

Frequency and extent of bromine oxide formation over the Dead Sea

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[1] A study has been performed in an attempt to better understand and characterize BrO formation in the Dead Sea region. The DOAS technique was employed to quantify BrO levels at three sites along the Dead Sea representing three different Br⁻ and pH levels of the water. In order to characterize the spatial extent of BrO formation, measurements were performed at a site south of the Dead Sea itself and also at a site 400 m above the water level. Additionally, measurements were concurrently performed for ozone, nitrogen oxides and meteorological parameters at each of the campaign sites. The results showed that BrO was produced everywhere in the Dead Sea region up to maximum levels of around 200 ppt. The frequency and intensity of BrO production was more intense in the southern part of the Dead Sea corresponding to the increased acidity and bromide content of the water and increased solid salt depositions. Maximum BrO production during the winter was similar to that of BrO produced during summer. BrO was also observed at 4 km inland from the Dead Sea shores and at heights 400 m above the water. However, these levels were less than half the concentration measured at the water level. While it would appear that the Br⁻ content and pH of the Dead Sea water are the two major factors responsible for the elevated BrO levels observed at the Dead Sea, the presence of NO₂, up to levels of several parts per billion, might also play an important role in the BrO production. Additional factors influencing BrO production could be the extensive salt deposition at the Dead Sea as well as the high sulfate aerosol levels present in the region.

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1. Introduction

[2] A summertime study performed at a site situated midway along the Dead Sea in Israel showed that the reactive halogen species BrO was present at levels of 150 ppt and above [Hebestreit *et al.*, 1999; Matveev *et al.*, 2001]. This was the first study to show the existence of tropospheric BrO at midlatitudes in contrast to previous studies performed in the Polar Regions. The BrO levels observed at the Dead Sea were higher by a factor of at least 6 compared to those measured in the Polar Regions [Hausmann and Platt, 1994; Kreher *et al.*, 1997; Tuckermann *et al.*, 1997].

[3] The above investigations further showed that the presence of elevated BrO levels was always accompanied by extensive ozone destruction to almost zero levels [Matveev *et al.*, 2001]. Ozone depletion events at the Dead Sea therefore give an indirect indication of BrO formation. A related investigation was therefore performed during a 15-month period to examine the frequency of ozone depletion episodes over the entire Dead Sea [Tas *et al.*,

2003]. The conclusions obtained from the above study indicated that ozone destruction events occur all over the Dead Sea during all seasons of the year. Ozone depletion episodes were observed even at altitudes of (approximately) 400 m above the Dead Sea water level. The study also showed that ozone destruction and hence BrO formation appeared to be more intensive toward the south of the Dead Sea, where salt evaporation ponds are located, as compared to the north.

[4] Measurements performed at the salt lakes in the vicinity of Salt Lake City, Utah [Stutz *et al.*, 2002] measured maximum BrO levels of up to 6 ppt. The salinity of these lakes is lower than the Dead Sea by a factor of about 3 to 4 (60 g/L Cl⁻). However, the Br⁻/Cl⁻ ratio of the salt lakes is very low (= 0.0007) as compared to 0.025 for the Dead Sea and 0.0034 for normal ocean water. A recent study performed at the world's largest saltpan (Salar de Uyuni, Bolivia), observed BrO levels of up to 20 ppt [Honninger *et al.*, 2004]. The maximum bromine content in the brine was reported as 300 mg/L as compared to at least 6 g/L at the Dead Sea (see Table 2 in section 2). Thus it appears that it is primarily the higher bromine salt levels present at the Dead Sea that strongly influence BrO production and hence cause repeated ozone depletion events.

[5] The Dead Sea region offers a unique site for studying the various factors that influence BrO formation, being one

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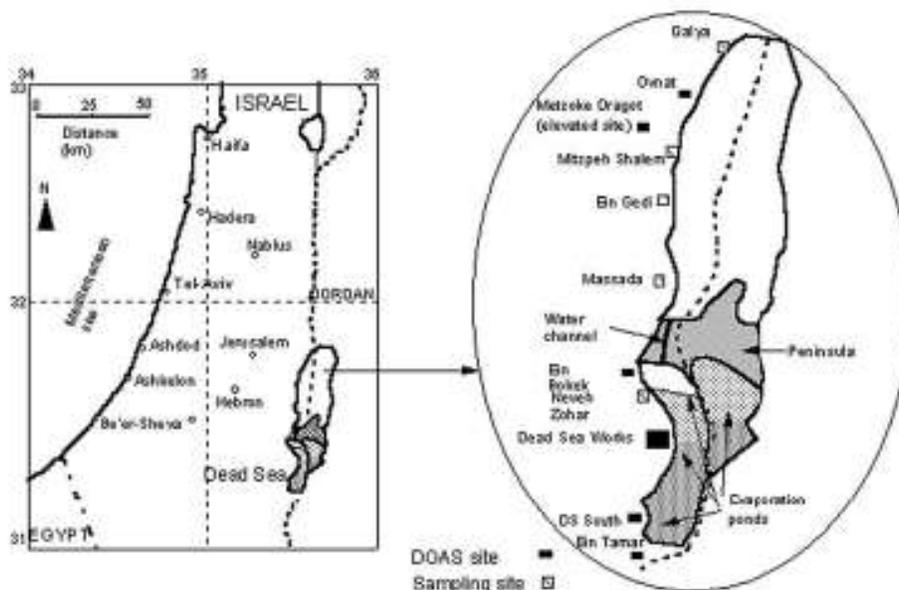


Figure 1. Map of Dead Sea region showing DOAS measuring sites.

of the most saline lakes in the world containing 5.6 g/L bromide and 225 g/L chloride (as reported by *Niemi et al.* [1997]) in contrast to 0.065 g/L bromide and 19 g/L chloride in standard ocean water [*Sverdrup et al.*, 1942]. The Dead Sea's geographical position is between $N31^{\circ}50'$ and $N31^{\circ}$, $E035^{\circ}30'$, and its dimensions are about 75 km long and 15 km wide (see Figure 1).

[6] Having no outlet, the Dead Sea is a "terminal lake" which loses significant amounts of water by evaporation into the hot dry air. The region, except for the Dead Sea Works situated at the south, is essentially a recreation region with a large hotel center at Ein Bokek, midway along the Dead Sea, and also a number of smaller resort sites on the northern part. The Dead Sea Works utilizes the high concentration of salts in the water to produce a number of products, including carnallite, potash, chlorine, bromine, magnesium metal, etc. The Dead Sea is separated into two basins by a peninsula, the southern part being in reality a series of solar evaporation ponds covering an area of about 100 km² for first-stage evaporation and "carnallite ponds" over an area of 40 km² for second-stage evaporation. The residual brine contains about 350g/L chloride and up to 11–12 g/L bromide and is used for the production of bromine. The Dead Sea Works has its own power plant (110 MW) that operates on heavy fuel oil. This power plant is the main

source of anthropogenic pollution in the region apart from limited pollution emitted by vehicles traveling on the road bordering the Dead Sea. Air pollutants may also be transported to the Dead Sea valley from outside of the area [*Matveev et al.*, 2002b].

[7] The question addressed in the present study is whether the elevated bromide levels present in the water are solely responsible for the high BrO levels observed at the Dead Sea, or whether the presence of solid salt deposits, low pH value of the water, or other factors such as the presence of NO₂ may also play a contributing role in the chemistry of BrO production. The present paper reports the results of a study aimed at measuring BrO formation along the Dead Sea, as well as outside the water boundaries and also at an elevated site 400 m above the water level.

2. Experimental

[8] An active long-path differential absorption optical spectroscopy (LP-DOAS) technique was employed to measure BrO levels in the ambient air over the Dead Sea [*Platt*, 1994]. The DOAS instruments used in the present study were capable of detecting BrO down to levels of less than 10 ppt, depending on the optical path length for each specific site and the specific instrument. For the first two

Table 1. List of Research Campaigns

Number	Date	Site	Light Direction	Light Path, km	Investigation Conditions
1	27 July to 10 Aug. 2001	Ovnat (north)	NW–SE	2.5–4.6	light path (LP) over land, west of the Dead Sea
2	20 July to 4 Aug. 2001	Ein Bokek (mid)	W–E	8.5	LP directly over Dead Sea water
3	2 to 12 Aug. 2001	Evaporation ponds DSW (South DS)	W–E	5.8	summer conditions, LP directly over most concentrated salt ponds
4	24 Dec. 2001 to 4 Jan. 2002	Evaporation ponds DSW (South DS)	W–E	5.8	winter conditions, LP directly over most concentrated salt ponds
5	17 June to 8 July 2002	Metzoke Dragot	N–S	4.1	elevated site (+400 m above DS); LP over land
6	18 Aug. to 2 Sept. 2002	Ein Tamar	SW–NE	5.8	south of evaporation ponds; LP over land

Table 2. Chloride and Bromide Levels in the Dead Sea Water and Enrichment Factors

Site	pH	Cl ⁻ , g/L	Br ⁻ , g/L	Br ⁻ /Cl ⁻ , × 10 ³	Br ⁻ Enrichment DS/OW
Ocean Water (OW)		19	0.065	3	
North Dead Sea (Qalya)	5.9	225	6.1	27	94
Mid North DS (Mitzpeh Shalem)	5.7	255	6.9	27	106
Mid DS (Ein Gedi)	5.8	236	6.4	27	98
Ein Bokek evaporation ponds	5.5	306	8.3	27	128
Neveh Zohar	5.0	354	9.6	27	148
South Dead Sea	4.9	405	11.0	27	169

campaigns, the DOAS instrument composed of a coaxial double Newton-type mirror telescope, (1500-mm focal length, mirror diameter 30 mm), an 0.5 m Czerny-Turner, ACTON spectra Pro 500, 600g/mm spectrograph and a 1024 pixel photo diode array. For all the other measurements, a commercially available Hoffmann HMT DOAS, consisting of a double Newton-type mirror telescope in coaxial arrangement (600-mm focal length, mirror diameter 20 mm), an 0.32-m Czerny-Turner, Triax 320,1200g/mm spectrograph, and a 1024 pixel photo diode array, was employed. The general evaluation procedure for the retrieval of optical densities from DOAS spectra is described in detail elsewhere [Stutz and Platt, 1997].

[9] The various research campaigns and conditions are summarized in Table 1 together with their site positions along the Dead Sea as shown in Figure 1. Table 2 shows the results of chloride and bromide concentrations and pH values measurements performed at various sites along the Dead Sea (the measuring sites are marked on the map in Figure 1). The table shows that the northern parts of the Dead Sea (Qalya, Mitzpeh Shalem, and Ein Gedi sites) all have similar bromide and chloride levels with pH levels slightly below a value of 6. From the land peninsula, southward from Ein Bokek, the water show increasingly higher acidity values with pH levels less than 5 and bromide and chloride salt concentrations continuously increasing to around 11 and 400 g/L, respectively.

[10] Three simultaneous research campaigns (campaigns 1–3) were performed during summer 2001, from Ovnat in

the north, at Ein Bokek at the middle, to a site almost at the southern tip of the Dead Sea. These sites cover three different salt concentration areas, from “normal” Dead Sea in the north to highly concentrated solutions in the southern evaporation ponds. The bromide almost doubles in concentration between the northern and southern sites. The purpose of this study was to determine the spatial extent of BrO formation over the Dead Sea Valley and examine the effects of the various compositions of the water and the surrounding deposits.

[11] The effect of winter conditions on the extent of BrO formation, as compared to the summer, was investigated during the fourth campaign (campaign 4), which was performed at the same site as campaign 3 and under identical experimental conditions.

[12] The next campaign (campaign 5) attempted to identify the presence of BrO at a site some 400 m above the Dead Sea level (~0 m above sea level) and some 1300 m inland from the waterline. The above study was performed during early summer.

[13] Since it appeared that the Dead Sea salt water and/or salt deposits may be instrumental in BrO formation, it was therefore assumed that BrO would be detected at a site south of the Dead Sea only when wind came from the north, from over the evaporation ponds. To test this assumption, campaign 6 was performed at Ein Tamar, a site 4 km south of the southernmost evaporation ponds.

[14] In addition to the BrO measurements, the DOAS spectra were also evaluated to simultaneously obtain the NO₂ concentration in the air mass under examination. A continuous monitor (TEII model 42), with an external converter, was utilized at the measuring sites to measure for total nitrogen oxides (NO_x) content as well as the NO levels. Continuous measurements of ozone and meteorological parameters (wind speed and direction, relative humidity, temperature) were performed. In addition, the noontime boundary layer mixing height was measured daily.

3. Results

[15] The BrO concentrations measured at three sites along the Dead Sea during 2001 for the entire measurement campaign (campaigns 1–3) are shown in Figure 2. The

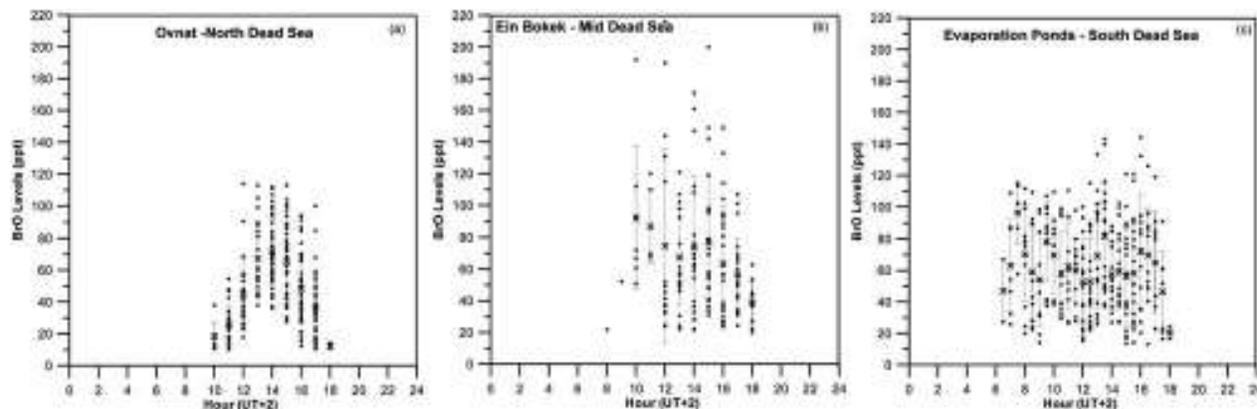


Figure 2. BrO levels at three sites along the Dead Sea, summer 2001. Values are presented in half hourly or hourly bins; crosses indicate the average for each bin, and bars represent standard deviation limits.

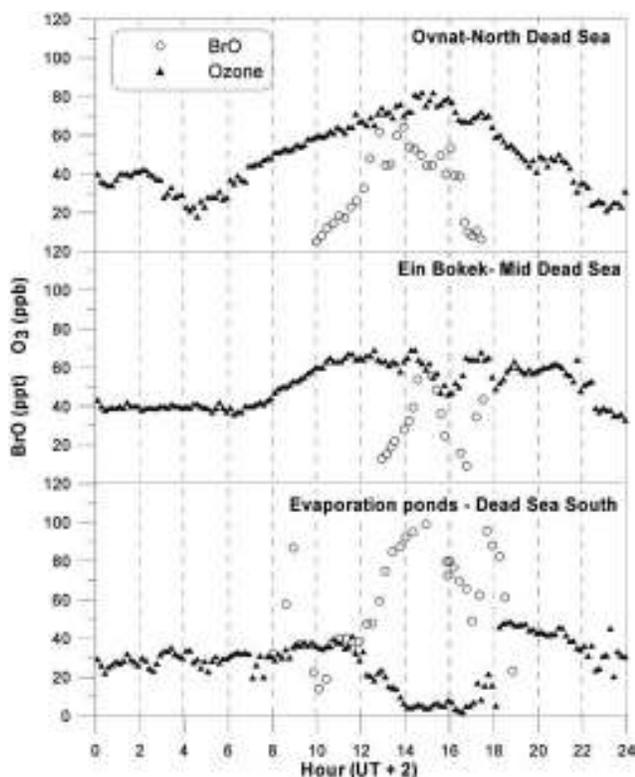


Figure 3. BrO and O₃ levels as measured simultaneously at three sites along the Dead Sea, 3 August 2001.

results are grouped into hourly or half-hourly (southern site) concentration bins. Additionally, standard deviations bars are shown together with the average value for each concentration bin. No BrO, above instrument detection limits, was observed during the nighttime. The results clearly indicate that BrO is formed all over the Dead Sea region during August. BrO was observed for all the days when measurements were available. The highest BrO levels were observed at Ein Bokek with a maximum value of almost 220 ppt; over the evaporation ponds values reached 150 ppt, while in the north at Ovnat, maximum levels reached only 120 ppt. The results for Ein Bokek campaign during May–June 1997 [Matveev *et al.*, 2001] were slightly lower (~180 ppt) than those observed in the present study. The formation of BrO begins in the early morning at around 0700 (UT+2) for the southern site (evaporation ponds), around 0800 to 0900 for the middle site, and not before 1000 for the northern Ovnat site. BrO formation continues at all sites through the morning hours, through the afternoon, and continuing until at least 1800 in the evening. Sunrise in the Dead Sea Valley is around 0500, and sunset at 1830 (UT+2). Between 1800 in the evening and about 0600 in the morning, BrO levels were below detection limits.

[16] The results for 3 August 2001 (Figure 3) shows that BrO was observed simultaneously all along the Dead Sea. The highest levels of 120 ppt were observed at the southern site over the evaporation ponds, while for the other two sites highest BrO levels of around 60 ppt were recorded. The simultaneous appearance of BrO at all three sites indicates

that BrO can be formed all over the Dead Sea region and is not a result of transportation from the more concentrated evaporation ponds/salt pans in the south. For example, transportation time from the salt pans to Ovnat would take at least 3 hours at typical wind speeds. Additionally, wind directions during BrO formation at the southern and Ein Bokek site are mainly from the NNE, ruling out transportation of BrO or its precursors from over the southern evaporation ponds as being the predominant source. Ozone depletion at both the middle and southern site was extensive, while the northern site showed only limited ozone depletion.

[17] The results for the winter campaign (campaign 4) are shown in Figure 4. BrO was observed on only 4 out of 10 measuring days in contrast to summer when BrO was observed everyday. On those days that BrO was observed, levels of more than 100 ppt were recorded, with a maximum observed value of almost 150 ppt. The high BrO levels observed during winter, while less frequent than during summer, reach similar maximum levels. This is in spite of the fact that the average daily maximum temperature at the Dead Sea during winter is almost 20°C as compared to above 35°C during summer. Similarly, the monthly average daily global radiation intensity decreases from around 8 kW/m² in summer to less than half that value during winter [Kudish *et al.*, 1997]. Correspondingly, the monthly average UVA radiation peaks at almost 400 W/m³ during the summer months as compared to values below 150 W/m³ for the winter, while the winter UVB radiation intensity is reduced to almost 20% of its summer value [Kudish *et al.*, 1997]. Owing to instrumental failure, no measurements of the mixing depth were available for the winter study. Long-term measurements in Israel have shown

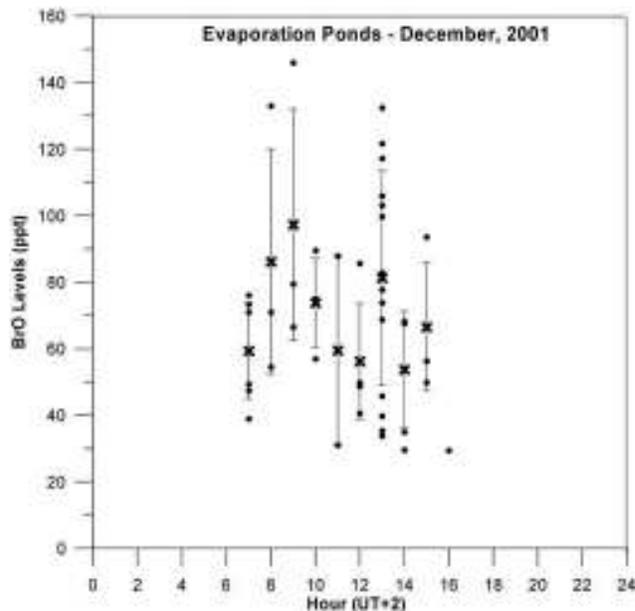


Figure 4. Wintertime BrO levels over Dead Sea southern site averaged only for days on which BrO was detected. Values are presented in hourly bins; crosses indicate the average for each bin, and bars represent standard deviation limits.

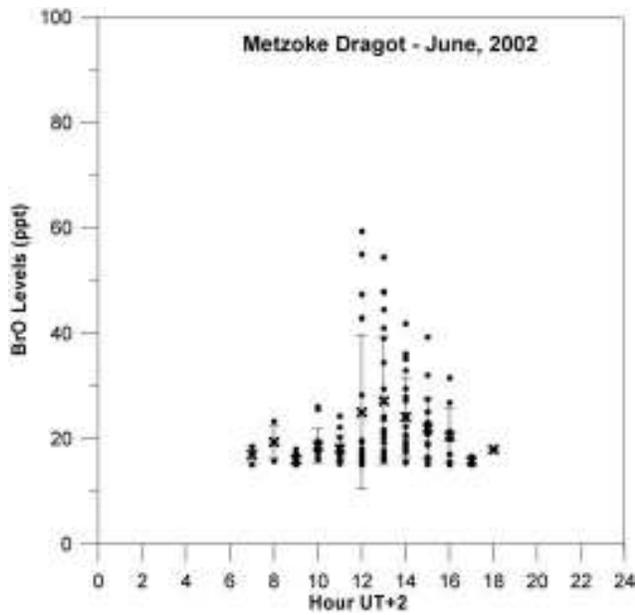


Figure 5. Summertime BrO levels at the elevated site. Values are presented in hourly bins; crosses indicate the average for each bin, and bars represent standard deviation limits.

that while the mean mixing depth during winter is twice that for summer, the ventilation rates (mixing depth multiplied by zonal wind) range from 3 times the maximum summer values to rates similar to summer levels [Matveev *et al.*, 2002b]. The ventilation rate is a better indicator of dispersion effects than simply the mixing depth. It is therefore possible that for days for which no BrO was detected the ventilation rate was high in contrast to the days with elevated BrO levels. It is therefore possible that the dispersion conditions may play a crucial factor in BrO buildup.

[18] The BrO concentrations measured during the fifth campaign at the elevated site are shown in Figure 5. The levels observed at this site were lower than measured at the Dead Sea level and limited to mainly the midday period. While BrO was observed on almost all of the 21 days during the measuring period, elevated levels above 40 ppt were recorded on only five of these days. The maximum BrO level observed at the elevated site was only 60 ppt, half the amount measured at the Dead Sea Ovnat site (Figure 2a). It should be noted that the elevated BrO levels were only observed for those days for which the boundary-mixing layer was less than 300 m above the site ground level. The limited mixing height restrains the BrO and its precursors from dispersing into the free troposphere and allows elevated BrO levels. During a study performed at the same site in early spring, BrO levels were below the detection limit of 10 ppt during the entire 10-day measuring period. The reason that no BrO was observed during the spring could also be related to the boundary-mixing layer height, since all other conditions were similar to those during the summer campaign. While no boundary layer measurements were performed at that time, a previous study has shown that for Israel the mixing depth and ventilation rates observed during March

are at least twice that measured during the summer [Matveev *et al.*, 2002b].

[19] The results for the sixth measurement campaign performed during August at the Ein Tamar site (situated 4 km south of the most southern edge of the Dead Sea Works evaporation ponds and saltpans) is shown in Figure 6, together with the corresponding wind rose pattern. It was assumed that only when the wind was coming from the north would BrO be evident in the air masses. The results showed that BrO was observed not only under northerly wind flow but also when the wind came from the south. While the maximum BrO level observed during the Ein Tamar campaign was almost 100 ppt when the wind came from the north, values of almost 80 ppt were observed even when the winds flowed from the south. The daily average BrO values were in the 20–30 ppt range. This compared to maximum BrO levels around 150 ppt and daily average

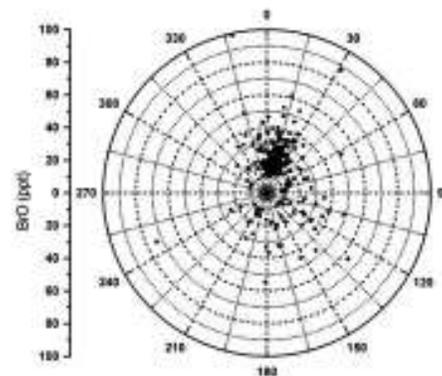
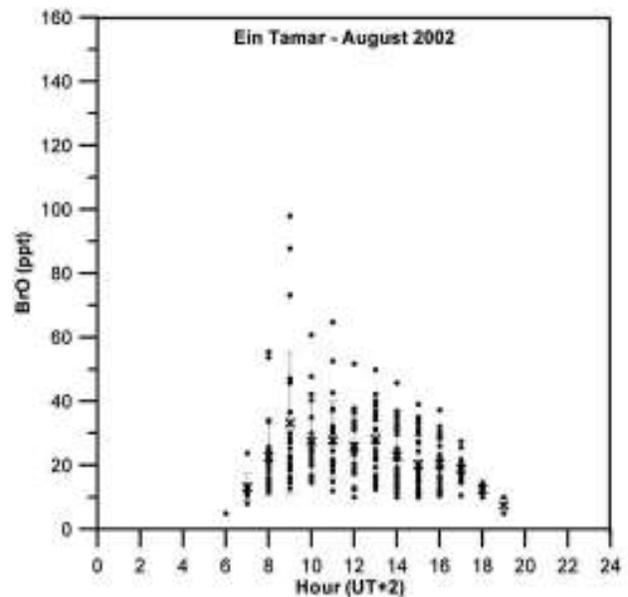


Figure 6. BrO levels and wind rose pattern at Ein Tamar site, summer 2002. Values are presented in hourly bins; crosses indicate the average for each bin, and bars represent standard deviation limits.

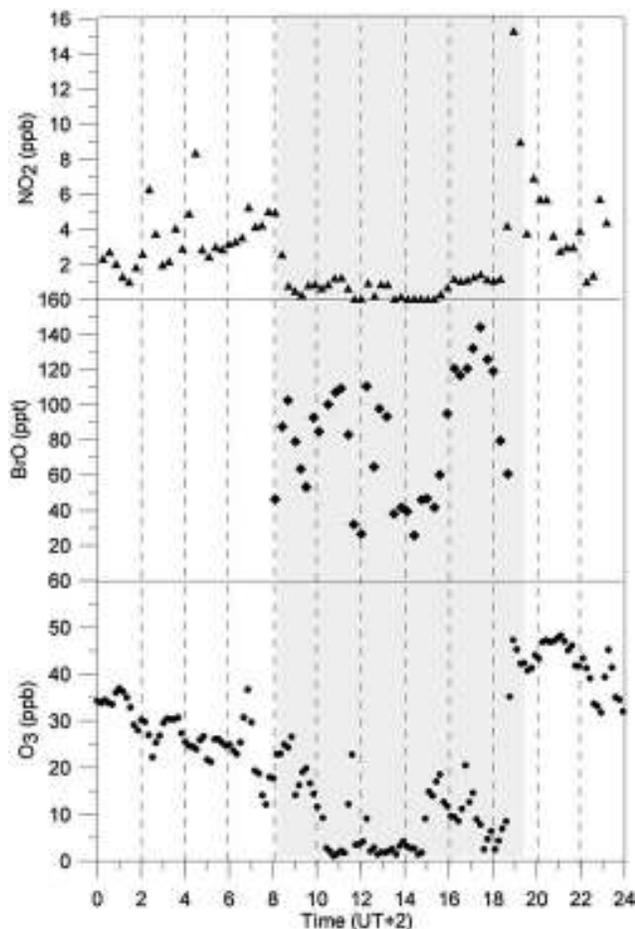


Figure 7. BrO, O₃ and NO₂ levels at the Dead Sea southern site, 5 August 2001. Shaded area indicates time period of BrO formation.

values at least twice as high for the Dead Sea South evaporation ponds site.

4. Discussion

[20] All of the above results clearly indicate that the BrO presence is very pronounced all over the Dead Sea valley even outside of the water boundaries and to heights of at least 400 m above the water level. The fact that BrO was detected (up to levels of 60 ppt, see Figure 6) at the Ein Tamar site even for air masses coming from the south suggests the possibility either of recirculated air masses that originated over the evaporation ponds/salt pans situated north of the site or the possibility that salt aerosols have been deposited in the vicinity of the Ein Tamar site. In either case the present study appears to indicate the possibility of BrO being present over a wide area outside and above the Dead Sea itself.

[21] The presence of elevated BrO levels, with repeated values to above 150 ppt is unique to the Dead Sea region. The maximum BrO levels recorded at salt lakes in the vicinity of Salt Lake City, Utah, was 6 ppt [Stutz *et al.*, 2002] and reached a maximum level of only 20 ppt at Salar de Uyuni in Bolivia [Honninger *et al.*, 2004]. Similarly, the maximum BrO level measured at Mace Head on the west

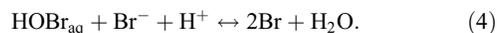
coast of Ireland was only 6.5 ppt [Saiz-Lopez *et al.*, 2004]. This raises the question whether it is solely the increased bromide levels at the Dead Sea that cause the exceptionally high BrO concentrations, or whether additional factors need to be taken into consideration.

[22] In order to elucidate the above question, attention needs to be turned to the nitrogen oxide chemistry at the Dead Sea and especially to the relationship between O₃, NO₂, and BrO. Figure 7 shows a typical example of the diurnal variation of O₃, BrO, and NO₂ for summer 2001 at the Dead Sea southern site (campaign 3). The shaded section shows the time period when a net BrO formation takes place. The BrO starts to appear from 0800 onward, peaking around noon with a value of around 120 ppt, declining to minimal values at 1400 before once again increasing to a second peak of almost 150 ppt around 1700 and finally dropping to below the detection limit at 1900. The ozone levels show a strong decline in parallel to BrO production, decreasing to below detection limit of 3 ppb, between 1000 and 1900 before returning to normal ozone levels of around 40 to 50 ppb. Strong anti-correlation was observed between BrO and ozone for all the sites. With respect to the NO₂, it decreases sharply at around 0800 from a value of 5 ppb to below 1 ppb levels. This low level was maintained throughout the day until about 1900 when a sudden increase was observed in parallel to ozone increase and BrO decline.

[23] The reactions leading to BrO formation and ozone depletion have been the subject of a number of investigations. The first stage towards BrO formation is the degassing of reactive bromine into the environment [Fan and Jacob, 1992; Sander and Crutzen, 1996; Vogt *et al.*, 1996] by the following reactions:



leading to the net reaction



The bromine activation cycle consumes H⁺ ions, which implies the need for acidification of the sea salt aerosol. Fickert *et al.* [1999] have shown in laboratory experiments that the above reactions occur only at pH < 6.5. Keene *et al.* [1998] showed that significant sea salt dehalogenation is limited to acidified aerosol but that differences between a pH of 5.5 and 3 were not significant. As shown in Table 2 the Dead Sea water contains elevated Br⁻ concentrations and the pH values are sufficiently acidic to enhance reaction (4).

[24] In the following stage, the bromine atoms formed in reaction (4) can react with ozone to form BrO as shown by several field campaigns and laboratory investigations [Barrie and Platt, 1997; Tuckermann *et al.*, 1997; Wayne *et al.*, 1995]. This oxide radical is a key species in the chemical mechanisms responsible for the destruction of ozone. Two

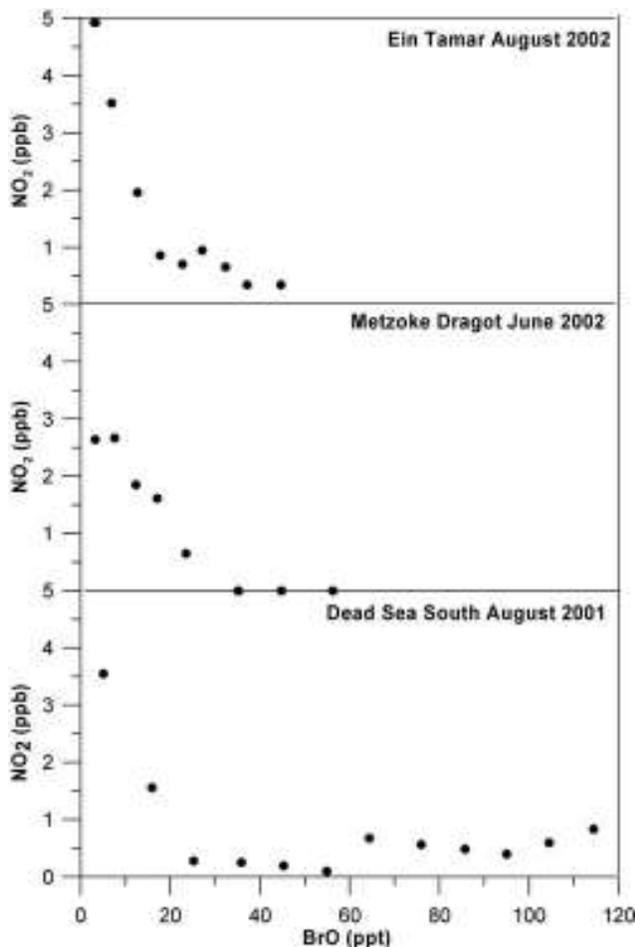
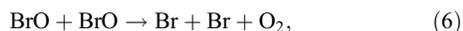
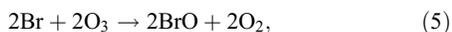


Figure 8. Correlation between BrO and NO₂ at Dead Sea at three sites. Values are presented in averaged bins.

main chemical mechanisms have been proposed as being responsible for BrO formation and ozone destruction.

Cycle A (BrO-cycle)

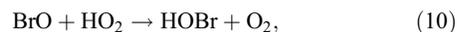
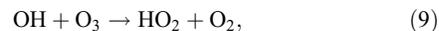
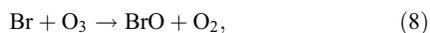


Net



As shown above, the halogen atoms are recycled and do not get lost in the cycle. As long as ozone is present (above 1–2 ppb), the rate dependent step is reaction (6). The second mechanism is initiated by the hydroperoxy radical as shown below.

Cycle B (HOBr-cycle)



Net



An alternative pathway is for the HOBr formed in reaction (10) to react with Br⁻ according to reaction (4) to produce a net free Br atom. It should be noted that the efficiency of cycle B is linearly dependent on the BrO concentration whereas the BrO dependence of cycle A is quadratic. Thus at high BrO levels, such as observed at the Dead Sea, cycle A is expected to dominate causing extensive ozone destruction.

[25] As observed in Figure 7, the onset of BrO formation is linked to a strong decline in NO₂ levels. The dependence between NO₂ and BrO at three different sites (directly over the evaporation ponds at the southern Dead Sea site, at the Ein Tamar site, and at the elevated site) is shown in Figure 8. The results show that the appearance of BrO is related to a sharp decrease in NO₂ concentrations to values below the detection level (<0.2 ppb). Before the onset of BrO formation is observed, NO₂ levels of between 3 and 5 ppb, depending on the site, were present. However, once BrO starts to form, there is an immediate reduction in NO₂ levels until at BrO levels of between 30 and 40 ppt, almost no NO₂ remains. Examination of the relation between NO₂ and NO_z is shown in Figure 9, for the elevated site (NO_z represents all nitrogen oxides minus NO and NO₂). The figure shows that

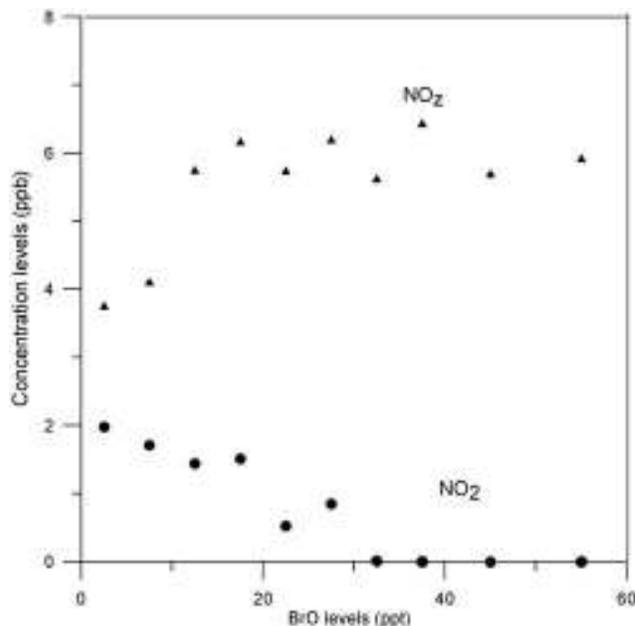
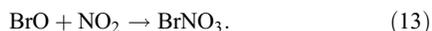


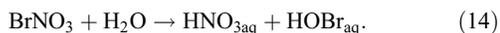
Figure 9. Comparison between NO₂ and NO_z at Metzoke Dragot. Values are presented in averaged bins.

NO₂ is reduced to zero values (below DOAS detection limits) at BrO levels above 30 ppt while the NO_z increases directly in proportion to the decrease of NO₂.

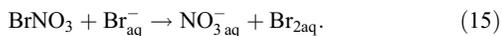
[26] A model study performed for a marine troposphere by Sander *et al.* [1999] has shown that the nitrogen and halogen chemistry is coupled through the gas-phase reaction to form BrNO₃,



The BrNO₃ is measured as part of the NO_z fraction and thus explains the increase of NO_z at the expense of NO₂. The bromine nitrate undergoes hydrolysis on sulfate or seas salt particles,



The HOBr can then react with Br⁻ as in reaction (4) to produce Br₂, which in turn produces additional BrO, and further enhance the ozone destruction cycle. The BrNO₃ can also react with bromide on sea-salt or sulfate particles in situations where sufficient Br⁻ is available, such as in the Dead Sea case, to release Br₂,



The Br₂ can then react as shown previously (reactions (2) and (3)) to produce Br that then take part in BrO formation and the ozone destruction cycle. Thus both of the above reactions lead eventually to increased BrO production. Additionally, the reactions lead to increased acidity of the sea salt/sulfate substrate, which also increases Br formation via reaction (4). Measurements performed at the Dead Sea have indeed shown that the NO₃⁻ levels present in aerosols collected over the water are relatively high and averaged around 6 μg/m³, with maximum levels almost double that value (V. Matveev *et al.*, unpublished data, 1997).

[27] The presence of sea salt and especially sulfate aerosols present in a marine atmosphere can influence BrO production. Chemical reactions on atmospheric particles and inside them have been suggested as having a significant influence on ozone chemistry in the gas phase [Jacob, 2000]. In the case of the Antarctic “ozone hole” where rapid O₃ destruction by halogen radicals takes place, interactions between the gas and the particulate phase (polar stratospheric clouds) are very important [see, e.g., Brasseur *et al.*, 1999]. Similarly, a model study on the halogen chemistry in the marine boundary layer, performed by von Glasow *et al.* [2002] has shown the importance of sulfate and sea salt aerosols in the marine atmosphere on the acid-catalyzed activation of bromine. They suggested that the large surface area of the sulfate aerosol (40 to 60 mm²/cm³ as compared to the sea salt surface area of 25 to 45 mm²/cm³) was the reason that HBr and HOBr are scavenged to a significant amount by the sulfate aerosol and are involved in reactions on and in the sulfate particles. Further due to the low pH, the acid-catalyzed cycle quickly transforms Br⁻ and HOBr to Br₂ that rapidly degases. The Br₂ then reacts to produce BrO and cause ozone depletion as previously described. The recycling of bromine species on sulfate

aerosol was shown to be higher than in sea salt aerosol by roughly a factor of 5 to 10. A study has shown that Israel is affected by long-range transportation of air pollutants originating over Europe [Luria *et al.*, 1996; Matveev *et al.*, 2002a] causing average yearly levels of around 10 μg/m³ SO₄²⁻ and summer levels above 25 μg/m³. The polluted air arriving from Europe also affects inland Israel, and sulfate levels between 10 and 20 μg/m³ are regularly observed in the Dead Sea region [Matveev *et al.*, 2002b]. These relatively high sulfate particle levels may therefore play an important part in recycling of less reactive to bromine species in the Dead Sea region.

[28] The model study performed by von Glasow *et al.* [2002] indicated that the pH of the sea salt and sulfate aerosols decreases with increasing height above the sea level. An implication of the vertical gradient of the sea salt particle pH is that acid-catalyzed bromine activation is more efficient in higher layers of the mixing boundary layer and thus increased BrO levels are to be expected. The present study, however, shows that BrO levels were lower at the elevated site (+400 m) and were less than half those measured at the Dead Sea level. There might be several reasons for this. First and probably primary, the lower than expected BrO levels can be explained by dilution processes as the BrO and precursors disperse into the free troposphere above the Dead Sea. Second, the relatively low pH levels already present at the Dead Sea itself and possibly also the relatively lower NO₂ concentration at the elevated site as compared to the Dead Sea sites could be contributing factors. The latter reason would indicate the importance of NO₂ in the BrO formation process.

5. Conclusions

[29] The present study shows that BrO is present all over the Dead Sea valley, even outside of the water boundary (an area of more than 1500 km²) and at heights of at least 400 m above the water level. The maximum BrO levels recorded at the Dead Sea were higher by a factor of about 30 than values reported at other midlatitude sites. The main contributor to these high BrO levels is most likely the high bromide content in the Dead Sea water. The intensity and frequency of BrO production increased toward the southern parts of the Dead Sea corresponding to the increased salinity of the water, the increase of bromide content, and the decrease in pH (see Table 2). This indicates the dependence of BrO formation on the Br⁻ content and pH values in the water. It is, however, also possible that the extensive solid salt depositions around the evaporation ponds play a contributing role in BrO formation and ozone destruction processes in a similar manner to the stratospheric clouds in the polar regions.

[30] However, the relatively high NO₂ levels (several ppb) present at the Dead Sea, as compared to the other sites where BrO has been identified, may play an important role by producing BrNO₃ that hydrolyzes to HOBr, which intensifies further BrO formation. Additionally, the elevated sulfate aerosol levels present in the area may also influence the halogen activation cycle. In conclusion, it would appear that several major factors, Br⁻ content and pH of the water, the presence of NO₂, and salt depositions and sulfate particulates, together contribute toward the elevated BrO

levels and strong ozone destruction effects observed at the Dead Sea.

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References

- Barrie, L. A., and U. Platt (1997), Arctic tropospheric chemistry: An overview, *Tellus, Ser. B*, *49*(5), 450–454.
- Brasseur, G. P., J. J. Orlando, and G. S. Tyndall (Eds.) (1999), *Atmospheric Chemistry and Global Change*, Oxford Univ. Press, New York.
- Fan, S.-M., and D. J. Jacob (1992), Surface ozone depletion in the Arctic spring sustained by bromine reactions on aerosols, *Nature*, *359*, 522–524.
- Fickert, S., J. W. Adams, and J. N. Crowley (1999), Activation of Br₂ and BrCl via uptake of HOBr onto aqueous salt solution, *J. Geophys. Res.*, *104*, 23,719–23,727.
- Hausmann, M., and U. Platt (1994), Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, *99*, 25,399–25,414.
- Hebestreit, K., J. Stutz, D. Rosen, V. Matveev, M. Peleg, M. Luria, and U. Platt (1999), DOAS measurements of tropospheric BrO in mid latitudes, *Science*, *283*, 55–57.
- Honninger, G., N. Bobrowski, E. R. Palenque, E. R. Torrez, and U. Platt (2004), Reactive bromine and sulfur emissions at Salar de Uyuni, Bolivia, *Geophys. Res. Lett.*, *31*, L04101, doi:10.1029/2003GL018818.
- Jacob, D. J. (2000), Heterogeneous chemistry and tropospheric ozone, *Atmos. Environ.*, *34*, 2131–2159.
- Keene, W. C., R. Sander, A. A. P. Pszenny, R. Vogt, P. J. Crutzen, and J. N. Galloway (1998), Aerosol pH in the marine boundary layer: A review and model evaluation, *J. Aerosol Sci.*, *29*, 339–356.
- Kreher, K., P. V. Johnston, S. W. Wood, and U. Platt (1997), Ground-based measurements of tropospheric and stratospheric BrO at Arrival Heights, Antarctica, *Geophys. Res. Lett.*, *24*, 3021–3024.
- Kudish, A. I., E. Evseev, and A. P. Kushelevsky (1997), The analysis of ultraviolet radiation in the Dead Sea Basin, Israel, *Int. J. Climatol.*, *17*, 1697–1704.
- Luria, M., M. Peleg, G. Sharf, D. Siman Tov-Alper, N. Schpitz, Y. Ben Ami, Z. Gawi, B. Lifschitz, A. Yitzchaki, and I. Seter (1996), Atmospheric sulfur over the east Mediterranean region, *J. Geophys. Res.*, *101*, 25,917–25,930.
- Matveev, V., M. Peleg, D. Rosen, D. Siman Tov-Alper, J. Stutz, K. Hebestreit, U. Platt, D. Blake, and M. Luria (2001), Bromine oxide-ozone interaction over the Dead Sea, *J. Geophys. Res.*, *106*, 10,375–10,387.
- Matveev, V., M. Luria, D. Siman Tov, and M. Peleg (2002a), Long range transportation of air pollutants from Europe to Israel, *Isr. J. Earth Sci.*, *51*, 17–28.
- Matveev, V., U. Dayan, E. Tas, and M. Peleg (2002b), Atmospheric sulfur flux rates to and from Israel, *Sci. Total Environ.*, *291*, 143–154.
- Niemi, T. M., Z. Ben-Avraham, and J. R. Gat (Eds.) (1997), *The Dead Sea: The Lake and Its Setting*, Oxford Monogr. Geol. Geophys., vol. 36, Oxford Univ. Press, New York.
- Platt, U. (1994), Differential optical absorption spectroscopy (DOAS), in *Air Monitoring by Spectroscopic Techniques*, edited by M. W. Sigrist, chap. 2, pp. 27–84, John Wiley, Hoboken, N. J.
- Saiz-Lopez, A., J. M. C. Plane, and J. A. Shillito (2004), Bromine oxide in the mid-latitude marine boundary layer, *Geophys. Res. Lett.*, *31*, L03111, doi:10.1029/2003GL018956.
- Sander, R., and P. J. Crutzen (1996), Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, *J. Geophys. Res.*, *101*, 9121–9138.
- Sander, R., Y. Rudich, R. von Glasow, and P. J. Crutzen (1999), The role of BrNO₃ in marine tropospheric chemistry: A model study, *Geophys. Res. Lett.*, *26*, 2857–2860.
- Stutz, J., and U. Platt (1997), Improving long-path differential optical absorption spectroscopy with a quartz-fiber mode mixer, *Appl. Opt.*, *36*, 1105–1115.
- Stutz, J., R. Ackermann, J. D. Fast, and L. Barrie (2002), Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah, *Geophys. Res. Lett.*, *29*(10), 1380, doi:10.1029/2002GL014812.
- Sverdrup, H. U., M. W. Johnson, and R. H. Fleming (1942), *The Oceans, Their Physics, Chemistry and General Biology*, Prentice-Hall, Upper Saddle River, N. J.
- Tas, E., V. Matveev, J. Zingler, M. Luria, and M. Peleg (2003), Frequency and extent of ozone destruction episodes over the Dead Sea, Israel, *Atmos. Environ.*, *37*, 4769–4780.
- Tuckermann, M., R. Ackermann, C. Golz, H. Lorenzen-Schmidt, T. Senne, J. Stutz, B. Trost, W. Unold, and U. Platt (1997), DOAS-observation of halogen radical-catalyzed Arctic boundary layer ozone destruction during the ARCTOC-campaigns 1995 and 1996 in Ny-Alesund, Spitsbergen, *Tellus, Ser. B*, *49*, 533–555.
- Vogt, R., P. J. Crutzen, and R. Sander (1996), A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer, *Nature*, *383*, 327–330.
- von Glasow, R., R. Sander, A. Bott, and P. J. Crutzen (2002), Modeling halogen chemistry in the marine boundary layer: 1. Cloud-free MBL, *J. Geophys. Res.*, *107*(D17), 4341, doi:10.1029/2001JD000942.
- Wayne, R. P., et al. (1995), Halogen oxides: Radicals, sources and reservoirs in the laboratory and in the atmosphere, *Atmos. Environ.*, *29*, 2675–2884.

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