M. F., Amiruddin, A. M., Banan, N., and Hanafiah, M. M.: Bromocarbons in the tropical  
 1345 coastal and open ocean atmosphere during the 2009 Prime Expedition Scientific Cruise (PESC-09),  
 1346 *Atmos Chem Phys*, 14, 8137-8148, 10.5194/acp-14-8137-2014, 2014.
- 1347 Niemi, T. M., Ben-Avraham, Z., and Gat, J.R., : *The Dead Sea: The Lake and Its Setting*, Oxford Monographs  
 1348 in Geophysics, vol. 36, Oxford Univ. Press, New York., 1997.
- 1349 O'Brien, L. M., Harris, N. R. P., Robinson, A. D., Gostlow, B., Warwick, N., Yang, X., and Pyle, J. A.:  
 1350 Bromocarbons in the tropical marine boundary layer at the Cape Verde Observatory - measurements  
 1351 and modelling, *Atmos Chem Phys*, 9, 9083-9099, 10.5194/acp-9-9083-2009, 2009.
- 1352 O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hameri, K., Pirjola, L., Kulmala, M.,  
 1353 Jennings, S. G., and Hoffmann, T.: Marine aerosol formation from biogenic iodine emissions, *Nature*,  
 1354 417, 632-636, DOI 10.1038/nature00775, 2002.
- 1355 Obrist, D., Tas, E., Peleg, M., Matveev, V., Fain, X., Asaf, D., and Luria, M.: Bromine-induced oxidation of  
 1356 mercury in the mid-latitude atmosphere, *Nature Geoscience*, 4, 22-26, 10.1038/Ngeo1018, 2011.
- 1357 Oren, A., and Shilo, M.: Factors Determining the Development of Algal and Bacterial Blooms in the Dead-  
 1358 Sea - a Study of Simulation Experiments in Outdoor Ponds, *Fems Microbiol Ecol*, 31, 229-237, 1985.
- 1359 Oren, A., Ionescu, D., Hindiyeh, M., and Malkawi, H.: Microalgae and cyanobacteria of the Dead Sea and  
 1360 its surrounding springs, *Isr J Plant Sci*, 56, 1-13, Doi 10.1560/Ijps.56.1-2.1, 2008.
- 1361 Osman, K. T.: Forest soils: properties and management. In 'Physical properties of forest soils', 19-28,  
 1362 2013.
- 1363 Pasquill, F., and Smith, F. B.: The physical and meteorological basis for the estimation of the dispersion of  
 1364 windborn material, in (H. M. Englund and W. T. Beery, Eds.), *Proceedings of the Second International*  
 1365 *Clean Air Congress*, Washington, DC, 1970, pp. 1067-1072, Academic Press, New York, , 1971.
- 1366 Pedersen, M., Collen, J., Abrahamsson, K., and Ekdahl, A.: Production of halocarbons from seaweeds: An  
 1367 oxidative stress reaction?, *Scientia Marina*, 60, 257-263, 1996.
- 1368 Pen-Mouratov, S., Myblat, T., Shamir, I., Barness, G., and Steinberger, Y.: Soil Biota in the Arava Valley of  
 1369 Negev Desert, Israel, *Pedosphere*, 20, 273-284, Doi 10.1016/S1002-0160(10)60015-X, 2010.

- 1370 Pyle, J. A., Ashfold, M. J., Harris, N. R. P., Robinson, A. D., Warwick, N. J., Carver, G. D., Gostlow, B.,  
1371 O'Brien, L. M., Manning, A. J., Phang, S. M., Yong, S. E., Leong, K. P., Ung, E. H., and Ong, S.: Bromoform  
1372 in the tropical boundary layer of the Maritime Continent during OP3, *Atmos Chem Phys*, 11, 529-542,  
1373 10.5194/acp-11-529-2011, 2011.
- 1374 Quack, B., and Wallace, D. W. R.: Air-sea flux of bromoform: Controls, rates, and implications (vol 17, art  
1375 no 1023, 2003), *Global Biogeochem Cy*, 18, Artn Gb100410.1029/2003gb002187, 2004.
- 1376 Quack, B., Atlas, E., Petrick, G., and Wallace, D. W. R.: Bromoform and dibromomethane above the  
1377 Mauritanian upwelling: Atmospheric distributions and oceanic emissions, *J Geophys Res-Atmos*, 112,  
1378 Artn D0931210.1029/2006jd007614, 2007.
- 1379 Rhew, R. C., Miller, B. R., and Weiss, R. F.: Natural methyl bromide and methyl chloride emissions from  
1380 coastal salt marshes, *Nature*, 403, 292-295, Doi 10.1038/35002043, 2000.
- 1381 Rhew, R. C., Miller, B. R., Vollmer, M. K., and Weiss, R. F.: Shrubland fluxes of methyl bromide and methyl  
1382 chloride, *J Geophys Res-Atmos*, 106, 20875-20882, Doi 10.1029/2001jd000413, 2001.
- 1383 Rhew, R. C., Miller, B. R., Bill, M., Goldstein, A. H., and Weiss, R. F.: Environmental and biological controls  
1384 on methyl halide emissions from southern California coastal salt marshes, *Biogeochemistry*, 60, 141-  
1385 161, Doi 10.1023/A:1019812006560, 2002.
- 1386 Rhew, R. C., Aydin, M., and Saltzman, E. S.: Measuring terrestrial fluxes of methyl chloride and methyl  
1387 bromide using a stable isotope tracer technique, *Geophys Res Lett*, 30, Artn  
1388 210310.1029/2003gl018160, 2003.
- 1389 Rhew, R. C., Teh, Y. A., Abel, T., Atwood, A., and Mazeas, O.: Chloroform emissions from the Alaskan Arctic  
1390 tundra, *Geophys Res Lett*, 35, Artn L2181110.1029/2008gl035762, 2008.
- 1391 Rhew, R. C., Whelan, M. E., and Min, D. H.: Large methyl halide emissions from south Texas salt marshes,  
1392 *Biogeosciences*, 11, 6427-6434, 10.5194/bg-11-6427-2014, 2014.
- 1393 Rousseaux, M. C., Ballare, C. L., Giordano, C. V., Scopel, A. L., Zima, A. M., Szwarcberg-Bracchitta, M.,  
1394 Searles, P. S., Caldwell, M. M., and Diaz, S. B.: Ozone depletion and UVB radiation: Impact on plant DNA  
1395 damage in southern South America, *Proceedings of the National Academy of Sciences of the United  
1396 States of America*, 96, 15310-15315, DOI 10.1073/pnas.96.26.15310, 1999.
- 1397 Ruecker, A., Weigold, P., Behrens, S., Jochmann, M., Laaks, J., and Kappler, A.: Predominance of Biotic over  
1398 Abiotic Formation of Halogenated Hydrocarbons in Hypersaline Sediments in Western Australia,  
1399 *Environ Sci Technol*, 48, 9170-9178, 10.1021/es501810g, 2014.
- 1400 Schmugge, T. j., and André, J.-C.: Land surface evaporation: measurement and parameterization: Springer  
1401 Science & Business Media, 1991.
- 1402 Simmonds, P. G., Derwent, R. G., Manning, A. J., O'Doherty, S., and Spain, G.: Natural chloroform  
1403 emissions from the blanket peat bogs in the vicinity of Mace Head, Ireland over a 14-year period, *Atmos  
1404 Environ*, 44, 1284-1291, 10.1016/j.atmosenv.2009.12.027, 2010.
- 1405 Simpson, W. R., Brown, S. S., Saiz-Lopez, A., Thornton, J. A., and von Glasow, R.: Tropospheric Halogen  
1406 Chemistry: Sources, Cycling, and Impacts, *Chemical Reviews*, 115, 4035-4062, 10.1021/cr5006638,  
1407 2015.
- 1408 Sive, B. C., Varner, R. K., Mao, H., Blake, D. R., Wingenter, O. W., and Talbot, R.: A large terrestrial source  
1409 of methyl iodide, *Geophys Res Lett*, 34, Artn L1780810.1029/2007gl030528, 2007.
- 1410 Stull, R. B.: An introduction to boundary layer meteorology. Kluwer, Dordrecht 1988.
- 1411 Sverdrup, H. U., Johnson, M.W., and Fleming, R.H.: The Oceans, Their Physics, Chemistry and General  
1412 Biology, Prentice-Hall, Englewood Cliffs, N.J., 1942.
- 1413 Tas, E., Matveev, V., Zingler, J., Luria, M., and Peleg, M.: Frequency and extent of ozone destruction  
1414 episodes over the Dead Sea, Israel, *Atmos Environ*, 37, 4769-4780, 10.1016/j.atmosenv.2003.08.015,  
1415 2003.
- 1416 Tas, E., Peleg, M., Matveev, V., Zingler, J., and Luria, M.: Frequency and extent of bromine oxide formation  
1417 over the Dead Sea, *J Geophys Res-Atmos*, 110, Artn D1130410.1029/2004jd005665, 2005.

1418 Tas, E., Peleg, M., Pedersen, D. U., Matveev, V., Biazar, A. P., and Luria, M.: Measurement-based modeling  
1419 of bromine chemistry in the boundary layer: 1. Bromine chemistry at the Dead Sea, *Atmos Chem Phys*,  
1420 6, 5589-5604, 2006.

1421 Tas, E., Obrist, D., Peleg, M., Matveev, V., Fain, X., Asaf, D., and Luria, M.: Measurement-based modelling  
1422 of bromine-induced oxidation of mercury above the Dead Sea, *Atmos Chem Phys*, 12, 2429-2440,  
1423 10.5194/acp-12-2429-2012, 2012.

1424 Varner, R. K., Crill, P. M., and Talbot, R. W.: Wetlands: a potentially significant source of atmospheric  
1425 methyl bromide and methyl chloride, *Geophys Res Lett*, 26, 2433-2435, Doi 10.1029/1999gl900587,  
1426 1999.

1427 Warwick, N. J., Pyle, J. A., and Shallcross, D. E.: Global modelling of the atmospheric methyl bromide  
1428 budget, *J Atmos Chem*, 54, 133-159, 10.1007/s10874-006-9020-3, 2006.

1429 Watling, R., and Harper, D. B.: Chloromethane production by wood-rotting fungi and an estimate of the  
1430 global flux to the atmosphere, *Mycol Res*, 102, 769-787, Doi 10.1017/S0953756298006157, 1998.

1431 Weissflog, L., Lange, C. A., Pfennigsdorff, A., Kotte, K., Elansky, N., Lisitzyna, L., Putz, E., and Krueger, G.:  
1432 Sediments of salt lakes as a new source of volatile highly chlorinated C1/C2 hydrocarbons, *Geophys Res*  
1433 *Lett*, 32, Artn L0140110.1029/2004gl020807, 2005.

1434 Wishkerman, A., Gebhardt, S., McRoberts, C. W., Hamilton, J. T. G., Williams, J., and Keppler, F.: Abiotic  
1435 methyl bromide formation from vegetation, and its strong dependence on temperature, *Environ Sci*  
1436 *Technol*, 42, 6837-6842, 10.1021/es800411j, 2008.

1437 WMO, W. M. O.: *Guide to Meteorological Instruments and Methods of Observation*, 2008.

1438 Xiao, X., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Weiss, R. F., O'Doherty, S., Miller, B. R., Salameh, P. K.,  
1439 Harth, C. M., Krummel, P. B., Porter, L. W., Muhle, J., Grealley, B. R., Cunnold, D., Wang, R., Montzka, S.  
1440 A., Elkins, J. W., Dutton, G. S., Thompson, T. M., Butler, J. H., Hall, B. D., Reimann, S., Vollmer, M. K.,  
1441 Stordal, F., Lunder, C., Maione, M., Arduini, J., and Yokouchi, Y.: Optimal estimation of the surface fluxes  
1442 of methyl chloride using a 3-D global chemical transport model, *Atmos Chem Phys*, 10, 5515-5533,  
1443 10.5194/acp-10-5515-2010, 2010.

1444 Yang, K., Tamai, N., and Koike, T.: Analytical solution of surface layer similarity equations, *J Appl Meteorol*,  
1445 40, 1647-1653, Doi 10.1175/1520-0450(2001)040<1647:Asosl>2.0.Co;2, 2001.

1446 Yassaa, N., Wishkerman, A., Keppler, F., and Williams, J.: Fast determination of methyl chloride and methyl  
1447 bromide emissions from dried plant matter and soil samples using HS-SPME and GC-MS: method and  
1448 first results, *Environmental Chemistry*, 6, 311-318, 10.1071/En09034, 2009.

1449 Yokouchi, Y., Ikeda, M., Inuzuka, Y., and Yukawa, T.: Strong emission of methyl chloride from tropical  
1450 plants, *Nature*, 416, 163-165, DOI 10.1038/416163a, 2002.

1451 Yokouchi, Y., Inagaki, T., Yazawa, K., Tamaru, T., Enomoto, T., and Izumi, K.: Estimates of ratios of  
1452 anthropogenic halocarbon emissions from Japan based on aircraft monitoring over Sagami Bay, Japan, *J*  
1453 *Geophys Res-Atmos*, 110, Artn D0630110.1029/2004jd005320, 2005.

1454 Yokouchi, Y., Saito, T., Ishigaki, C., and Aramoto, M.: Identification of methyl chloride-emitting plants and  
1455 atmospheric measurements on a subtropical island, *Chemosphere*, 69, 549-553,  
1456 10.1016/j.chemosphere.2007.03.028, 2007.

1457 Zhou, Y., Varner, R. K., Russo, R. S., Wingenter, O. W., Haase, K. B., Talbot, R., and Sive, B. C.: Coastal water  
1458 source of short-lived halocarbons in New England, *J Geophys Res-Atmos*, 110, Artn  
1459 D2130210.1029/2004jd005603, 2005.

1460 Zhou, Y., Mao, H. T., Russo, R. S., Blake, D. R., Wingenter, O. W., Haase, K. B., Ambrose, J., Varner, R. K.,  
1461 Talbot, R., and Sive, B. C.: Bromoform and dibromomethane measurements in the seacoast region of  
1462 New Hampshire, 2002-2004, *J Geophys Res-Atmos*, 113, Artn D0830510.1029/2007jd009103, 2008.

1463 Zingler, J., and Platt, U.: Iodine oxide in the Dead Sea Valley: Evidence for inorganic sources of boundary  
1464 layer IO, *J Geophys Res-Atmos*, 110, Artn D0730710.1029/2004jd004993, 2005.

1465 Ziska, F., Quack, B., Abrahamsson, K., Archer, S. D., Atlas, E., Bell, T., Butler, J. H., Carpenter, L. J., Jones, C.  
1466 E., Harris, N. R. P., Hepach, H., Heumann, K. G., Hughes, C., Kuss, J., Kruger, K., Liss, P., Moore, R. M.,  
1467 Orlikowska, A., Raimund, S., Reeves, C. E., Reifenhäuser, W., Robinson, A. D., Schall, C., Tanhua, T.,

1468 Tegtmeier, S., Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., and  
1469 Yokouchi, Y.: Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide,  
1470 Atmos Chem Phys, 13, 8915-8934, 10.5194/acp-13-8915-2013, 2013.

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