

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 (CH₃Br, perhaps also CH₃Cl, CHCl₃, and CH₂Br₂) 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 (CH₃Br, 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 C₂HCl₃ and CH₃I, 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 CH₃I and C₂HCl₃) 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 CH_3I with CHCl_3 and C_2HCl_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 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 ≤ 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 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 CHCl_3 considering the relatively low incidence of positive flux from sites which were identified as a source for 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 CH_3I and C_2HCl_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 CHCl_3 . Further from the coastal area, the bare soil sites were sources for CHBrCl_2 , CHBr_2Cl , CHCl_3 , and apparently also for CH_2Br_2 and CH_3I , and the agricultural vegetation site was a source for CHBr_3 , CHBr_2Cl and CHBrCl_2 . Our measurements reinforce reports of CHCl_3 and 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 CHBr_2Cl and emission of CH_2Br_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 CHCl_3 , CHBr_2Cl , CHBr_3 and particularly CHBrCl_2 , are associated with the highest number of sites at which their flux was, on average, positive, while CHBr_3 , CHBr_2Cl and 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 CHBr_2Cl and 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 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 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 CH_3I ." (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 CH_3Br and CH_3Cl 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 CH_3I emission than those reported by Keppler et al. (2000), pointing to emission of CH_3I via other mechanisms. The high correlation of

CH₃I emission with that of CHCl₃ and C₂HCl₃, particularly at the SD sites, together with findings by Weissflog et al. (2005), of various chlorinated VHOCs emission, including CHCl₃ and C₂HCl₃, from salt lake sediments, suggests that the Dead Sea, particularly the SD, sites probably act as an emission source for CHCl₃, C₂HCl₃ and CH₃I 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 CHCl₃ and C₂HCl₃ 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 CHC₃I ($0.05 > p < 0.1$; 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 CH₃I emission than of CH₃Br and CH₃Cl emissions as a function of halides in the soil, compared to those reported by Keppler et al. (2000), pointing to emission of CH₃I via other mechanisms. The strong correlation between both fluxes and mixing ratios of CH₃I, CHCl₃ and C₂HCl₃, particularly at the SD sites, strongly suggests that the coastal area of the Dead Sea acts as an emission source for CHCl₃, C₂HCl₃ and CH₃I via similar mechanisms, although these sites were associated with only moderate statistical significance ($p \leq 0.1$) as a net source for CHCl₃. The emission of CHCl₃ and C₂HCl₃ from these sites is in line with findings by Weissflog et al. (2005) of emission of various chlorinated VHOCs, including CHCl₃ and C₂HCl₃, 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 CH₃I and both CHCl₃ and C₂HCl₃ 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 C₂HCl₃ 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 C₂HCl₃, 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 C₂Cl₄, which strongly support the origin of C₂HCl₃ 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 C₂HCl₃, 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 C₂HCl₃ 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 C₂HCl₃, 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 C₂Cl₄ (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 CH₃I, 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 CH₃I 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 CH₃I 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 CHCl_3 , CH_2Cl_3 and CH_3I (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 ≤ 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 CHCl_3 and C_2HCl_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 (CHCl_3), L73 chloroethane ($\text{C}_2\text{H}_5\text{Cl}$), L112 iron (Fe), L115 potassium bromide (KBr), nitric acid (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 “...C₂H₅Cl, 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 CH₃Cl. 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 CHBr₃ in Zhou et al., 2005 – how do these compare with the Dead Sea?

Answer: Information about mixing ratios of CHBr₃ as well as fluxes for CH₂Br₂ and CH₂Br₂ 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 C₂HCl₃ and CH₃I - 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 CHCl₃, C₂HCl₃ and CH₃I. Note that as explained above, C₂HCl₃ 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 CH₃I 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 CH₃I reported by Sive et al. (2007) at Duke Forest, averaging ~0.27 nmol m⁻² d⁻¹ (range, ~ 0.11–4.1 nmol m⁻² d⁻¹)." (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 CHBr₃ and CH₂Br₂ were greater than for most reported emissions in the MBL (e.g., CHBr₃, 25.2–62.88 nmol m⁻² d⁻¹ for the Mauritanian upwelling (Quack et al., 2007); CH₂Br₂, 0.14–0.29 nmol m⁻² d⁻¹ 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⁻² d⁻¹, respectively) and than the average flux from the New Hampshire coast as reported by Zhou et al. (2005) (~620 ± 1370 nmol m⁻² d⁻¹ and 113 ± 130 nmol m⁻² d⁻¹, respectively)." (lines 428-434).

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

Answer: Corrected (line 473)

L360: For "nmol m⁻²-d⁻¹" 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 C₂HCl₃/C₂Cl₄ 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 CHCl₃ and CHBr₃. 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 - C₂HCl₃ 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 C₂HCl₃ (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 C₂HCl₃ was associated with C₂Cl₄, 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 ~ 40 °C decreasing gradually until winter, to a corresponding temperature of ~ 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 VLSL 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 VLSL, except for the Abstract, Introduction and twice in the Results and discussions, where we specifically refer to VLSL (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 CHCl₃

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 CHCl₃ and CHClBr₂.

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 CHCl₃ 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 CHBr_3 and CHBr_2Cl were observed at the agricultural field, even higher emission rates for these species were observed at the coastal sites, and for CHBr_2Cl 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 CHBr_2Cl and 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 CHBrCl_2 , CHBr_2Cl and 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 CH_3Br , and more statistically significantly so for CH_3Cl and CH_3I , 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 CH₃I-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 CHCl₃ 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 CHCl₃ and the methyl halides, the related discussion is as follows: "Interestingly, in agreement with Table 4, Table 5 also shows relatively high correlations between CHCl₃ and all methyl halides, particularly for the BARE sites (CH₃I, $r = 0.68$, $p < 0.15$; CH₃Br, $r = 0.83$, $p < 0.05$; CH₃Cl, $r < 0.86$, $p < 0.05$), and SD sites (CH₃I, $r = 0.99$, $p < 0.05$; CH₃Br, $r = 0.59$, $p > 0.15$; CH₃Cl, $r = 0.91$, $p < 0.1$). Remarkably, a high correlation was found for CH₃I with CHCl₃ and C₂HCl₃ 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 CHCl_3 (Table 2). Weissflog et al. (2005) found that emission of C_2HCl_3 , 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 CHCl_3 , C_2HCl_3 and CH_3I at the SD sites, where statistically significant fluxes were frequently measured for these species, reinforce the colocalized emission of CHCl_3 and C_2HCl_3 from salt lake sediments, as indicated by Weissflog et al. (2005), and suggest that CH_3I can be emitted in a similar fashion. The fact that the relative emission efficiency of CH_3I 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 CH_3I at the Dead Sea (Sect. 3.2.3)." (lines 883-898). Hence, we believe that the integrated analyses indicate a common source for CHCl_3 , C_2HCl_3 and CH_3I . 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).

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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 (CH_3X ; X
34 = Br, Cl and I) and very short-lived halogenated substances [VSLs; bromoform (CHBr_3),
35 dibromomethane (CH_2Br_2), bromodichloromethane (CHBrCl_2), trichloroethylene (C_2HCl_3),
36 chloroform (CHCl_3) and dibromochloromethane (CHBr_2Cl)] 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 CH_3I and~~
49 C_2HCl_3 over the vegetated sites. were highly variable. Fluxes (and mixing ratios) for the
50 investigated VHOCs ranged as follows: CHBr_3 from -79 to -187 $\text{nmol m}^{-2} \text{d}^{-1}$ (1.9 to
51 -22.6 pptv), CH_2Br_2 from -55 to -71 $\text{nmol m}^{-2} \text{d}^{-1}$ (0.7 to -19 pptv), CHBr_2Cl from $-$
52 408 to -768 $\text{nmol m}^{-2} \text{d}^{-1}$ (0.4 to -11 pptv), CHBrCl_2 from -29 to -45 $\text{nmol m}^{-2} \text{d}^{-1}$ (0.5
53 to -9.6 pptv), CHCl_3 from -577 to -883 $\text{nmol m}^{-2} \text{d}^{-1}$ (15 to -57 pptv), C_2HCl_3 from $-$
54 74 to -884 $\text{nmol m}^{-2} \text{d}^{-1}$ (0.4 to -11 pptv), methyl chloride (CH_3Cl) from -5300 to
55 $-10,800$ $\text{nmol m}^{-2} \text{d}^{-1}$ (530 to -730 pptv), methyl bromide (CH_3Br) from -111 to -118
56 $\text{nmol m}^{-2} \text{d}^{-1}$ (7.5 to -14 pptv) and methyl iodide (CH_3I) ~~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 ~~CHCl₃, CHBr₃, CH₂Br₂, CHBr₂Cl, CHBrCl₂, CHCl₃, C₂HCl₃, CH₃Cl, CH₃Br and CH₃I.~~ ~~F~~;
61 ~~further away from the coastal area, the bare soil sites were found as a sources for CHBrCl₂,~~
62 ~~CHBr₂Cl, CHCl₃, and probably also for CH₂Br₂ and CH₃I,~~ and the agricultural ~~vegetated~~ sites
63 ~~were sources for CHBr₃, CHBr₂Cl and CHBrCl₂.~~ In contrast to previous reports, we also
64 observed emissions of brominated trihalomethanes, with net molar fluxes ordered as follows:
65 CHBr₂Cl > > CHCl₃ > CHBr₃ > CHBrCl₂, and lowest positive flux incidence for CHCl₃ among
66 ~~all trihalomethanes~~ > CHCl₃; ~~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 CHBr₂Cl and CHBrCl₂, and likely also for CHBr₃. ~~all the above~~
69 ~~trihalomethanes but also for CH₂Br₂.~~ ~~There are~~ ~~were~~ no indications for correlation of the
70 ~~brominated trihalomethanes with CHCl₃.~~ Also in line with previous reports, we observed
71 elevated emissions of CHCl₃ and C₂HCl₃ 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~~ CH₃I); suggested that at least CH₃I is also emitted via similar
74 mechanisms or is subjected to similar controls. Overall, our results indicate elevated ~~d~~ 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 (CH₃X; X = Br, Cl
82 and I) and very short-lived halogenated substances (VSLSS; ~~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 (O₃ destruction), changes in atmospheric oxidation capacity, and radiative forcing (Simpson et al., 2015). Depletion of O₃ 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, O₃ ~~depletion~~ destruction is of great importance, given that O₃ 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 (CHCl₃) and chloroethane, originate primarily from anthropogenic sources (Carpenter et al., 2014). Methyl iodide (CH₃I), having a relatively short lifetime, is also classified as a VSLSS, and contributes significantly to tropospheric O₃ 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 (CHBr₃), methylene bromide (CH₂Br₂), and dibromochloromethane (CHBr₂Cl)] and iodinated (e.g., methyl iodide (CH₃I)) 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 (CH₃Br), and a significant (~19-%) source of methyl chloride (CH₃Cl) (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 CH₃Br and CH₃Cl 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 CH₃Cl
120 (Yokouchi et al., 2007), and the results of recent [modeling](#) indicate that about 55% of the
121 global sources of CH₃Cl originate from tropical lands (Xiao et al., 2010;Carpenter et al., 2014).
122 It [has](#) also [been](#) suggested that natural terrestrial sources of CH₃Br, 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). CHCl₃ ~~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 CH₃Br, CH₃Cl, and CH₃I, 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 CHCl₃ 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 O₃-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⁻¹; Shafir and Alpert, 2010), while ~~and~~ ~~with a very high~~ seawater evaporation rates are
191 high, estimated at about ~~rate of~~ 400 cm y⁻¹ (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⁻¹ Br⁻ bromide and 225 g L⁻¹ Cl⁻ chloride (Br⁻/Cl⁻ ratio ≈ 0.025) (Niemi,
194 1997), whereas normal ocean water contains 0.065 g L⁻¹ Br⁻ bromide and 19 g L⁻¹ Cl⁻ chloride
195 (Br⁻/Cl⁻ 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 CHCl₃ and CHBr₃.

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 km² 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 m² cultivated watermelon
239 agricultural field with cultivated watermelon located surrounded by a larger agricultural area of
240 ~3 km², 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~~ (CHBr_3), ~~trichloroethene~~ (C_2HCl_3), ~~methylene~~
269 ~~bromide~~ (CH_2Br_2), ~~dibromochloromethane~~ (CHBr_2Cl), ~~bromodichloromethane~~ (CHBrCl_2),
270 ~~trichloroethene~~ (C_2HCl_3), ~~chloroform~~ (CHCl_3), ~~methyl iodide~~ (CH_3I), ~~methyl bromide~~ (CH_3Br)
271 and ~~methyl chloride~~ (CH_3Cl). 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 CH_3Cl , 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 (Local local)	Site name / measurement abbreviation ^a	Sampling heights (m)	Total samplings	Seawater ^b	Precipitation (days before sampling) ^c
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 *	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</u> , <u>2.0</u> , <u>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	WM 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 ^a The suffixes "s" and "w" refer to ~~samplings~~ samples taken during the spring and winter, respectively. "SD", MD",
 286 and "LD" refer to relatively short, medium, and long distance from the coastline, respectively (see Sect. 2.1).

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

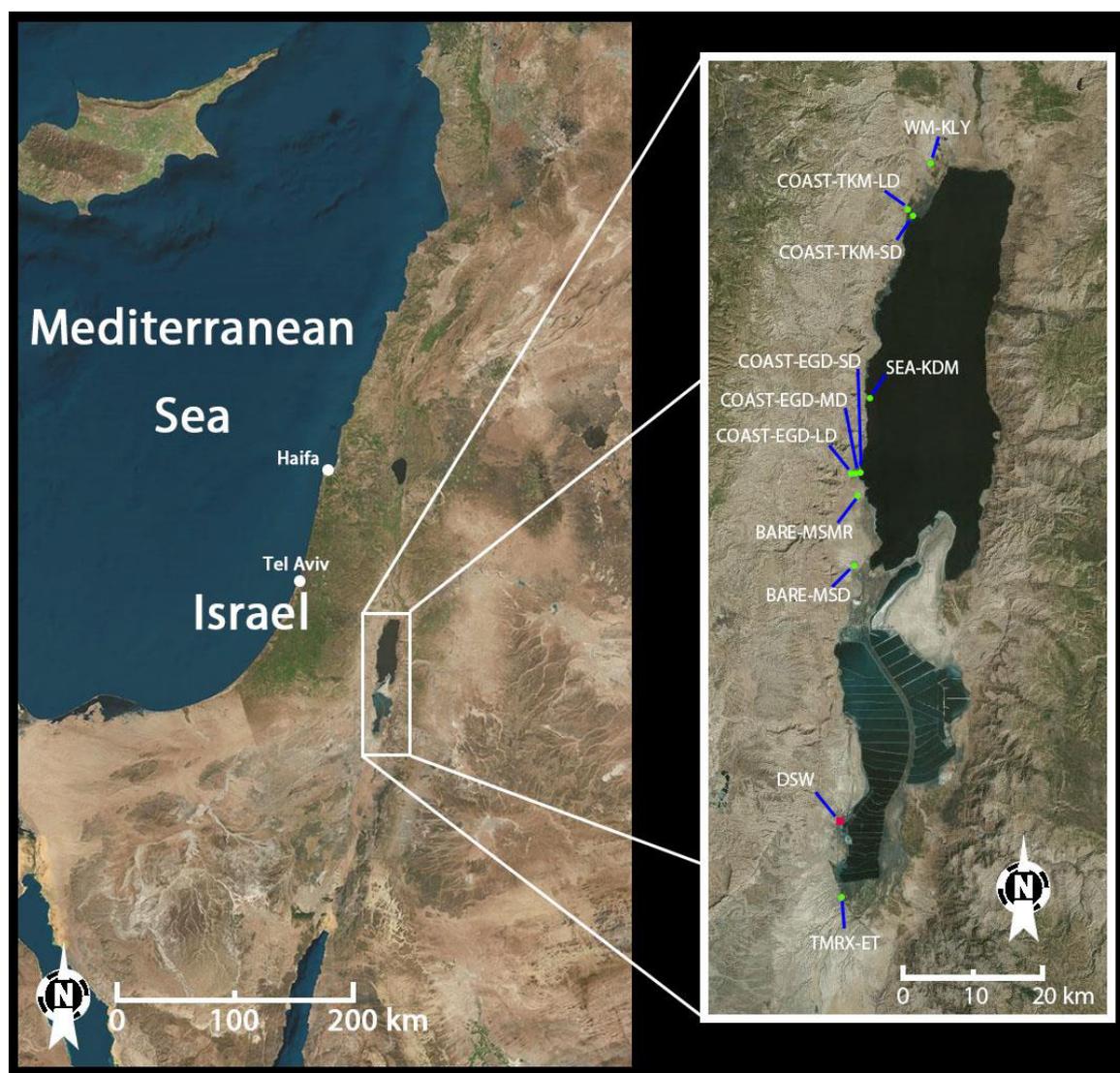
289 ^c Values indicate the number of days before sampling during-on which precipitation occurred.

290 Additional abbreviations: MSD, Masada; MSM^{SR}, 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 CH₃Cl 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 ϕ_c is a universal function of the dimensionless parameter ζ . According to MOST, vertical
309 fluxes in the surface layer can be evaluated on the basis of the dimensionless length parameter,
310 ζ , 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 ϕ_c is similar to ϕ_h for chemical species
315 with a relatively long lifetime (Dearellano et al., 1995), and calculated ϕ_h using the following
316 equation for the relationship between ϕ_h and ζ , 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 ψ_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 ψ_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 HNO₃ (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 AgNO₃.

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 (HNO₃ (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**

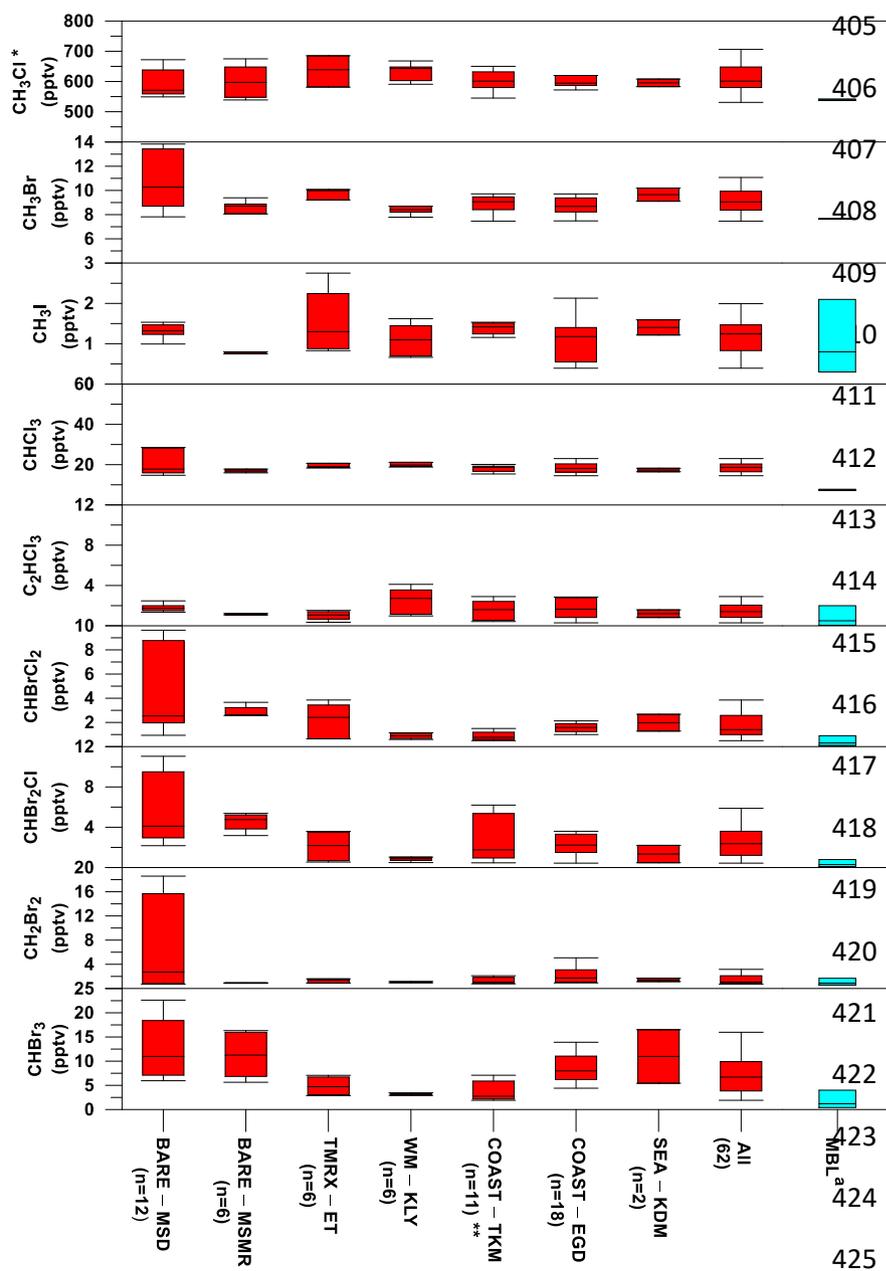
357 **3.1 VHOC flux and mixing ratio**

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 C₂HCl₃ was associated with C₂Cl₄, 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 VSLSS and ~1.5, 1.3
375 and 1.1 for CH₃I, CH₃Br and CH₃Cl, 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, CHBr₃ and CH₂Br₂ are the most
386 extensively studied VSLSS in the MBL (Hossaini et al., 2010). The mixing ratios of CHBr₃ and
387 CH₂Br₂ 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 CHBr₃ and CH₂Br₂ 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 CHBr₃ and CH₂Br₂, 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 CHBr₃ 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 CH₂Br₂, 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).^a -Values for CH₃Cl and CH₃Br 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 CH₃Cl 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 C₂HCl₃ and CH₃I, 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 CHCl₃, C₂HCl₃ and CH₃I. Note that as explained above, C₂HCl₃ 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 CHCl₃, C₂HCl₃ and CH₃I. 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 ~~pues are used here to ,pues of and also indicated when present~~The flux magnitudes for
463 CHBr₃ and CH₂Br₂ were ~~higher greater~~ than for most reported emissions ~~at-in~~ the MBL ~~((e.g.,~~
464 ~~CHBr₃, 25.2–62.88 nmol m⁻² d⁻¹ for the Mauritanian upwelling (Quack et al., 2007); CH₂Br₂,~~
465 ~~0.14–0.29 nmol m⁻² d⁻¹ 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⁻² d⁻¹~~), respectively) ~~and from than the average flux from~~
468 ~~the New Hampshire coast as reported by Zhou et al. (2005) (~620 ± 1370 nmol m⁻² d⁻¹ and~~
469 ~~113 ± 130 nmol m⁻² d⁻¹, respectively).~~ ~~In some cases, however, the fluxes of both species~~
470 ~~were higher than these values.~~

471 Relatively high positive CHCl₃ fluxes were measured for ~~CHCl₃ emission rates were~~
472 ~~positive for most measurements and particularly high for including BARE-MSMR (247 nmol~~
473 ~~m⁻² d⁻¹), TMRX-ET-2 (213 nmol m⁻² d⁻¹) and for, COAST-EGD-SD-s (883 nmol m⁻² d⁻¹),~~
474 ~~and although the two latter two sites were not identified as a net source for CHCl₃ (Table 2).~~
475 ~~BARE-MSMR-1 (247 nmol m⁻² d⁻¹) (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⁻² d⁻¹ 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 ~~CHBr₂Cl₇ and CHBrCl₂ were positive for all sites except for CHBr₂Cl at COAST-TKM (Fig.~~
487 3). The mixing ratios of CHBr₂Cl and CHBrCl₂ were higher by factors of ~ 4 – 14 and ~ 5 – 11 ,
488 respectively, than the average reported values for the MBL₂ and were also higher than the
489 ~~measured~~ mixing ratios measured in nearby coastal areas, except for the extremely high
490 CHBr₂Cl 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 CHBr₂Cl and CHBrCl₂ 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 CHBr₂Cl and CHBrCl₂ mixing
494 ratios of 0.07–0.15 ppt and 0.15–0.22 ppt, respectively, in the tropics. The measured CHBr₂Cl
495 fluxes ~~that we obtained~~ for CHBr₂Cl 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 CHBrCl₂ ~~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⁻² d⁻¹.

501 COAST-TKM and COAST-EGD-SD were found asto be the only net source sites for
502 CH₃Cl ~~The CH₃Cl 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 CH_3Br (Table 2). In contrast to CH_3Cl ,
515 emissions of CH_3Br 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 CH_3I measured at the Dead Sea was negative in 60 % of the~~
521 ~~measurements~~ Similar to CH_3Br and CH_3Cl , for CH_3I , 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 CH_3I . 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 CH_3I 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 CH_3I reported by Sive et al. (2007) at Duke Forest, averaging ~ 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 suggest ing 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.

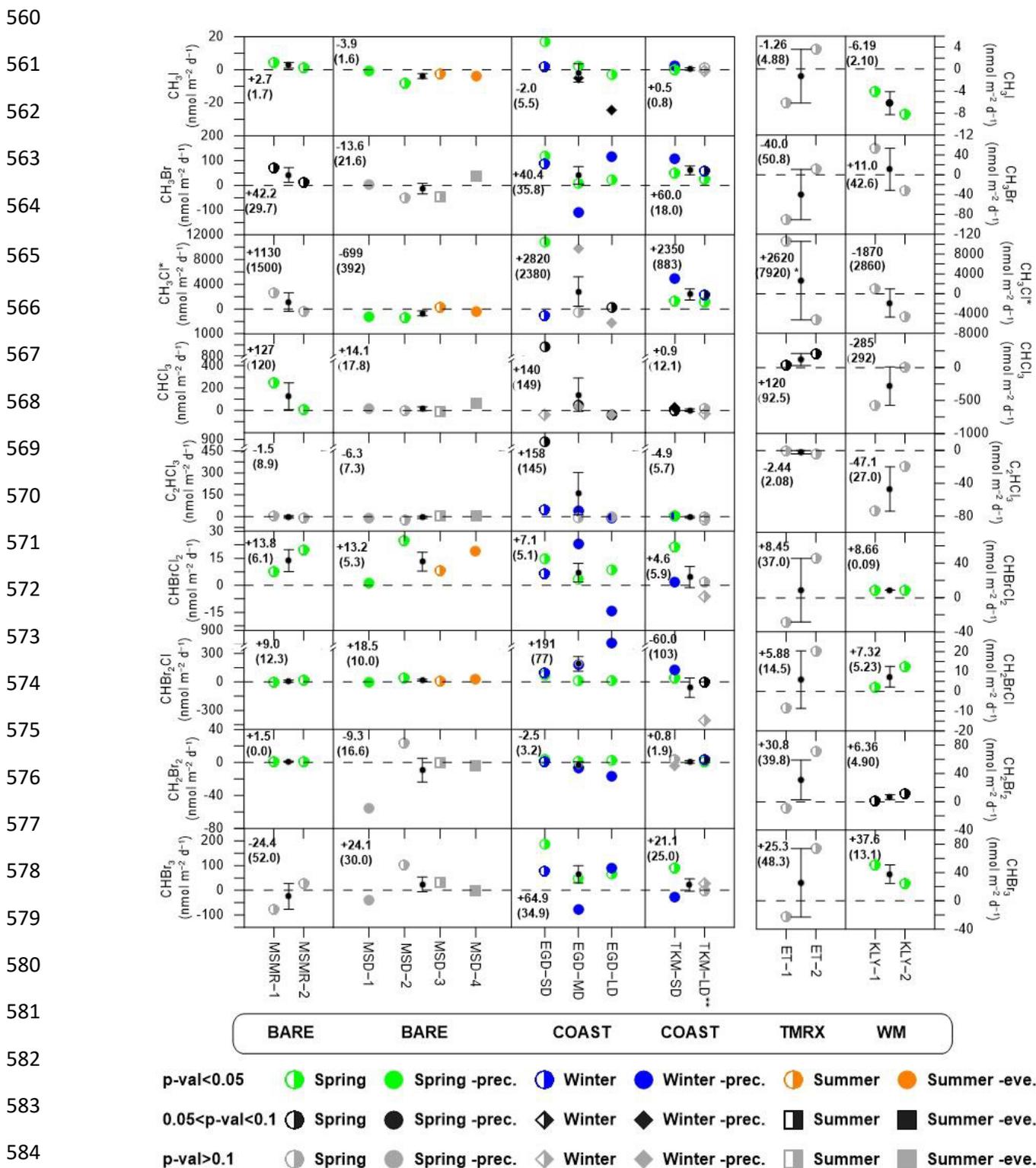
545 **Table 42.** VHOC fluxes for the different measurement sites and its correspondence with mixing ratios. Shown are
546 the measured flux ($\text{nmol m}^{-2} \text{d}^{-1}$); obtained for the different measurements. Values in bold and in parentheses
547 indicate that the related measurement site 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 ₂ Br ₂	CHBr ₃	CHBr ₂ Cl	CHBrCl ₂	CHCl ₃	C ₂ HCl ₃	CH ₃ Cl	CH ₃ Br	CH ₃ I	X (%)	
BARE-MSMR-1	1.43	(-76.5)	-3.27	7.68	247	(7.33)	(2629)	71.9^{b9a}	4.42	33 (78)	
BARE-MSMR-2	1.51	(27.6)	21.3	19.9	6.51	(-10.4)	(-378)	12.6^{b6a}	1.00	44 (78)	
BARE-MSD-1	(-55.4)	(-37.7)	-3.58	1.32	(12.1)	-11.0^{e0b}	-1266	(5.26)	-0.73	11 (33)	
BARE-MSD-2	(23.5)	(103)	41.8	24.5	(-6.02)	-24.8^{e8b}	-1368	(-50.3)	-8.14	22 (44)	
BARE-MSD-3	(-0.60)	(32)	8.69	7.92	(-14.6)	4.32^{e32b}	311	(-47.9)	-2.95	22 (56)	
BARE-MSD-4	(-4.61)	(-1.41)	26.96	19.1	(64.7)	6.39^{e39b}	-472	(38.44)	-3.58	22 (56)	
COAST-EGD-SD-w	0.85	78.1	90.0	6.63	(-42.8)	47.3	-1040	88.4	1.45	78 (78)	
COAST-EGD-MD-w	-6.53	-79.0	187	23.1	(38.5)	37.5	(9719)	-111	-5.46^{b16a}	33 (56)	
COAST-EGD-LD-w	-16.7	88.7	768	-14.2	(-43.7)	-8.97	(-2281)	116	-24.5^{b5a}	33 (33)	
COAST-EGD-SD-s	3.71	187	72.3	14.8	883 ^b	884^{b884a}	10817	118	17.0	78 (100)	
COAST-EGD-MD-s	1.35	48.6	13.4	3.42	46.4^{b4a}	-8.39^{e39b}	(-530)	8.10	2.27	67 (78)	
COAST-EGD-LD-s	2.52	66.0	13.8	8.68	-40.8^{b8a}	-2.03^{e03b}	261^{b261a}	22.3	-2.96	56 (67)	
COAST-TKM-SD-w	-4.45^{e15b}	-28.1	123	1.62	22.8^{b8a}	0.89	4895	110	2.42	67 (78)	
COAST-TKM-LD-w	2.95	(28.5)	(-408)	(-6.2)	(-32.9)	-22.0^{e0b}	2200	57.3	(-1.03)	33 (44)	
COAST-TKM-SD-s	3.80^{e80b}	87.7	42.7	21.4	0.99^{b99a}	2.00	1210	49.3	-0.38	67 (89)	
COAST-TKM-LD-s*	0.56	(-3.83)	2.07^{b07a}	(1.67)	(12.6)	-0.34^{e31b}	1100	23.6	(0.97)	33 (78)	
TMRX-ET-1**	(-8.93)	(-23.0)	(-8.64)	(-28.5)	27.6^{b6a}	-0.36^{e36b}	(10500*)	(-90.8)	(-6.14)	0 (11)	
TMRX-ET-2	(70.6)	(73.7)	(20.4)	(45.4)	213^{b213a}	-4.53^{e53b}	(-5300)	(10.9)	(3.61)	0 (78)	
WM-KLY-1	1.45^{b45a}	50.7	2.09	8.57	(-577)	-74.4^{e1b}	(983)	(53.5)	-4.01	33 (56)	
WM-KLY-2	11.3^{b3a}	24.5	12.6	8.76	(6.31)	-20.0^{e0b}	(-4730)	(-31.6)	-8.29	33 (67)	
Mean	S NS	-0.84 (1.43)	52.4 (32.3)	88.5 (51.1)	10.2 (8.78)	70.9 (41.2)	-2.2 (40.1)	1640 (1360)	48.2 (22.7)	-2.75 (-1.74)	
Mean positive	S NS	1.86 (9.66)	78.9 (68.9)	102 (90.4)	11.8 (13.2)	127 (122)	21.9 (124)	3400 (4060)	65.9 (52.4)	6.17 (4.14)	
X (%)	S NS	40 (65)	40 (65)	70 (80)	75 (85)	10 (65)	20 (40)	30 (55)	45 (75)	20 (40)	

555 ^a $0.05 < p < 0.1$ for a measurement site as net source or sink for a specific species.
 556 ^b $0.1 < p < 0.15$ 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 CH_2Cl 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 CH_3Cl 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 CH_3Cl measurement in TMRX-ET-1~~
603 ~~(see Sect. 2.1.2).~~

604

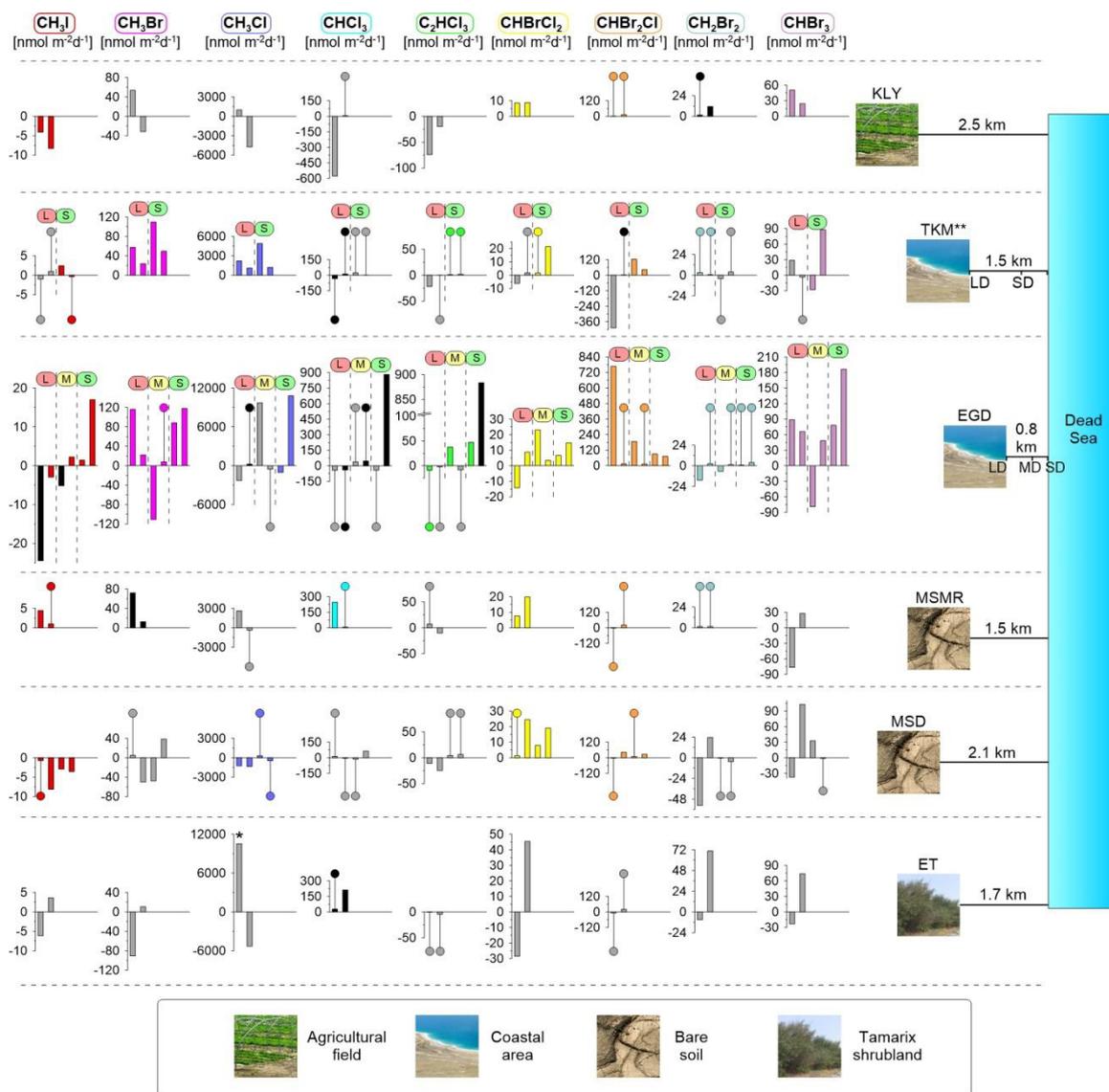
605 **3.2 Factors controlling the VHOC flux of VHOCs**

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 CH_3I , CHCl_3 and C_2HCl_3 .
609 ~~For All~~ of the investigated VHOCs, ~~a except C_2HCl_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 (CH_2Br_2 , CHBr_2Cl , CHBrCl_2 and 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 C₂HCl₃ and CH₃Cl, ~~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. * $\text{-CH}_3\text{Cl}$ 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.**

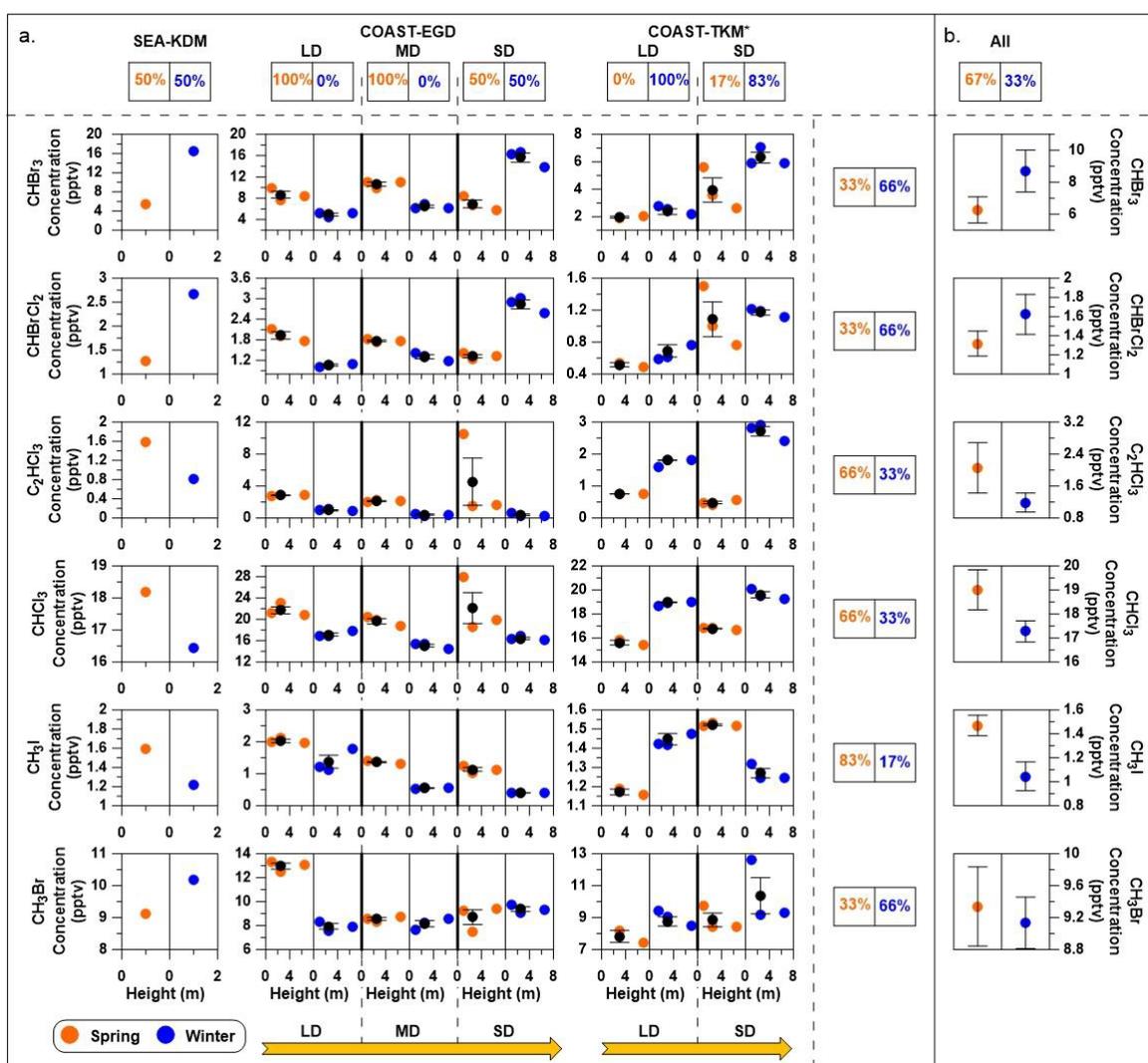
640 Our findings on the effects of season and distance from the sea on the measured fluxes are
641 presented in Fig. 23, which shows the measured fluxes for spring and winter and for different
642 distances from the sea at COAST-EGD and COAST-TKM. Differences in VHOCs emissions
643 between winter and 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 CH₃I and CH₂Br₂ 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 CH₃I, CHBrCl₂ and CH₂Br₂ 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 CH₃I 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 spring 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⁻¹ and 6.1–120 g kg⁻¹, 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-SD₂ both soil
740 water and OM content were relatively high, for COAST-EGD-SD₂ 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 C₂HCl₃ and CH₃Cl (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~~ CH₃Cl positive fluxes ~~and~~ CHCl₃. 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 C₂HCl₃), 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 CHBr₃ and CH₃Br). 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⁻¹</u>	<u>Br</u> <u>µg kg soil dw⁻¹</u>	<u>Cl</u> <u>µg kg soil dw⁻¹</u>	<u>Fe</u> <u>mg kg soil dw⁻¹</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 CH₃Cl 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 CHCl₃ 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 (CHBr₂Cl > CHBr₃ > CHBrCl₂ > CHCl₃; see Table 4). ~~The overall average net flux of the~~
 812 trihalomethanes decreased according to CHBr₂Cl > CHCl₃ > CHBr₃ > CHBrCl₂, while CHCl₃
 813 showed the lowest incidence of positive and highest mean positive fluxes among all
 814 trihalomethanes. ~~When averaging over the positive fluxes only, CHCl₃ 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~~ CHCl₃ 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 ≥ 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 ($\sim 7.4\text{--}7.9$; 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 CHCl_3 and 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 CHBr_2Cl and 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 CHBr_2Cl and 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 enrichment mainly enhances the emission of CHBr_3 and CHBr_2Cl ,
852 rather than that of CHBrCl_2 , supports the former possibility, namely, relatively elevated
853 emission of CHBr_2Cl and 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 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 CHCl_3 , the methyl halides CH_3Cl , CH_3Br , and CH_3I , and more statistically
870 significantly so for CH_3Cl and CH_3I , 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 CH_3Cl 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 CH_3Cl (Rhew et al., 2003). The relatively high positive net fluxes of CH_3Cl and
876 CH_3Br 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 CH_3I 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 CH_3I flux of $\sim 0.27 \text{ nmol}$
886 $\text{m}^{-2} \text{d}^{-1}$ on average (ranging from ~ 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 CH_3I fluxes
890 were higher in spring than in winter, except for COAST-TKM-SD (Fig. 23). Also, in 83% of
891 the measurements the CH_3I mixing ratios were higher in spring than in winter As discussed in

892 Sect. 3.2.1, the mixing ratios of CH₃I 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 CH₃Cl and CH₃Br, and to a lesser extent of CH₃I, 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 CH₃Br and CH₃Cl, 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 CH₃I > CH₃Br > CH₃Cl (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 ~~57.715:1.564:1~~ for CH₃I, CH₃Br and CH₃Cl, 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:~~ CH₃Cl < CH₃Br < CH₃I, in agreement with
921 Keppler et al. (2000), ~~suggesting. These findings suggest~~ that at least the methylation and
922 emission of CH₃Br and CH₃Cl in our study were controlled by abiotic mechanisms similar to
923 those reported by Keppler et al. (2000). The apparently higher relative efficiency of CH₃I
924 emission may ~~point to indicate~~ emissions of CH₃I 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 CH₃I-emission efficiency ~~of CH₃I~~
929 calculated by Keppler et al. (2000) and by us.

930 ~~C₂HCl₃: C₂HCl₃ is associated with~~ hasd -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 ~~C₂HCl₃, 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 C₂HCl₃ 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 CHCl₃ and CH₃Cl, 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 ~~CH₂Br₂: CH₂Br₂ 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 CH₂Br₂ 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 (~~r² < 0.1~~), but were
954 substantially higher for the brominated trihalomethanes [~~CHBr₃-CHBrCl₂ (r² = 0.6279),~~
955 ~~CHBr₂Cl-CHBrCl₂ (r² = 0.7587), and CHBr₂Cl-CHBr₃ (r² = 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 CH₃Cl
959 and CH₃Br (~~r² = 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 C₂HCl₃ and CHCl₃. 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 CHCl₃ with all the methyl halides CH₃Cl, CH₃Br~~
966 ~~and CH₃I (with r² 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, $p > 0.15$; ^a $p < 0.1$; ^b $p < 0.15$.

		CHBrCl ₂	CHBr ₃	CHBr ₂ Cl	CHCl ₃	CH ₂ Br ₂	C ₂ HCl ₃	CH ₃ Cl	CH ₃ Br
CH ₃ I	NO-KDM (n=20)	(-0.23)	(-0.15)	(-0.15)	0.45	(0.12)	(0.17)	(0.31)	0.36
	ALL (n=22)	(-0.23)	(-0.15)	(-0.15)	0.45	(0.10)	(0.16)	(0.31)	0.36^b36^a
	BARE (n = 6)	0.76^e76^b	0.90^b90^a	0.84^b84^a	(0.32)	(-0.12)	(0.18)	(0.38)	(0.34)
COAST (n = 10)*		0.78	(0.39)	(0.57)	(0.42)	(0.24)	(0.29)	0.86	(0.55)
	SD (n = 4)	-0.95	(0.21)	(0.14)	(-0.23)	(-0.06)	(-0.41)	(0.60)	(0.63)
VEG (n = 4)		(-0.49)	(-0.45)	(-0.51)	0.86^e86^b	(0.79)	(-0.11)	0.85^eb	(0.62)
CH ₃ Br	ALL-NO-KDM	(0.19)	0.37 ^b	(0.26)	0.43	0.52	(0.19)	0.75	
	ALL	(0.18)	0.38 ^b	(0.25)	0.42	0.51	(0.17)	0.75	
	BARE (n = 6)	(0.00)	(0.01)	(-0.05)	(0.49)	0.98	(0.08)	(0.38)	
COAST (n = 10)*		(0.22)	(0.60)	(0.46)	(0.54)	(0.32)	(0.39)	0.86	
	SD (n = 4)	(-0.58)	0.88^b88^a	(0.77)	(0.56)	(0.41)	(0.41)	0.99	
VEG (n = 4)		(0.27)	(0.30)	(0.22)	(0.76)	0.93^b93^a	(-0.73)	(0.78)	
CH ₃ Cl ^{a,**}	ALL-NO-KDM	(0.04)	(0.21)	(0.13)	0.53	(0.08)	(0.12)		
	ALL	(0.00)	(0.04)	(0.02)	0.28	0.01	0.12		
	BARE (n = 6)	(0.39)	(0.71)	(0.53)	(0.70)	(0.29)	(0.18)		
COAST (n = 10)*		(0.39)	(0.50)	(0.45)	(0.36)	(0.21)	(0.29)		
	SD (n = 4)	(-0.51)	0.94^b94^a	(0.71)	(0.63)	(0.30)	(0.47)		
VEG (n = 4)		(-0.39)	(-0.35)	(-0.44)	1.00	0.95	(-0.59)		
C ₂ HCl ₃	ALL-NO-KDM	(0.11)	(0.18)	(0.16)	(0.26)	(-0.01)			
	ALL	(0.12)	(0.09)	(0.17)	0.27	0.00			
	BARE (n = 6)	(0.78)	(0.56)	(0.75)	(0.63)	(-0.12)			
COAST (n = 10)*		(0.39)	(0.50)	(0.38)	0.93	(0.24)			
	SD (n = 4)	(0.50)	(0.79)	(0.56)	0.98	(0.26)			
VEG (n = 4)		(-0.30)	(-0.32)	(-0.25)	(-0.56)	(-0.70)			
CH ₂ Br ₂	ALL-NO-KDM	(0.06)	(0.23)	(0.12)	(0.17)				
	ALL	(0.07)	(0.20)	(0.12)	(0.17)				
	BARE (n = 6)	(-0.19)	(-0.13)	(-0.24)	(0.32)				
COAST (n = 10)*		(0.67)	(0.77)	(0.52)	(0.42)				
	SD (n = 4)	(-0.18)	(0.41)	0.87^e87^b	(0.26)				
VEG (n = 4)		(-0.10)	(-0.06)	(-0.15)	0.95				
CHCl ₃	ALL-NO-KDM	0.35 ^b	(0.27)	(0.24)					
	ALL	(0.35)	(0.21)	(0.24)					
	BARE (n = 6)	0.84^b84^a	0.77 ^b ^e	0.84^b84^a					
COAST (n = 10)*		(0.51)	(0.59)	(0.57)					
	SD (n = 4)	(0.34)	0.89^b89^a	(0.63)					
VEG (n = 4)		(-0.41)	(-0.38)	(-0.46)					
CHBr ₂ Cl	ALL-NO-KDM	0.87	0.85						
	ALL	0.87	0.75						
	BARE (n = 6)	0.97	0.90						
COAST (n = 10)*		(0.17)	(0.39)						
	SD (n = 4)	(-0.25)	(0.81)						
VEG (n = 4)		1.00	1.00						
CHBr ₃	ALL-NO-KDM	0.79							
	ALL	0.69							
	BARE (n = 6)	0.76^e76^b							
COAST (n = 10)*		0.78^b78^a							
	SD (n = 4)	(-0.13)							
VEG (n = 4)		(0.76)							

974 ^aCorrelations for CH₃Cl over VEG sites were excluded one CH₃Cl 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 CH₃Cl 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 CHBr_3 and
1005 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 CHBr_3 and 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 CH_2Br_2 and both $\text{CH}_2\text{Br}_2\text{Cl}$ ($p < -0.15$) and CHBrCl_2 ($p < 0.1$) at these sites further
1011 suggests common controls for CH_2Br_2 , and the brominated trihalomethanes (see Table 5).
1012 ~~Correlation of CHCl_3 with the brominated trihalometahanes are generally either insignificant or~~
1013 ~~negative.~~

1014 ~~We also observed high correlations of CH_2Br_2 with all trihalomethanes, particularly for the~~
1015 ~~vegetated sites ($r \geq 0.77$), and somewhat lower correlations with CHCl_3 ($r = 0.55$). CH_2Br_2 also~~
1016 ~~showed high correlations with CHBrCl_2 ($r = 0.90$) and CHBr_3 ($r = 0.88$) at the SD sites,~~
1017 ~~suggesting a common emission mechanism for CH_2Br_2 and the other trihalomethanes.~~

1018 Correlation of CH_2Br_2 with CHBr_2Cl at the SD sites was strongly negative ($r = -0.93$; $p <$
1019 0.1), similar to the negative correlation between CHBr_2Cl and the other brominated
1020 trihalomethanes, CHBrCl_2 ($r = -0.98$; $p < 0.05$) and 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 CHBr_2Cl and ~~both~~ CHBrCl_2
1023 and potentially also 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 CHBr_2Cl too can~~

1028 ~~be emitted via mechanisms similar to those of the other two brominated trihalomethanes and~~
1029 ~~CH₂Br₂.~~

1030 Table ~~6-5~~ also indicates overall low correlations between CHCl₃ and all of the brominated
1031 trihalomethanes, mostly resulting from negative correlations at the ~~bare soil~~ BARE sites. There
1032 ~~anticorrelation of CHCl₃ with trihalomethanes increased in the order CHBrCl₂ < CHBr₂Cl <~~
1033 ~~CHBr₃. The incidence of the chlorinated~~ was also a higher incidence of positive fluxes at the
1034 ~~bare soil sites for the~~ trihalomethanes (CHCl₃ and CHBrCl₂), compared to the less chlorinated,
1035 ~~ones~~ (CHBr₃ and CHBr₂Cl) also tended to be higher at the BARE sites compared to the other
1036 sites (Table 42). Hence, the negative correlation between CHCl₃ 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 CHCl₃ at the expense of the more
1040 brominated species (e.g., (Albers et al., 2017; Huber et al., 2009)), particularly CHBr₃ and
1041 CHBr₂Cl. ~~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 CHBr₂Cl and CHBrCl₂,~~ 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 CHCl₃ and all methyl halides, ~~particularly for~~ the BARE sites (CH₃I, ~~r = 0.68, p <~~
1048 ~~0.15; CH₃Br, r = 0.83, p < 0.05; CH₃Cl, r < 0.86, p < 0.05), -and (r ≥ 0.68) and at the~~ SD sites
1049 (~~CH₃I, r ≥ = 0.5999, p < 0.05; CH₃Br, r = 0.59, p > 0.15; CH₃Cl, r = 0.91, p < 0.1). We also~~
1050 ~~found high correlations for the SD sites between C₂HCl₃ and all methyl halides (r ≥ 0.59).~~
1051 Remarkably, a high ~~correlation was found~~ correlations were obtained between CH₃I and the
1052 ~~brominated trihalomethanes and CH₂Br₂ at the vegetated sites (r ≥ 0.57), and for CH₃I with~~
1053 CHCl₃ and C₂HCl₃ at the SD sites (r = 0.99, ~~p < 0.05~~ in both cases). ~~In most cases the flux of~~

1054 ~~CH₃I was negative at the vegetated sites; therefore, it is not clear whether the strong correlations~~
1055 ~~between CH₃I and the brominated trihalomethanes at these sites point to common sources or~~
1056 ~~sinks. In contrast, p~~Positive fluxes of ~~both CH₃I and the brominated trihalomethanes and~~
1057 ~~CH₂Br₂~~the three species were observed at the SD sites in most cases, although with only
1058 moderate statistical significance for ~~C₂HCl₃ and CHCl₃ (Table 2), pointing to a common source~~
1059 ~~of these species at the SD sites.~~ Weissflog et al. (2005) found that emission of C₂HCl₃, CHCl₃
1060 and other chlorinated VHOCs can occur from salt lakes via the activity of halobacteria in the
1061 presence of dissolved Fe₂(III) and crystallized NaCl. The strong correlations of CHCl₃, C₂HCl₃
1062 and CH₃I (~~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 CHCl₃
1064 and C₂HCl₃ from salt lake sediments, as indicated by Weissflog et al. (2005), and ~~may also~~
1065 ~~indicate~~suggest that CH₃I can be emitted in a similar fashion. The fact that the relative emission
1066 efficiency of CH₃I 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 CH₃I at the Dead Sea
1069 (Sect. 3.2.3).

1070 ~~The relatively high correlations between fluxes of CHCl₃ and C₂HCl₃ and the other methyl~~
1071 ~~halides, CH₃Br and CH₃Cl, 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, $p > 0.15$; ^a $p < 0.1$; ^b $p < 0.15$.

		CHBrCl ₂	CHBr ₃	CHBr ₂ Cl	CHCl ₃	CH ₂ Br ₂	C ₂ HCl ₃	CH ₃ Cl	CH ₃ Br
CH ₃ I	All (n = 20)	0.34 ^b _e	(0.13)	-0.56	0.59	(0.19)	0.59	0.45	(0.23)
	BARE (n = 6)	(-0.54)	-0.85	-0.78	0.68 ^e 68 ^b	(-0.32)	(0.54)	0.73 ^b 73 ^a	0.77 ^b 77 ^a
	COAST (n = 10)*	0.50 ^e 50 ^b	(0.26)	-0.64	0.66	0.81	0.63	0.54 ^b	(0.08)
	SD (n = 4)	(0.13)	(0.72)	(-0.05)	0.99	(0.35)	0.99	0.90 ^b	(0.69)
	VEG (n = 4)	(0.76)	(0.72)	(0.57)	(0.31)	0.88 ^{eb}	(0.16)	(0.11)	0.45
CH ₃ Br	All (n = 20)	(-0.08)	0.39 ^b 39 ^a	(0.22)	(0.20)	(-0.06)	0.33 ^c	(0.30)	
	BARE (n = 6)	(-0.22)	-0.83	(-0.45)	0.83	(-0.21)	(0.57)	(0.61)	
	COAST (n = 10)*		0.65	(0.19)	(0.29)	(-0.04)	(0.33)	(-0.24)	
	SD (n = 4)	0.51 ^b 51 ^a	(0.07)	(0.69)	(0.59)	(-0.40)	(0.59)	(0.69)	
	VEG (n = 4)	(0.67)	0.87 ^e 87 ^b	(0.47)	(-0.57)	(0.36)	(-0.76)	0.94	
CH ₃ Cl**	All (n = 19)	(0.27)	(0.05)	(0.00)	-0.37 ^b	(-0.15)	0.54		
	BARE (n = 6)	(-0.33)	(-0.63)	(-0.54)	0.86	(0.21)	0.74 ^e 71 ^b		
	COAST (n = 10)*	0.58 ^b 58 ^a	(-0.09)	(-0.16)	0.69	(0.14)	0.66		
	SD (n = 4)	(0.07)	(0.45)	(0.08)	0.94 ^b 91 ^a	(0.12)	0.86 ^e 86 ^b		
	VEG (n = 3)	(0.45)	(0.68)	(0.31)	(-0.75)	(0.06)	(-0.91)		
C ₂ HCl ₃	All (n = 20)	(0.10)	0.53	(0.05)	0.83	(0.02)			
	Bare (n = 6)	(-0.41)	-0.66 ^e 66 ^b	(-0.52)	(0.56)	(-0.10)			
	COAST (n = 10)*	(0.30)	0.65	(-0.01)	0.99	(0.26)			
	SD (n = 4)	(0.26)	(0.81)	(-0.19)	0.99	(0.48)			
	VEG (n = 4)	(-0.05)	(-0.34)	(0.12)	0.96	(0.33)			
CH ₂ Br ₂	All (n = 20)	0.62	0.36 ^e 36 ^b	(-0.17)	(0.15)				
	BARE (n = 6)	0.77 ^b 77 ^a	(0.58)	0.68 ^c	(0.08)				
	COAST (n = 10)*	(0.45)	(0.26)	-0.85	(0.27)				
	SD (n = 4)	0.90 ^b 90 ^a	0.88 ^c	-0.93 ^b 93 ^a	(0.45)				
	VEG (n = 4)	0.94 ^b 91 ^a	0.77 ^b	0.87 ^e 87 ^b	(0.55)				
CHCl ₃	All (n = 20)	(0.01)	(0.30)	(0.01)					
	BARE (n = 6)	(-0.25)	-0.74 ^b 74 ^a	(-0.46)					
	COAST (n = 10)*	(0.31)	0.60 ^b 60 ^a	(-0.04)					
	SD (n = 4)	(0.27)	(0.77)	(-0.18)					
	VEG (n = 4)	(0.22)	(-0.09)	(0.40)					
CHBr ₂ Cl	All (n = 20)	(-0.11)	(0.16)						
	Bare (n = 6)	0.95	0.86						
	COAST (n = 10)*	(-0.22)	(0.11)						
	SD (n = 4)	-0.98	(-0.65)						
	VEG (n = 4)	0.94	(0.82)						
CHBr ₃	All (n = 20)	(0.22)							
	BARE (n = 6)	0.72 ^b 72 ^a							
	COAST (n = 10)*	(-0.04)							
	SD (n = 4)	(0.65)							
	VEG (n = 4)	0.95							

1078 ^a - Correlations for CH₃Cl over VEG sites were excluded one CH₃Cl measurement in at TMRX-ET-1 (see Sect.
 1079 2.1.2).

1080 ^{*} - Correlations calculations for COAST-TKM-LD excluded one sampling canister (see Sect. 2.1.2).

1081 ^{**} - Correlation calculation for CH₃Cl₂ 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 ~~CHCl₃, 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 CH₃I
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 partsome 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 fewThe 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 CHCl₃, which were
1102 ambiguousFurther from the coastal area, the bare soil sites were found as a sources for
1103 CHBrCl₂, CHBr₂Cl, CHCl₃, and apparently also for CH₂Br₂ and CH₃I, and the agricultural
1104 vegetation site was a source for CHBr₃, CHBr₂Cl and CHBrCl₂. Our measurements reinforce
1105 reports of -CHCl₃ and CHBrCl₂ 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 CHBr₂Cl and emission of CH₂Br₂ 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 CH₃I and C₂HCl₃ 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 CHCl₃, CHBr₂Cl, CHBr₃ and particularly CHBrCl₂, are~~
1128 ~~associated with the highest number of sites at which their flux was, on average, positive, while~~
1129 ~~CHBr₃, CHBr₂Cl and CHBrCl₂ 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 CHBr₂Cl and CHBrCl₂, 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 CHBr₃ 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 ~~CH₂Br₂ via mechanisms that are common to the trihalomethanes. Correlation of the brominated~~
1138 ~~trihalomethanes with CHCl₃ was lower.~~ Whereas Albers et al. (2017) suggested that CHBr₃ and
1139 CHBr₂Cl are emitted from soil only in relatively small amounts compared to CHCl₃, 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 CHBr₂Cl > CHCl₃ >
1142 CHBr₃ > CHBrCl₂ > CHCl₃, while CHCl₃ 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 CHBr₃ and CHBr₂Cl rather~~
1146 ~~than of CHBrCl₂ 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 CH₃I. Comparing the proportion of Br and Cl in the soil
1151 ~~for the various sites with proportions of measured positive flux of CH₃Br and CH₃Cl 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 CH₃I emission than of CH₃Br and CH₃Cl 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 CH₃I via other mechanisms. The strong correlation between both fluxes and mixing
1157 ratios of CH₃I, CHCl₃ and C₂HCl₃, ~~high correlation of CH₃I emission with that of CHCl₃ and~~
1158 ~~C₂HCl₃,~~ particularly at the SD sites, strongly suggests that, the coastal area of the Dead Sea acts
1159 as an emission source for CHCl₃, C₂HCl₃ and CH₃I via similar mechanisms, although these sites
1160 were associated with only moderate statistical significance ($p < 0.1$) as a net source for CHCl₃.

1161 The emission of CHCl₃ and C₂HCl₃ from these sites is in line with findings by
1162 Weissflog et al. (2005), of emission of various chlorinated VHOCs, including CHCl₃
1163 and C₂HCl₃, from salt lake sediments, ~~suggests that the Dead Sea, particularly the SD, sites~~
1164 ~~probably act as an emission source for CHCl₃, C₂HCl₃ and CH₃I 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 CH₃I and both CHCl₃ and C₂HCl₃ 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, CHBr₃ showed the
1174 highest enrichment with respect to MBL mixing ratios. Owing to the relatively short
1175 tropospheric lifetime of CHBr₃, its photolysis contributes significantly to reactive bromine
1176 formation in the MBL. However, although relatively high, the elevated CHBr₃ 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 CH₃I
1181 photolysis is the only source of reactive iodine species, the measured fluxes and elevated
1182 mixing ratios of CH₃I are not high enough to account for the high iodine monoxide(?) in this
1183 area. Given their relatively fast photolysis, however, CH₃I and CHBr₃, as well as CH₂Br₂, 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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1207

1208 **References**

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