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Frequency and extent of ozone destruction episodes over the Dead Sea, Israel

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Abstract

A previous study performed at the Dead Sea during the summer (J. Geophys. Res. 106 (2001) 10375) has shown frequent ozone depletion episodes, when the mixing ratio of ozone was reduced to less than 5 ppb. These episodes were accompanied by the presence of high BrO levels (up to a level above 150 ppt). In order to establish the temporal and spatial extent of ozone depletion and subsequently indirect evidence of BrO formation, continuous ozone measurements were performed at three sites along the Dead Sea for a 14-month period starting from February 2001. The results indicated that extensive ozone depletion effects occur along the entire region of the Dead Sea basin during all periods of the year. The depletion effects were more pronounced in the southern areas (mid and south sites) than the north site. Since ozone depletion occurs with higher frequency in the south closer to the evaporation ponds and saltpans, it appears to be related to a higher sea-salt aerosol concentration in that region. Ozone depletion effects were also observed during a short-term study performed at a site situated approximately 1 km west and 400 m above the Dead Sea. Further, the ozone depletion effects appear to be more pronounced during summer than winter times. Additionally, these effects are prevalent during all periods of the year. Comparison of the Dead Sea data with ozone levels measured simultaneously at Beer Sheva, a site some 60 km west and outside of the Dead Sea Valley, demonstrates the extent of the ozone depletion. Further, while the Beer Sheva site showed the typical diurnal ozone cycle with ozone peaking at midday, the Dead Sea sites show a reverse situation and had decreased midday levels during the summer period. The present study indicates that ozone depletion events, and hence BrO production, occur all along the entire Dead Sea Valley and extend to a significant distance vertically and horizontally away from the water level. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Ozone depletion; Dead Sea; Reactive halogen species

1. Introduction

This phenomenon of complete boundary layer ozone depletion was first discovered about a decade ago and observed at several Arctic sites such as Alert, Canada (Bottenheim et al., 1990); Barrows, Alaska (Sturges et al., 1993), Spitsbergen, Norway (Solberg et al., 1996), Thule and Sandre-Stromfjord in Greenland (Rasmussen et al., 1996). Similar phenomenon was reported also for

*Corresponding author. Fax: +972-2-6584020. E-mail address: pelegm@pob.huji.ac.il (M. Peleg). several Antarctic stations: Syowa, between August and early October of 1989 (Murayama et al., 1992), Neumayer (Fries et al., 1999), and Arrival Heights (Kreher et al., 1997). The key species proposed to be responsible in the chemical mechanisms causing destruction of boundary layer ozone are the halogen atoms X,Y and their oxide radicals XO and YO (X,Y=Cl, Br, I) (Finlayson-Pitts et al., 1992; Wayne et al., 1995; Le Bras and Platt, 1995; Platt and Lehrer, 1997; Barrie and Platt, 1997). The presence of BrO was unequivocally verified in the Arctic boundary layer (Hausmann and Platt, 1994; Tuckermann et al., 1997).

Later studies have shown that ozone depletion episodes, not caused by anthropogenic nitrogen oxides titration reactions, can also occur at mid-latitudes within the tropospheric boundary layer at salt lake sites (Hebestreit et al., 1999; Matveev et al., 2001; Stutz et al., 2002). Studies performed at a site situated midway along the Dead Sea, during a 3-week period (late May/ early June) in 1997, showed repeated ozone depletion events, to almost zero levels, during most of the days sampled (Hebestreit et al., 1999). Aircraft flight measurements performed in summer 1997 showed that the ozone depletion episodes on several occasions covered almost the entire Dead Sea region (Matveev et al., 2001). Concurrent measurements using the Long Path-Differential Optical Absorption Spectroscopy (LP-DOAS) technique indicated that BrO produced was mainly responsible for the ozone destruction. As previously reported (Hebestreit et al., 1999; Matveev et al., 2001), BrO levels of up to 176 ppt were observed during the summer at a site situated in the middle of the Dead Sea adjacent to the shoreline. Later studies have confirmed that high BrO levels above 100 ppt are regularly observed at the Dead Sea (Zingler et al., 2003).

The present paper reports the results of 15 months of continuous ozone measurements performed at three sites at the Dead Sea in an attempt to better quantify the extent of ozone depletion both on a spatial and temporal

basis. The purpose of the study was to ascertain the frequency of ozone depletion episodes during the entire year and the spatial extent of the phenomenon. Further, since ozone loss was always accompanied by the presence of BrO (Matveev et al., 2001), ozone depletion events can therefore give an indication of the spatial and temporal extent of BrO formation. The above is therefore a qualitative substitute for DOAS BrO measurements and hence a simplified method for obtaining indirect information on long-term observations of BrO formation.

2. Experimental

The Dead Sea is a unique location, situated at the lowest point on the earth's surface, some 415 m below sea level and is part of the Syrian-East African Rift Valley. The Dead Sea valley is flanked by the Judean Mountains to the west and the Jordanian Moab Mountains to the east. Both mountain ridges reach a height of around 1000 m above sea level. The Dead Sea's geographical position is between N31°50′ and N31°, E35°30′, and its dimensions are about 75 km long and 15 km wide (see Fig. 1). The Dead Sea is fed mainly by the river Jordan in the north and by perennial springs and streams from the east and west. Having no outlet,

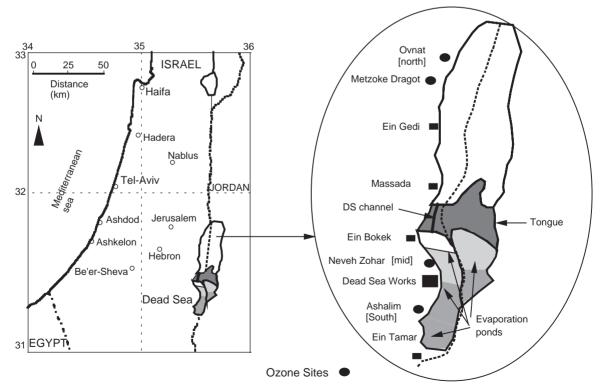


Fig. 1. Map of Israel with inset of the Dead Sea region indicating the measuring sites.

the Dead Sea is a "terminal lake" which looses huge amounts of water by evaporation into the hot dry air. The Dead Seas is one of the most saline lakes in the world containing 5.6 g bromide 1⁻¹ and 225 g chloride 1⁻¹ (Niemi et al., 1997). It is almost 12 times more saline than standard ocean water (Sverdrup et al., 1942). The Dead Sea is separated into two basins by a peninsula, the southern part being a series of solar evaporation ponds, which increase in salinity towards the south (see Fig. 1). An artificial channel allows water to be pumped from the northern section to the southern part.

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 and also a number of smaller resort sites along the northern part. The Dead Sea Works utilizes the high concentration of salts in the water to produce a number of products, including carnalite, potash, chlorine, bromine, magnesium metal, etc. The southern area consists of 'salt ponds' covering an area of about 100 km² for first-stage evaporation and 'carnalite ponds' over an area of 40 km² for second-stage evaporation. The residual brine contains about 11-12 g/l bromide and is used for the production of bromine. The 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 west bank of the Dead Sea.

Continuous ozone measurements were performed for almost 15 months, starting from February 2001, at three different positions along the Dead Sea as indicated in Fig. 1. The northern most site was at Ovnat, a

community college, some 8 km south of the northern tip of the Dead Sea and about 1km west of the shoreline. This site is situated some 50 km north of the evaporation ponds situated at Ein Bokek. The mid site at Neveh Zohar was situated about 3km north of the main evaporation ponds of the Dead Sea Works and almost on the water line. The third instrument was placed at a southern site about 2km north of the southern edge of the large salt evaporation ponds and about half a kilometer west of the ponds. For a limited period between 21 July and 11 August, an additional ozone monitor was operated at Metzoke Dragot, an elevated site some 400 m above the Dead Sea (~0 m absolute elevation above ocean sea level). This site was some 1.5 km west of the Dead Sea and about 10 km south of the Ovnat Dead Sea level site (Fig. 1). The ozone monitors were periodically calibrated in order to be certain that all the instruments were measuring comparable values.

3. Results

A summary of the results for the continuous ozone measurements is shown in Table 1. The table shows the maximum, minimum and monthly average of half-hourly ozone levels for the three different sites at the Dead Sea. The results reported are only for the daytime period when photochemical activity is pronounced. The data coverage of the ozone monitors (see Table 2) was not as high as scheduled and occasionally dropped below 75% of the time per month, due to various

Table 1 Maximum, minimum and average ozone levels at the Dead Sea during photochemical activity period; 09:00–17:00 (LT=UT+2)

Site position	North	Mid	South	North	Mid	South	North	Mid	South	
Midday half-hour values		Maximum (ppb)		Minimum (ppb)		Average (ppb)				
Year	Month									
2001	February	86	73	74	4	7	6	47	38	44
	March	83	83	80	6	7	9	55	50	47
	April		102	97		5	6		52	46
	May	88	99	98	3	1	8	59	63	53
	June	85	115	82	2	3	3	57	61	45
	July	94	103	74	2	3	2	50	48	37
	August	84	92	74	3	3	2	46	43	33
	September	79	83	65	4	8	7	50	46	32
	October	83	88		7	9		55	50	
	November	63	69	80	8	4	2	40	37	35
	December	51	61		6	3		34	26	
2002	January	69	72		5	3		42	41	
	February	80	77		9	2		48	43	
	March	83	77	92	20	18	5	55	60	43
	April	73	73	88	3	3	3	42	37	41

Table 2			
Instrument data coverage	(%) at the	three Dea	d Sea sites

Year	Month	Site position				
		North	Mid	South		
2001	February	84	25	99		
	March	54	79	77		
	April	0	85	85		
	May	57	97	100		
	June	77	100	99		
	July	80	91	81		
	August	93	98	94		
	September	73	41	40		
	October	23	34	0		
	November	39	95	76		
	December	21	69	0		
2002	January	66	65	6		
	February	92	97	0		
	March	79	14	37		
	April	77	58	80		

problems such as power cuts, vandalism and theft of one of the monitors, etc.

Examination of Table 1 does not show any distinct seasonal trends although a tendency to higher ozone levels during spring and summer is evident, as is to be expected for the more photochemically active periods, in contrast to the winter season. Of special importance is the level of the minimal values reported during the entire measuring period. Midday values below 10 ppb were recorded during all the months and at all of the sites (excluding March 2002). Such low values indicate that ozone depletion processes must be occurring all along the Dead Sea during all seasons.

Figs. 2 and 3 show the diurnal ozone variations for the three measuring sites for February and August 2001, respectively. These months are representative of winter and summer respectively. Also included for comparison in the figures are data from a site situated at Beer Sheva (residential area, 15 m above ground level) supplied by the Israeli National Air Quality Monitoring Network. The Beer Sheva site is situated 60 km west of the Dead Sea (see map in Fig. 1) and at a height of about 200 m above sea level. Beer Sheva is a town with a population of some 180,000, whose air quality is mainly affected by local transportation effects. Thus, these results should represent a site unaffected by the Dead Sea ozone depletion effects. The ozone results as reported for Beer Sheva represent typical urban behavior with peak ozone levels corresponding to peak photochemical activity at midday. The figures show all the data for each month grouped into hourly averages for the Dead Sea data and half-hourly averages for the Beer Sheva results. Additionally, the standard deviations (marked by bars) and the mean values (closed diamond shape) are plotted.

Examination of the data for both February and August show that all sites have typical diurnal variation with minimum values during early morning and maximum levels during the afternoon hours. However, a number of differences can be observed between the urban site and the Dead Sea sites. The standard deviations of ozone concentrations for Beer Sheva are limited and much smaller than for the Dead Sea sites. especially so for the midday periods. Further, during periods of high photochemical activity (between 09:00 and 17:00 during summer and between 10:00 and 16:00 in winter), the ozone levels for Beer Sheva never dropped below 20 ppb. This is in strong contrast to the Dead Sea sites that showed repeatedly low concentration levels approaching almost zero. Conversely, elevated ozone levels, even higher than values noted for Beer Sheva, are also observed at the Dead Sea sites for the midday period. This wide dispersion of ozone levels, from high to almost zero levels, indicates that on certain days strong ozone depletion takes place while for the remaining days normal photochemical peaking is recorded. It should also be noted that the mean hourly values (closed diamond symbols) for the Dead Sea sites do not show any distinct peaking during midday for August and in fact show a slight decrease in ozone levels around 14:00. Conversely, single measurement data points show that during midday at the Dead Sea, strong ozone depletion occurs and only once this being terminated at around 17:00, a slight ozone increase can be observed before again decreasing as photochemical activity is reduced during the evening hours. The order of the mean ozone levels for August was around 30 ppb for the south site, followed by the mid site slightly above 40 ppb, 45 ppb for the north site, and above 60 ppb for Beer Sheva. For February, all three Dead Sea sites and Beer Sheva show similar mean ozone values of around 45 ppb during the midday period. However, while during the midday period, the Beer Sheva site does not show ozone levels above 50 ppb or below 25 ppb, the Dead Sea sites show maximum values approaching 80 ppb together with minimum levels approaching zero.

Fig. 4 shows the ozone measurements for a single day, 7 July 2001, at the three sites. Ozone depletion occurred at all three sites almost simultaneously on that day beginning at around 12:00. The above and similar results indicate that ozone depletion occurs along the entire Dead Sea region probably caused by the presence of BrO formed over the Dead Sea. The other possibility of ozone reduction due to titration with NO can be ruled out due to the low levels (generally less than 5 ppb) of this pollutant present at the Dead Sea (Matveev et al., 2001), especially so in the northern parts.

During the period between 21 July and 11 August, additional ozone measurements were performed at the Metzoke Dragot elevated site. Ozone depletion effects were observed at Metzoke Dragot on 3 days during the

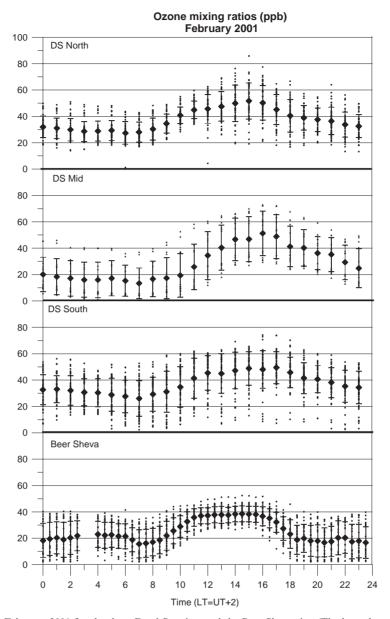


Fig. 2. Ozone levels for February 2001 for the three Dead Sea sites and the Beer Sheva site. (The bars show the standard deviations and the mean values by closed diamond shapes.) Time is Israeli local time (UT+2).

22-day measuring period. For 26 July 2001, a time-correlated ozone loss could be detected at Metzoke Dragot and at all three of the Dead Sea sites, see Fig. 5. From this figure it is clear that the ozone depletion begins at around 11:00 at both Metzoke Dragot and the north site followed by the mid and south sites at 12:00. From the results of Figs. 4 and 5, it is obvious that ozone depletion occurs all over the Dead Sea region and is not limited to the Dead Sea surface but affects regions at least 400 m above the water level and a kilometer west of the Dead Sea.

4. Discussion

Several field campaigns and laboratory investigations have shown that halogen atoms and their oxide radicals are key species in the chemical mechanisms responsible for the destruction of ozone (Barrie and Platt, 1997; Tuckermann et al., 1997; Wayne et al., 1995; Matveev et al., 2001). A number of studies (Hebestreit et al., 1999; Matveev et al., 2001) performed at the Dead Sea have clearly shown the role of BrO in causing ozone depletion. Two main chemical mechanisms have been

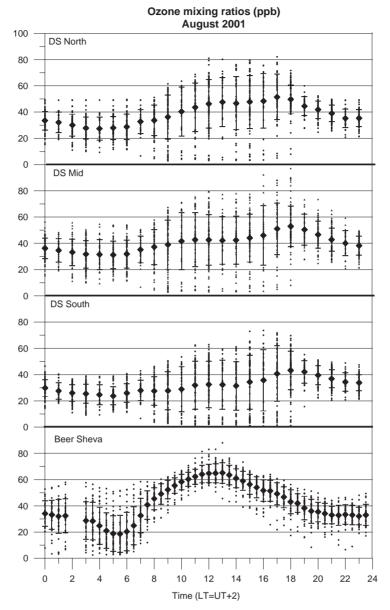


Fig. 3. Ozone levels for August 2001 for the three Dead Sea sites and the Beer Sheva site. (The bars show the standard deviations and the mean values by closed diamond shapes.) Time is Israeli local time (UT+2).

(3)

proposed as being responsible for ozone destruction at the Dead Sea.

Cycle A (BrO-cycle):

$$2Br + 2O_3 \rightarrow 2BrO + 2O_2,$$
 (1)

$$BrO + BrO \rightarrow Br + Br + O_2.$$
 (2)

Net:

$$2O_3 \rightarrow 3O_2$$
.

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

Cycle B (HOBr-cycle):

$$Br + O_3 \rightarrow BrO + O_2,$$
 (4)

$$OH + O_3 \rightarrow HO_2 + O_2, \tag{5}$$

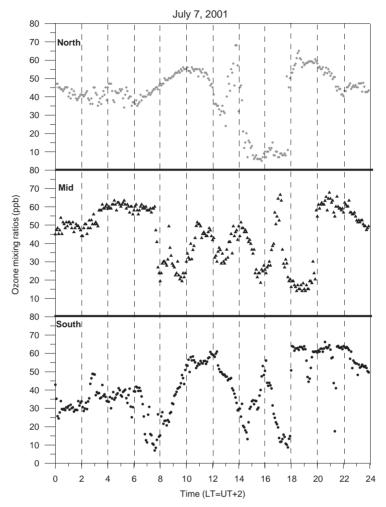


Fig. 4. Diurnal ozone concentrations at the three Dead Sea sites for 7 July 2001. Time is Israeli local time (UT+2).

$$BrO + HO_2 \rightarrow HOBr + O_2,$$
 (6)

$$HOBr + hv \rightarrow Br + OH.$$
 (7)

Net:

$$2O_3 \to 3O_2$$
. (8)

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 (Matveev et al., 2001), cycle A will dominate.

As shown above, bromine atoms are a prerequisite for initiating both cycle A and cycle B. Halogen release mechanisms have been the subject of a number of computational, laboratory and field investigations. The main source, relevant for the Dead Sea, is the release of reactive halogens from sea salt. The release of bromine

(or other halogens) from sea salt is based on the uptake of HOBr (reaction 6) on acidic salt surfaces (Fan and Jacob, 1992; Tang and McConnel, 1996; Vogt et al., 1996) followed by the formation of a halogen molecule.

$$HOBr + Br^{-} + H^{+} \rightarrow Br_{2} + H_{2}O,$$
 (9)

$$Br_2+h\nu\rightarrow 2Br,$$
 (10)

The released halogen atoms then react as shown previously

$$2Br + 2O_3 \rightarrow 2BrO + 2O_2$$
,

$$BrO + HO_2 \rightarrow HOBr + O_2$$
.

Giving rise to the net reaction:

$$BrO + HO_2 + Br^- + H^+ + 2O_3$$

 $\rightarrow 2BrO + H_2O + 3O_2.$ (11)

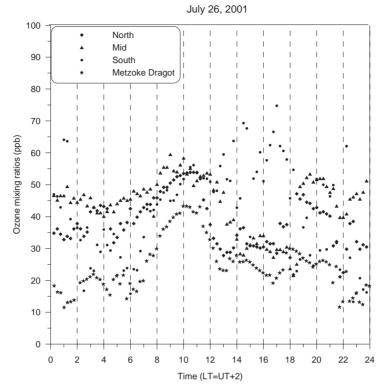


Fig. 5. Diurnal ozone concentrations at the three Dead Sea sites and Metzoke Dragot for 26 July 2001. Time is Israeli local time (UT+2). Time is Israeli local time (UT+2).

The above net reaction has been proposed by Platt and Lehrer (1997) as a 'bromine explosion mechanism'. The halogen oxide molecule acts like a catalyst promoting the oxidation of Br to Br by O₃. This reaction sequence has been demonstrated in several laboratory (Rudich et al., 1996) and modeling (see e.g. Lehrer, 2000) investigations. This reaction occurs only at pH < 6.5 (Fickert et al., 1999). The Dead Sea waters are characterized by pH values between 6 and 6.35 (Nishri and Stiller, 1997) and are strongly buffered solutions. The above heterogeneous processes only lead to an exponential increase in gaseous reactive bromine if more than one bromine atom is produced for each scavenged HOBr molecule. This is the case as long as the release of Br₂ is preferred to that of BrCl (by reacting with the Cl⁻ also present in the waters) as reported by Fickert et al. (1999). Since the Dead Sea waters contain 5.6 g/l bromide (as compared to 0.07 g/l for normal sea water) and has a Br⁻/Cl⁻ ratio of 0.025 as compared to a ratio of 0.0034 in normal seawater (enrichment factor of 7), it is to be expected that the 'bromine explosion mechanism' will be especially effective over the Dead Sea. It is therefore to be expected that the 'bromine explosion mechanism' will occur not only at the salt surface but also over the waters themselves and at the salt aerosol surfaces.

Since, as shown above, the ozone destruction depends on the presence of a Br atom, processes that remove Br will interfere with ozone depletion and the reformation of BrO. Bromine atoms can react with oxidized or unsaturated hydrocarbons (e.g. formaldehyde, olefins) and HO₂ to form HBr.

$$Br + RH \rightarrow HBr + R.$$
 (12)

This reaction effectively reduces the number of Br available for ozone destruction. However, as long as ozone is not completely depleted, almost all Br atoms will prefer to react with the ozone leading to no net BrO loss (reaction (1) above). Comparison of reaction rates shows that the effective conversion time of BrO to HBr will be more than 1 h (Stutz et al., 1999). Since the daytime lifetime of BrO is determined by the rate of formation of HBr, it is therefore expected that this will be of the order of 1–2 h.

In our previous reports (Hebestreit et al., 1999; Matveev et al., 2001), it has been suggested that the evaporation ponds/salt pans situated in the southern area of the Dead Sea were assumed to be responsible for BrO production and hence ozone depletion. However, the present study shows (see Figs. 4 and 5) that ozone depletion occurs at the north simultaneously or even sooner than at the south or mid sites. Thus, BrO

formation at the ponds followed by transportation to the north cannot be the sole reason for ozone depletion at the north before or simultaneously occurring at the south of the Dead Sea. The distance between the northern and south sites is around 60 km. Even assuming a wind speed of 20 km/h (above average for midday), it would still take more than 2 h for any BrO or BrO precursors produced over the evaporation ponds/ saltpans to arrive at the northern site.

The major question regarding the source or sources of BrO production at the Dead Sea remains unanswered. Figs. 6 and 7 show the monthly ozone wind roses for February and August for the three sites when ozone levels dropped below 20 ppb during daytime (10:00–16:0 for winter and 09:00-17:00 for summer). The above months are representative of winter and summer respectively. The levels below 20 ppb for this time period, at completely rural sites, indicate that ozone depletion effects are taking place. Comparison of the 2 months indicates that during the winter months, there were much less ozone depletion episodes than for summer. The number of half-hourly periods that showed ozone levels below 20 ppb for February and August were 3 and 61, respectively, for the north site, 23 and 60 at the mid-position and 44 and 140 for the south site. Ozone depletion was observed at the south mainly (89% and 78% of the time for February and August respectively) under wind directions in the N-NE (0-120°) sector for both months, and also in the W-N $(270-360^{\circ})$ sectors during summer (25% of the time). At the mid site, ozone depletion during February occurs for 63% of the time under southerly wind flows (150–200°) and predominantly (78%) from the north $(330-40^{\circ})$ during August. At the north site, ozone depletion occurs for 85% of the time during August when the wind was in the east to south sector (60–180°). During February. only three depletion events could be recorded.

As previously observed it is the special chemical composition, and especially its bromine content, of the Dead Sea waters that appears to be responsible for BrO formation and subsequently ozone destruction. It is therefore to be expected that winds flowing over the waters and especially over the evaporation ponds/saltpans can give rise to ozone reduction. Examination of the predominant wind directions during the daytime shows that ozone depletion events correlate, more or less, with the predominant wind directions, and it is not possible to designate a specific direction as being solely responsible for ozone depletion. For example, during August, the south site shows that for 65% of the time, the wind direction is in the 0-120° segment and for 25% of the time in the 270–360° segment, corresponding respectively to 78% and 25% of the ozone depletion events. For the south site, all winds originating from the eastern sectors will have passed over the evaporation ponds/salt pan before reaching the measuring site and thus ozone

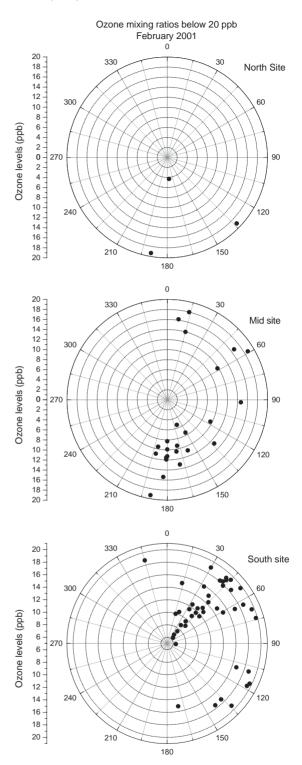


Fig. 6. Ozone wind roses for February 2001 for the three Dead Sea sites.

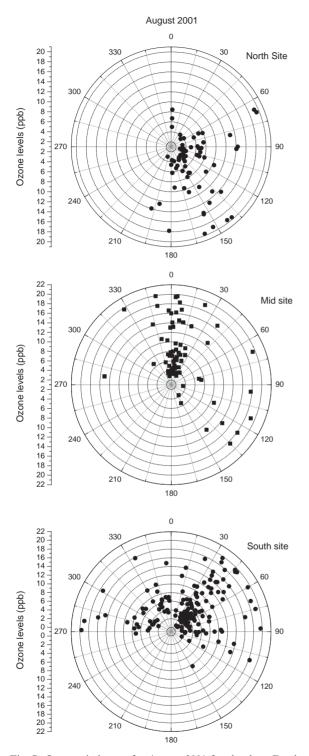


Fig. 7. Ozone wind roses for August 2001 for the three Dead Sea sites.

depletion events are to be expected. However, as observed in Fig. 7, ozone depletion was observed during August even when the winds flowed from the northwest. Since winds from the northwest have not passed directly over the evaporation ponds, it must be assumed that either recirculation of air masses that previously passed over the salt lakes has occurred or that deposition of salt spray outside the water bodies has taken place. The mid site is affected during summer by northerly wind flows and during the winter by winds from the south. Northerly winds will flow over the Dead Sea lake before reaching this measuring site, while the southerly winds will have passed mainly over the evaporation ponds/saltpans. The north site is affected by only southern wind flows during the daytime. These air masses have passed over the Dead Sea before reaching the north-measuring site. Since this site is distant from the evaporation ponds/saltpans, therefore, the only source of ozone depletion precursors must be from the Dead Sea waters.

In an attempt to quantify the effect of ozone depletion and its temporal variations, a comparison was made, as shown in Fig. 8, between the monthly mean ozone midday maximum levels as measured at the Beer Sheva air quality monitoring station and concurrently at the Dead Sea sites (obtained from figures similar to Figs. 2 and 3 for all the relevant months). As observed in Fig. 8, a distinct monthly pattern is obvious for all the sites. However, while Beer Sheva shows elevated ozone values for the summer months, as is normally expected, the Dead Sea sites show a reverse situation and have lower midday levels during summer than for the other periods of the year. This unique behavior further supports the fact that ozone depletion effects are effective at the Dead Sea. It should also be remembered that Beer Sheva, in contrast to the Dead Sea, is affected by local anthropogenic emissions of nitrogen oxides that cause titration, and hence lowering of the ozone levels. Thus, the difference between the Beer Sheva midday maximum ozone levels and the Dead Sea values should be even larger. For the remainder of the year, the ozone levels for Beer Sheva are similar to those for Dead Sea, especially with respect to the north site. Further, as noted in Fig. 8, the order of the mean midday ozone levels for the Dead Sea sites is lowest at the south site followed by the mid position and the highest monthly midday levels for the north. This would appear to further support, as noted previously, that the closer the measuring site is to the evaporation ponds/salt pans, the more extensive is the ozone depletion and hence the closer proximity to more intensive BrO production. While it is to be expected, BrO production is more intensive over the saltpans and evaporation ponds, in order to explain the ozone reductions in the northern parts of the Dead Sea, it must be assumed that the 'bromine explosion

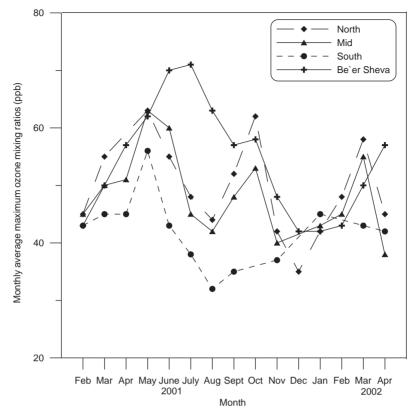


Fig. 8. Average monthly ozone maximum levels at the three Dead Sea sites and for Beer Sheva.

mechanism' occurs also over the waters and is not restricted to the solid phase.

Recent measurements performed at salt lakes in the vicinity of Salt Lake City, USA (Stutz et al., 2002) measured maximum BrO levels of only 6 ppt. The salinity of these lakes is lower than the Dead Sea by a factor of about 3–4 (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. Thus, it appears that it is primarily the higher bromine salt levels present at the Dead Sea that strongly influences BrO production and hence cause repeated ozone depletion events.

The fact that ozone depletion effects were also observed at the elevated site would indicate that the BrO is still available even after being transported to some 400 m above the Dead Sea. The minimum theoretical time (based on atmospheric stability, air mass density, ground temperature, etc) for an air mass to rise from the Dead Sea surface to a height of 400 m is at least 30 min. This is consistent with the expected BrO daytime lifetime of 1–2 h as explained previously.

Depending on the BrO lifetime, wind speed and meteorological conditions, it is reasonable to assume that ozone depletion events should take place outside of the Dead Sea region, up to distances of a number of kilometers.

5. Conclusions

The present study shows clearly that ozone depletion effects occur along the entire region of the Dead Sea basin during all periods of the year. The ozone reductions are more predominant in the southern areas (mid and south, closer to the evaporation ponds/salt pans corresponding to the higher salt concentration in that region) than at the north side. The depletion effects are more pronounced during the summer times than during winter. These effects do not occur only at the Dead Sea surface but affect areas even 400 m above the water level.

The ozone depletion mechanism has been shown to be related strongly to the presence of BrO species, as reported by Hebestreit et al. (1999) and Matveev et al. (2001). The ozone depletion results presented here indicate that the proposed 'bromine explosion mechanism' responsible for initiating the ozone depletion effects occurs not only over the solid salt deposits but also over

the Dead Sea waters themselves and more intensively over the evaporation ponds.

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