Supplement of Atmos. Chem. Phys., 19, 7667–7690, 2019
https://doi.org/10.5194/acp-19-7667-2019-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Emission of volatile halogenated organic compounds over various Dead Sea landscapes

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S1. Lifetime and main sink pathways for the investigated VHOCs

Table S1. Average lifetimes and primary removal pathways for the VHOCs[a].

Species	Average lifetime	Primary removal pathway
$CHBr_3$	15 days	J[c] >OH
CH_2Br_2	94 days	OH
$CHBr_2Cl$	32 days	OH>J
$CHBrCl_2$	41 days	OH>J
C_2HCl_3	5 days	OH
$CHCl_3$	112 days	OH
CH_3I	4 days	J>OH
CH_3Br	1.8 years [b]	OH>loss in soil>loss in ocean
CH_3Cl	1.57 years [b]	OH>loss in ocean>loss in soil

[a] See more details in (Carpenter et al., 2014).

[b] Partial lifetime against reaction with OH.

[c] J, photolysis first-order rate coefficient.

S2. Specification of the mass spectrometry instrumentation and techniques

Table S2. Specification of instrumentation and techniques used to analyze the sampled gas and corresponding precision.

Species	System[a]	Precision (%)
$CHBr_3$	D, MSD	1.6
CH_2Br_2	D	1.6
$CHBr_2Cl$	D	9.3
$CHBrCl_2$	D	2.0
CH_2Cl_2	C, MSD	4.5
C_2HCl_3	MSD	≤ 5.0
$CHCl_3$	C, D , MSD	1.1
CH_3I	C,D	1.1
CH_3Br	MSD	1.7
CH_3Cl	B, MSD	1.5

[a] Indicates the applied column and detector for quantifying species concentration: B, DB-1 column + flame ionization detector (FID); C, DB-5 column + electron-capture detector (ECD); D, RESTEK1701 column + ECD; MSD, DB-5 MS column + mass spectrometer.

S3. Measured VHOC mixing ratios

Table S3 compares the measured mixing ratios at the different measurement sites and reported values for the global marine boundary layer (MBL).

Table S3. Comparison of VHOC mixing ratios (in pptv) measured at the Dead Sea to their corresponding values at the marine boundary layer (MBL). Unless otherwise specified, the table presents median, minimum and maximum VHOC mixing ratios measured at different sites at the Dead Sea (see Table 1 in the main text for site abbreviations) and in the MBL as reported by Carpenter et al. (2014).

Species	Median/ range	BARE−MSMR	BARE−MSD	COAST−EGD	COAST−TKM	TMRX−ET	WM−KLY	SEA−KDM	All sites	MBL
$CHBr_3$	Median	11.3	11.0	8.0	2.6	4.7	3.1	11.0	**6.2**	**1.2**
	Range	5.6−16.3	6.0−22.6	4.4−16.8	3.6−1.9	2.9−7.1	2.3−3. 5	5.4−16.5	**1.9−22.6**	**0.4-4.0**
CH_2Br_2	Median	0.9	2.7	1.8	0.8	1.3	1.1	1.4	**1.1**	**0.9**
	Range	0.9−1.0	0.7−18.6	0.9−5.1	0.9−0.8	0.9−1.6	1.0−1.2	1.1−1.7	**0.7−18.6**	**0.6-1.7**
$CHBr_2Cl$	Median	4.8	4.1	2.2	1.2	2.2	0.9	1.3	**2.4**	**0.3**
	Range	3.2 −5.4	2.2−11.0	0.4−6.5	7.5−0.5	0.6−3.6	0.5−1.0	0.5−2.2	**0.4−11.0**	**0.1-0.8**
$CHBrCl_2$	Median	2.6	2.5	1.6	1.0	2.4	0.9	2.0	**1.4**	**0.3**
	Range	2.6−3.7	0.9−9.6	1.0−3.0	0.5−1.4	0.7−3.9	0.6−1.1	1.3−2.7	**0.5−9.6**	**0.1-0.9**
C_2HCl_3	Median	1.15	1.7	1.3	1.6	1.1	2.7	1.2	**1.5**	**0.5**
	Range	0.84-1.22	1.0−2.7	0.3−10.5	0.4−2.9	0.4−1.5	1.0−4.1	0.8−1.6	**0.4−10.5**	**0.05-2**
$CHCl_3$	Median	16.9	19.8	18.2	18.7	19.0	19.8	17.3	**18.63**	**7.5**
	Range	15.9−20. 5	18.8−25.3	14.5−27.9	15.4−20.1	18.4−57.2	18.8−5.3	16.5−18.2	**14.5−57.2**	**7.3-7.8**
CH_3I	Median	0.8	1.3	1.2	1.5	1.3	1.1	1.4	**1.2**	**0.8**
	Range	0.8−0.8	1.0−1.5	0.4−2.1	1.5−1.2	0.8−2.8	0.7−1.6	1.2−1.6	**0.4−2.8**	**0.3-2.1**
CH_3Br	Mean	8.6	10.6	9.29	9.12	10.2	8.45	9.65	**9.1**	**7.01[a]**
	Range	8.1−9.4	7.8−13.8	7.5−13.3	8.5−7.5	8.3−13.8	7.8−9.2	9.1−10.2	**7.5−13.8**	**6.95-7.07[a]**
CH_3Cl	Mean	601	592	617	614	744	633	596	**601**	**540[a]**
	Range	583−608	549−672	531−732	583−545	581−685*	591−668	583−608	**531−732***	**537-542[a]**

[a]Mean and range for 2012 based on flask measurements by the US National Oceanic and Atmospheric Administration (NOAA) (http://www.esrl.noaa.gov/gmd/dv/site/) and in situ measurements by the Advanced Global Atmospheric Gases Experiment (AGAGE) (http://agage.eas.gatech.edu/). Measurements are taken from ground stations, which do not represent the MBL in all cases. See Table 1 in the main text for site abbreviations.

*Calculation excludes one CH_3Cl measurement at TMRX−ET-1 (see Sect. 2.1.2 in main text).

Figure S1 compares the mixing ratios of the measured VHOCs at different distances from the seawater, and individually for winter and spring. No clear impact of season or distance from the seawater on the mixing ratios can be discerned in this figure, or for the sample taken at SEA−KDM, the latter directly representing air masses over the seawater (Sect. 2.1.1 in the main text). Additional discussion of these results is included in Sect. 3.2.1 in the main text.

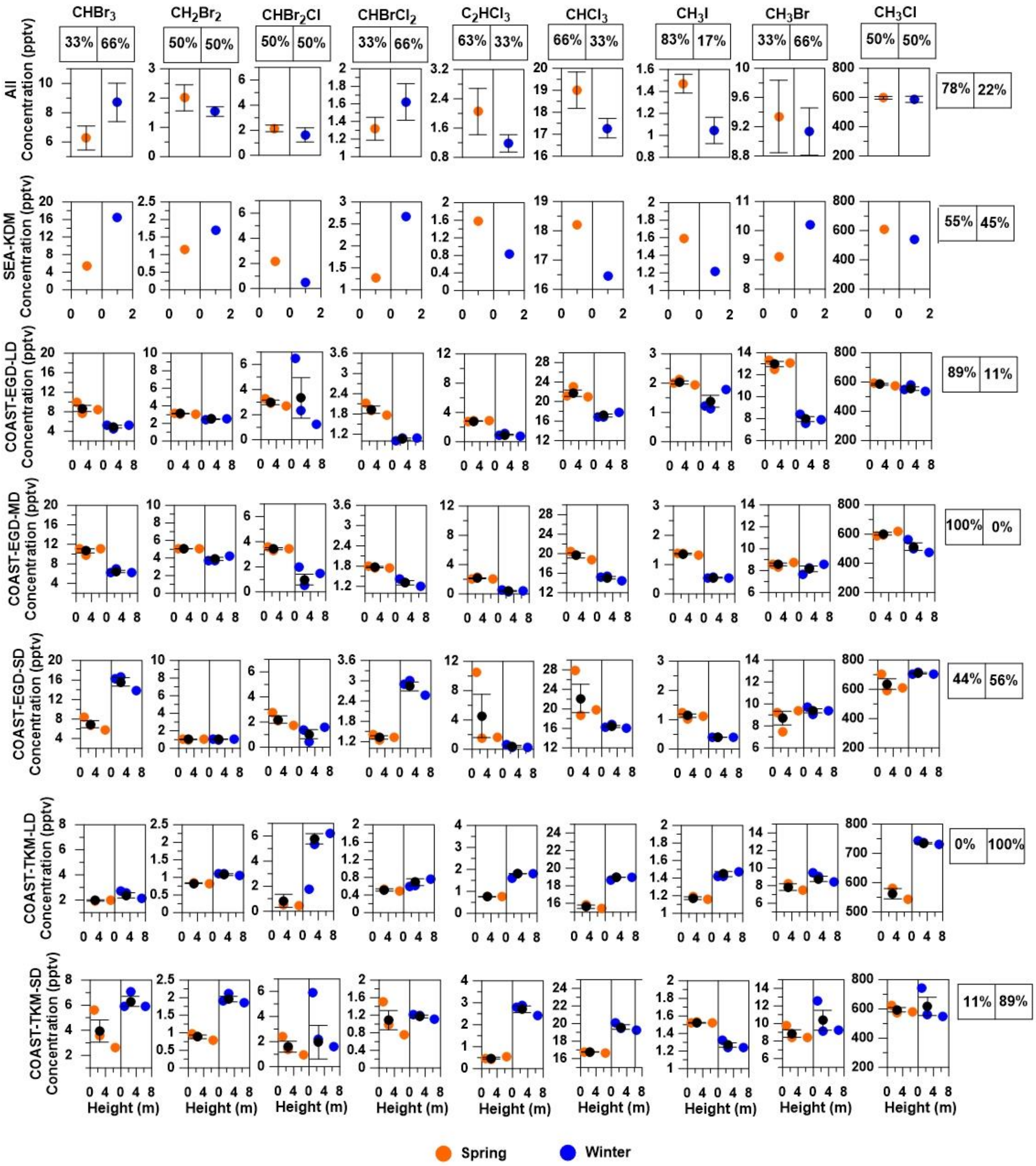

Figure S1. Seasonal and spatial influences on measured mixing ratios of VHOCs. Measured VHOC mixing ratios are presented vs. vertical height above surface level, separately for winter (blue) and spring (orange). Black filled circles and error bars represent average and standard error of the mean, respectively. Values above and to the right of the figure indicate the percentage of time during which average mixing ratios were higher in the spring (left box) or in the winter (right box), individually for COAST–TKM, COAST–EGD and SEA−KDM sites, and for all of these sites together (All), for all sites and all species, respectively (see Table 1 in the main text for measurement site abbreviations).

S4. Sampling footprints

Table S4. Calculated footprint following the methodology of Schuepp et al. (1990). The table shows the date, time, site name (and abbreviation), sampling heights and 80% and 90% footprints for the lowest (low) and highest (high) canister during each measurement.

Date dd/m/yyyy	Time (local)	Site name / measurement abbreviation [a]	Sampling height (m)	80% footprint low (m)	80% footprint high (m)	90% footprint low (m)	90% footprint high (m)
20/4/2016	08:45–08:55	BARE−MSMR / BARE−MSMR-1	2.5, 4.5, 7.0	293.5	954.9	621.7	2022.3
21/4/2016	08:45–08:55	WM−KLY / WM−KLY-1	1.0,2.0,4.0	105.7	502.6	223.9	1064.5
02/5/2016	08:45–08:55	TMRX−ET / TMRX−ET-1	4.5, 5.5, 7.5	135.6	444.2	287.2	940.8
03/5/2016	08:45–08:55	WM−KLY / WM−KLY-2	1.0, 2.0, 4.0	105.7	502.6	223.9	1064.5
25/5/2016	08:30–08:40	BARE−MSD / BARE−MSD-1	1.25, 2.5, 5	126.2	643.3	267.3	1362.4
26/5/2016	08:30–08:40	BARE−MSD / BARE−MSD-2	1.25, 2.5, 5	126.2	643.3	267.3	1362.4
30/5/2016	12:00–12:10	TMRX−ET / TMRX−ET-2	4.5, 5.5, 7.5	135.6	444.2	287.2	940.8
31/5/2016	12:00–12:10	BARE−MSMR / BARE−MSMR-2	2.5, 4.5, 7	293.5	954.9	621.7	2022.3
11/7/2016	12:00–12:20	BARE−MSD / BARE−MSD-3	1.25, 2.5, 5	126.2	643.3	267.3	1362.4
11/7/2016	18:00–18:20	BARE−MSD / BARE−MSD-4	1.25, 2.5, 5	126.2	643.3	267.3	1362.4
21/2/2017	11:20–11:40	COAST−TKM-SD / COAST−TKM-SD-w	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
22/2/2017	11:00–11:20	COAST−TKM-LD / COAST−TKM-LD-w	1.5, 3, 7	94.1	717.5	199.3	1519.6
28/2/2017	11:20–11:40	COAST−EGD-SD / COAST−EGD-SD-w	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
01/3/2017	11:07–11:27	COAST−EGD-MD / COAST−EGD-MD-w	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
02/3/2017	11:00–11:20	COAST−EGD-LD / COAST−EGD-LD-w	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
25/4/2017	11:30–11:50	COAS-EGD-SD / COAST−EGD-SD-s	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
26/4/2017	11:00–11:20	COAST−EGD-MD / COAST− EGD-MD-s	1, 2.5, 6.5	98.3	722.5	208.2	1530.2
27/4/2017	11:00-11:20	COAST−EGD-LD / COAST−EGD-LD-s	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
03/5/2017	12:10–12:30	COAST−TKM-SD / COAST−TKM-SD-s	1, 2.5, 6.5	126.8	932.0	268.6	1973.9
04/5/2017	10:30–10:50	COAST−TKM-LD / COAST−TKM-LD-s	1.5, 3, 7	94.1	717.5	199.3	1519.6

[a] Suffixes "s" and "w" refer to samples taken during the spring and winter, respectively. SD, MD, and LD refer to relatively short, medium, and long distance from the coastline, respectively (see Sect. 2.1 in the main text). Additional abbreviations: MSD, Masada; MSMR, Mishmar; KLY, Kalya; ET, Ein Tamar; KDM, Kedem; EGD, Ein Gedi; BARE, bare soil site; COAST, coastal soil–salt mixture site; WM, agricultural watermelon-cultivation site; TMRX, natural *Tamarix* site; SEA, sampling near the seawater (see Sect. 2.1.1 in the main text).

S5. Anthropogenic influence during the measurements

We used the measured mixing ratios of C_2HCl_3 and C_2Cl_4 to explore potential influences on the sampled air composition, considering that these two species typically have a dominant anthropogenic origin (Zhou et al., 2005). Table S5 presents the Pearson correlation coefficients for the correlations between the VHOCs that were investigated in this work. The table indicates a much higher correlation between C_2HCl_3 and C_2Cl_4 compared to all other correlations, indicating an anthropogenic source for C_2HCl_3 ($p < 0.05$).

Table S5. Pearson correlation coefficient for the correlation between the investigated VHOCs.

	C_2HCl_3	C_2Cl_4
$CHCl_3$	0.27	0.27
C_2HCl_3	1.00	0.73
C_2Cl_4	0.73	1.00
CH_3Cl	0.04	0.12
CH_3Br	0.12	0.16
CH_3I	0.21	0.22
CH_2Br_2	0.00	0.01
$CHBrCl_2$	0.04	-0.12
$CHBr_2Cl$	0.15	0.12
$CHBr_3$	0.02	-0.11

To further investigate the origin of C_2HCl_3 and C_2Cl_4, we plotted their measured mixing ratios as well as the $[C_2Cl_4]/[C_2HCl_3]$ ratio vs. corresponding wind direction (Fig. S2). The ratio between the two species can be used to evaluate the transportation duration of the sampled air masses between the anthropogenic origin and the sampling point, considering the significantly longer atmospheric lifetime of C_2Cl_4 (3.5–4 months; (Olaguer, 2002;Singh et al., 1996)), compared to C_2HCl_3 (~7 days; (Quack and Suess, 1999)). It should be emphasized, however, that the ratio [C_2Cl_4]/[C_2HCl_3] may vary with time for a specific emission source, and our measurements are also potentially exposed to more than a single anthropogenic origin. The apparently dominant origin in the study area is, however, the Dead Sea Works (DSW), located a few kilometers to the south of most measurement sites (see Fig. 1 in the main text). Other potential emission sources were generally located at least a few dozen kilometers from the study area. It should be further emphasized that Fig. S2a presents C_2Cl_4 and C_2HCl_3 mixing ratios and [C_2Cl_4]/[C_2HCl_3] collectively for all measurement sites located to the north of the DSW. The justification for this is the relatively short distances between these sites, compared to that between any of these sites and a potential origin for anthropogenic VHOC emission other than the DSW. Fig. S2b presents C_2Cl_4 mixing ratios and [C_2Cl_4]/[C_2HCl_3] individually for TMRX–ET, which is located ~1.7 km south of the DSW.

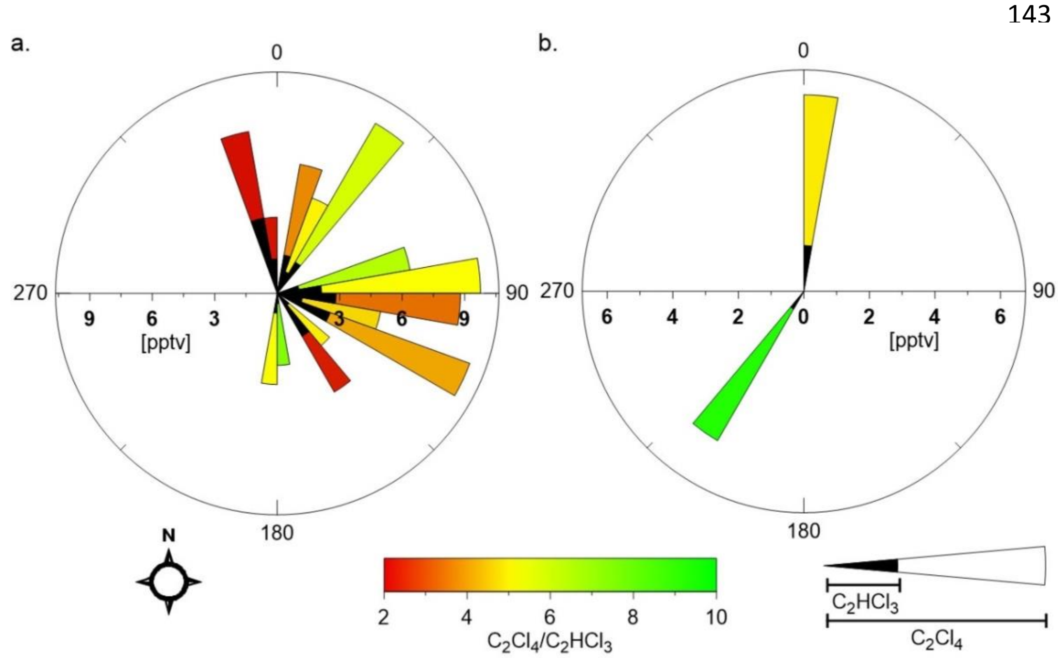

Figure S2. Anthropogenic impact on measured VHOCs. Presented are the C_2Cl_4 and C_2HCl_3 mixing ratios vs. 10° wind direction (WDD) sectors, as well as the [C_2Cl_4]/[C_2HCl_3] which is indicated by color, for all sites to the north of the Dead Sea Works (a) and TMRX–ET, which is located to the south of the Dead Sea Works (b).

Figure S2a shows elevated contribution from the eastern sector (apparently from the eastern coast of the Dead Sea, i.e., from Jordan) to the mixing ratios of C_2Cl_4 and to some extent also to those of C_2HCl_3, compared to the other wind sectors. It does not support contribution from the DSW which is located some dozens of kilometers to the south of these sites (see Fig. 1 in the main text). Potentially, the relatively small $[C_2Cl_4]/[C_2HCl_3]$ from the 140^o–150^o sector, suggesting relatively fresh emission, could be attributed to emission from the DSW, which could indicate no elevated contribution to C_2HCl_3 or C_2Cl_4 from the DSW. Furthermore, Fig. S2b demonstrates that the single measurement that can be attributed to emission from the DSW (from the 0^o–10^o sector) for TMRX–ET, which is significantly closer to the DSW than the other sites, corresponds to significantly less fresh emission compared with those measured at the other sites for the 140^o–150^o sector. Moreover, the mixing ratios of both C_2HCl_3 and C_2Cl_4, which correspond to the 0^o–10^o wind direction sector (Fig. S2b), seem to not be elevated compared to the corresponding mixing ratios measured at the other sites. Nevertheless, additional measurements are required to better analyze the contribution of anthropogenic origin to the mixing ratios of these species at the Dead Sea.

S6. In situ-measured meteorological parameters during the air sampling

Table S6. Summary of measured meteorological data during the different samplings. Summary of VHOCs over the Dead Sea. The table shows the date, time, site name (and abbreviation), as well as the average and standard deviation, in parentheses, for the following parameters: wind speed (WDS), wind direction (WDD) and wind vector (WDDV), temperature (T), relative humidity (RH), global solar radiation (GSR).

Date dd/m/yyyy	Time (local)	Site name / measurement abbreviation [a]	WDS (m/s)	WDD (◦)	WDDV (◦)	T (°C)	RH (%)	GSR (%)
20/4/2016	08:45−08:55	BARE−MSMR / BARE−MSMR-1	6.39 (0.52)	10.16 (1.57)	10.11 (1.22)	29.63 (0.24)	28.48 (0.99)	618.4 (13.0)
21/4/2016	08:45−08:55	WM−KLY / WM−KLY-1	6.27 (0.71)	13.65 (3.19)	13.91 (5.52)	27.72 (0.12)	20.98 (0.84)	332.5 (12.1)
02/5/2016	08:45−08:55	TMRX−ET / TMRX−ET-1	1.87 (0.29)	214.99 (16.78)	214.40 (12.35)	26.50 (0.12)	48.76 (0.46)	538.1 (8.9)
03/5/2016	08:45−08:55	WM−KLY / WM−KLY-2	3.74 (0.44)	340.19 (4.30)	340.33 (10.95)	25.93 (0.12)	45.71 (0.46)	225.5 (8.9)
25/5/2016	08:30−08:40	BARE−MSD / BARE−MSD-1	1.86 (0.27)	104.00 (15.65)	103.92 (19.44)	26.46 (0.13)	48.26 (0.52)	518.9 (10.6)
26/5/2016	08:30−08:40	BARE−MSD / BARE−MSD-2	2.56 (0.65)	141.03 (12.26)	141.71 (19.42)	28.48 (0.09)	34.06 (0.49)	497.6 (10.1)
30/5/2016	12:00−12:10	WM−ET / TMRX−ET-2	2.75 (0.52)	9.42 (18.42)	9.40 (13.50)	31.16 (0.32)	29.94 (0.89)	1044.5 (2.4)
31/5/2016	12:00−12:10	BARE−MSMR / BARE−MSMR-2	2.90 (0.34)	78.26 (8.52)	78.47 (5.40)	30.83 (0.29)	30.64 (0.97)	1027.4 (1.6)
11/7/2016	12:00−12:20	BARE−MSD / BARE−MSD-3	1.91 (0.65)	12.12 (39.32)	21.69 (12.47)	36.60 (0.35)	33.96 (0.87)	1000.7 (6.4)
11/7/2016	18:00−18:20	BARE−MSD / BARE−MSD-4	3.35 (0.38)	350.53 (9.46)	350.61 (9.53)	40.19 (0.15)	22.46 (0.30)	260.00 (24.9)
21/2/2017	11:20−11:40	COAST−TKM-SD / COAST−TKM-SD-w	2.36 (0.55)	111.13 (12.84)	111.95 (13.77)	18.50 (0.15)	37.32 (0.61)	790.1 (4.4)
22/2/2017	11:00−11:20	COAST−TKM-LD / COAST−TKM-LD-w	2.91 (0.52)	29.85 (12.11)	30.66 (5.35)	20.29 (0.16)	34.01 (0.28)	454.1 (47.9)
28/2/2017	11:20−11:40	COAST−EGD-SD / COAST−EGD-SD-w	7.90 (0.64)	13.60 (3.19)	13.61 (1.96)	24.71 (0.13)	27.70 (1.92)	314.1 (82.1)
01/3/2017	11:07–11:27	COAST−EGD-MD / COAST−EGD-MD-w	8.23 (1.05)	28.06 (5.08)	28.09 (1.34)	22.12 (0.38)	55.06 (0.58)	506.9 (93.9)
02/3/2017	11:00–11:20	COAST−EGD-LD / COAST−EGD-LD-w	8.32 (0.96)	182.17 (5.96)	182.28 (6.38)	23.49 (0.19)	44.43 (0.45)	345.5 (68.0)
25/4/2017	11:30–11:50	COAS-EGD-SD / COAST−EGD-SD-s	5.40 (0.31)	16.30 (3.97)	16.33 (2.88)	23.65 (0.16)	42.99 (1.03)	1031.5 (0.95)
26/4/2017	11:00–11:20	COAST−EGD-MD / COAST− EGD-MD-s	2.15 (0.25)	82.45 (8.05)	82.15 (6.42)	26.37 (0.29)	33.67 (0.38)	831.5 (10.8)
27/4/2017	11:00–11:20	COAST−EGD-LD / COAST−EGD-LD-s	2.39 (0.77)	104.12 (23.19)	98.01 (14.98)	27.03 (0.19)	42.27 (0.54)	707.9 (153.8)
03/5/2017	12:10–12:30	COAST−TKM-SD / COAST−TKM-SD-s	2.80 (0.41)	174.49 (19.14)	174.76 (21.93)	28.44 (0.33)	36.21 (1.05)	961.6 (7.4)
04/5/2017	10:30–10:50	COAST−TKM-LD / COAST−TKM-LD-s	2.70 (0.43)	132.88 (16.62)	132.16 (17.79)	26.11 (0.25)	45.25 (1.21)	871.8 (13.1)

[a] The suffixes "s" and "w" refer to samples taken during the spring and winter, respectively. SD, MD, and LD refer to relatively short, medium, and long distance from the coastline, respectively (see Sect. 2.1 in the main

text). Additional abbreviations: MSD, Masada; MSMR, Mishmar; KLY, Kalya; ET, Ein Tamar; KDM, Kedem; EGD, Ein Gedi; BARE, bare soil site; COAST, coastal soil–salt mixture site; WM, agricultural watermelon-cultivation site; TMRX, natural *Tamarix* site; SEA, sampling near the seawater (see Sect. 2.1.1 in the main text).

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