

Vertical distribution of physical and chemical properties of haze particles in the Dead Sea valley

Zev Levin*, Hezi Gershon, Eliezer Ganor

Department of Geophysics and Planetary Sciences, Tel-Aviv University, Ramat Aviv 67789, Israel

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Abstract

The chemical and physical properties of haze particles in the Dead Sea were measured using airborne and ground-based instruments. The results show a very distinct layering of the haze with two major layers, one below about 300 m ASL and the other at around -150 m ASL, which is around $+250$ m above the Dead Sea surface.

The lower layer was found to contain a large fraction of sodium nitrate particles with sizes larger than $1\ \mu\text{m}$. The particles in this layer are likely transported at night from pollution sources to the south west of the Dead Sea. The upper layer contained large concentrations of fine sulfate particles that are transported from distance sources such as the Israeli Mediterranean coastal regions or even from sources as far away as Europe. The two haze layers appear to be separated in the morning hours, but as the day marches on and the temperature of the land surface on both sides of the lake increases, thermal convection sets in and the two layers become homogenized. A third layer around 1000 m ASL is also observed. This layer is the commonly observed marine boundary layer over Israel and is not affected by the circulation in and around the Dead Sea.

In the afternoon the Mediterranean sea breeze reaches the Dead Sea valley and is diverted first into a weak easterly and then into stronger northerly winds, which clear the haze particles from the valley. The land breeze over the lake during the night brings new pollution particles from the Rotem Plato to the southeast of the Dead Sea and is responsible for the formation of the early morning lower haze layer.

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1. Introduction

The Dead Sea, besides being the lowest place in the world (currently around -415 m below the sea level), is a source of minerals, which are being harvested by both the Israeli and the Jordanian chemical industries. Fig. 1 presents the map of Israel and an enlarged map of the Dead Sea with the solar ponds in the southern end of the lake.

In addition, the combination of the Dead Sea minerals, with the low solar radiation that reaches the surface is thought to have some medical qualities, especially for several skin diseases (Shani et al., 1985, 1987). Therefore, changes in the transparency of the atmosphere above the Dead Sea have important economic as well as environmental implications.

A haze layer regularly appears above the Dead Sea valley, when the weather is fair and the atmospheric is stable. It forms in the early morning and disappears in the late afternoon, when the Mediterranean sea breeze reaches the valley. The reduction in solar radiation due

*Corresponding author. Fax: +972 3 6408274.

E-mail address: zev@hail.tau.ac.il (Z. Levin).

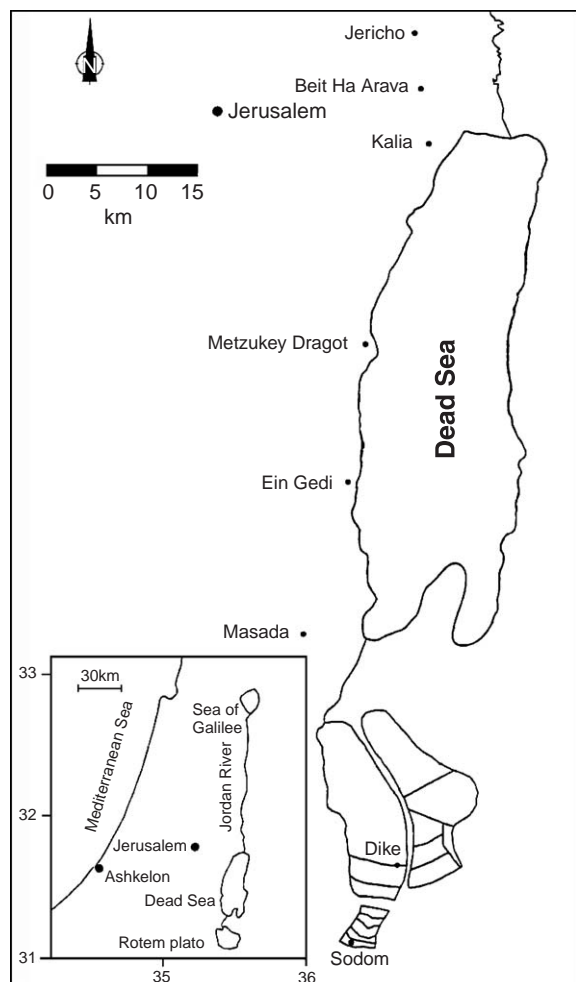


Fig. 1. A map of Israel with an enlargement of the Dead Sea region.

to the extinction by haze particles has been shown to reduce the net radiation reaching the surface and therefore, reduces the evaporation rate from the lake and from the solar ponds used for the extraction of potash (Stanhill, 1987). Stanhill and Moresht (1992) and Stanhill and Cohen (2001) relying among others, on measurements at the Dead Sea, suggested that a global reduction of incoming solar radiation, called “global dimming”, is taking place due to the increased concentrations of suspended atmospheric aerosols from air pollution.

A few investigations were carried out in order to study the chemical composition of the haze particles (e.g. Aharonson and Berenshtain, 1984; Levin and Ganor, 1984).

Both studies sampled the particles at different places around the shores of the Dead Sea (around 415 below sea level), and at Metzukey Dragot, located at about Sea

Level (see Fig. 1). Their results indicated that the particles, which were samples near the shores, were found to be similar to the composition of the water in the lake. However, the particles which were sampled at Metzukey Dragot were found to contain high concentrations of the element sulfur. Since there are very few local sources of sulfur they concluded that most sulfur containing particles must have originated from distant sources, such as the Israeli–Mediterranean coast or even from remote sources in Europe (e.g. Wanger et al, 2000). However, no direct measurements of the vertical concentrations and composition of the haze particles were ever made. In addition, there are no measurements or results from model simulations that give confidence to the conclusions made by Levin and Ganor (1984) that the source of most of the haze particles is the Mediterranean coast.

The aim of this paper is to address these last points by reporting on measurements carried out at the Dead Sea region from an airplane and from a ground-based station.

2. Method

The vertical distribution of the haze particle’s chemical composition, concentration and size distribution were determined during three typical hazy conditions in 1998 and 1999. The measurements were carried out from an airplane, on which a number of aerosol optical spectrometers and sampling systems were installed. In 1998 and in 1999, a two engine Cessna and a King Air airplane, respectively, were used.

Some of the flights were performed in both the morning and the afternoon hours, in order to study the temporal variations of the haze particles.

The Cessna was instrumented with a condensation nuclei (CN) counter (Environmental 1) mounted near the nose of the plane to obtain as much representative samples as possible. In addition, a 1” diameter sampling tube with a conical inlet with 6 mm diameter hole, for collecting particles on various substrates for subsequent chemical analysis, was installed, stretching from the front of the plane to the cabin. Filter holders and a cascade impactor were connected to the sampling tube on one side and to a pump on the other side.

The King Air airplane was instrumented with a PMS-FSSP-100 optical aerosols spectrometer (modified by DMT to SPP-100, with sizing range of 0.3–47 μ m), which was mounted under the wing. The sampling tube on the King Air airplane was mounted from the top of the cabin allowing near-isokinetic sampling of aerosols, smaller than about 5 μ m. The same inlet was used for the measurements with the CN counter. The collection of particles was performed on substrates similar to those used on the Cessna airplane.

Two different substrates were used for depositing the aerosols during the flights; aerosols were collected on grids coated with carbon, which were mounted in a single-stage Casella cascade impactor. Individual particles in the collected samples were later subjected to elemental analysis. The second type of substrate used was a filter made of Teflon (0.2 μm pores); samples collected with this substrate were later subjected to bulk chemical analysis.

Elemental analysis of individual particles was carried out using a scanning electron microscopy (SEM) (Jeol, JSM-6300), which had been previously calibrated for elemental mass based on the method of Pardess et al. (1992) and Levin et al. (1996).

Bulk chemical analyses were carried out using an inductively coupled plasma (ICP) analyzer by PE SCIEX ELAN 6000 ICP-MS.

The flights were conducted back and forth from above Jericho, just north of the Dead Sea to Sodom in the south. Initially, the plane flew at around 1700 m ASL for about 20 min, in order to allow us to collect a sample with sufficient material to carry out bulk chemical analysis. The plane then descended in steps of about 70 m until it reached an elevation of about 50–70 m above the Dead Sea surface (about 330 m below sea level). In each of these legs, aerosol samples were collected on grids for elemental analysis of individual particles. Throughout the flight our optical aerosol spectrometers measured particle concentrations and size.

In addition to the airplane measurements, a three-day field experiment at Metzukey Dragot, on the hills to the west of the Dead Sea (altitude about sea level, or about 400 m above the level of the Dead Sea) was conducted from 31st October until 2nd November, 1999. In this campaign aerosol size distributions were measured by an optical aerosol spectrometer SPP-200 (also known as PCASP, having a range of 0.1–3.0 μm).

A number of aerosol samples were collected everyday at the measuring site. They were later on used for analysis of the elemental and chemical composition of the particles. In addition, meteorological parameters such as temperature, wind speed and wind direction, were measured manually.

3. Results

3.1. Physical analysis of the haze layer

3.1.1. The airborne measurements

The average vertical profiles of particle concentration (the range of the measurements was about $\pm 10\%$ around the average) and temperature (about $\pm 5\%$ around the average value) from above the Dead Sea on the morning of 29 April 1999 are shown in Figs. 2 and 3. In this figure, one can identify two distinct sub-layers;

the upper one, which we will name “layer 2”, between 100 and 500 m ASL (in this layer a number of sub-layers appear, but we will consider them as one layer, due to the uncertainty expressed by the errors around the average measurements), and the lower one, named “layer 1”, around 150 m below sea level. The gap between these layers is characterized with relatively low particle concentration. It should be mentioned that this relative minima in particle concentration was found to be relatively constant during our flight at this time and height. A third peak, composed of a few sub-layers in the particle concentration, can be seen from around 750 to 1500 m ASL. This layer is named “layer 3”.

The temperature profile in Fig. 3 shows that three temperature inversions were present; one around 0 m, a second between 250 and 700 m ASL and the third at 1200 m ASL. Dayan (1986) showed that a marine

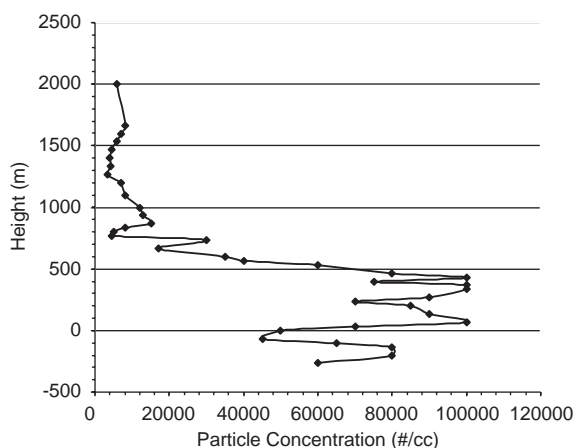


Fig. 2. The vertical profile of particle concentrations as measured by the CN counter (Environment 1) during a flight above the Dead Sea valley on 29 April 1999, (starting at 09:45 and ending at 10:15 LT).

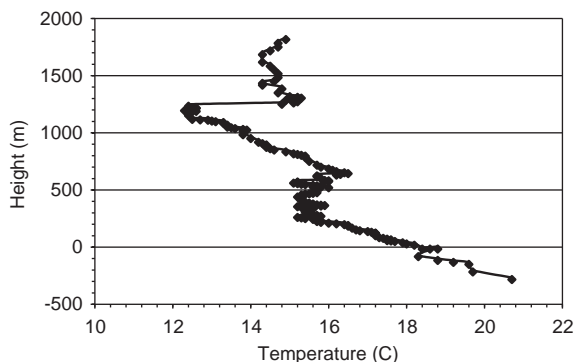


Fig. 3. The vertical profile of temperature measured during a flight above the Dead Sea on 29 April 1999 (starting at 09:45 and ending at 10:15 LT).

inversion layer around 1200 m ASL is usually present over Israel during the summertime. This marine inversion appears above the Dead Sea at around 1250 m (Fig. 3) and it is likely the cause of the formation of layer 3. However, a few additional weak irregularities in the temperature profile appear at lower levels. The local maxima in particle concentrations shown in Fig. 2 coincide with the locations of the lower thermal inversions (around 600 and 0 m, ASL) shown in Fig. 3.

Fig. 4 represents the particle concentration profiles over the Dead Sea during a summer day, 31 July, 1998. On this day, we carried out measurements in the morning and in the afternoon, in order to investigate the temporal variations in the vertical distribution of the haze. As can be seen, haze layers 1 and 2 exist in the morning hours, similar to the situation during our measurements in April 1999 (Fig. 2). But as the day progresses, and the land surface on the shores of the lake heats up, local convection sets in and the two lower haze layers merge into one semi-homogeneous layer over a larger vertical extend. This mixing and dilution of the haze leads to reduced particle concentrations and improved visibility. During the day the upper haze layer, layer 3, decreases in intensity by mixing with the air below (mixing of upper air at 1000 m ASL with air at around 600–800 m). At the time of our measurement (at 13:00) the upper layer was still apparent, but it disappeared around 16:00 when the Mediterranean sea breeze reached the Dead Sea valley.

The reasons for the differences between the particle concentrations in Figs. 2 and 4 stem at least in part, from the different seasons in which these measurements were conducted. Fig. 2 presents measurements taken during the spring time, when the temperatures are still

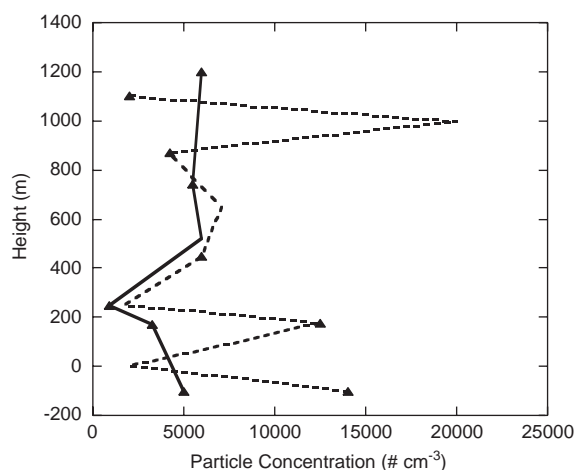


Fig. 4. Vertical profiles of average particle concentrations, measured on 31 July 1998. The dashed and solid curves represent the particle concentrations at 11:00 LT and at 13:00 LT, respectively.

low and the upper inversion above layer 2 is weaker and lower than in the summer. But, in spite of that, it is interesting to note that haze layers 1 and 2 in both seasons remain about the same. This suggests that the height of haze layers 1 and 2 are more affected by local conditions (the differences between the temperature of the Dead Sea water and the surrounding land) than by the larger synoptic scale, which controls the regional marine boundary layer over Israel and layer 3 over the Dead Sea.

Fig. 5 presents the size distribution of the particles in layers 1–3, as measured with our FSSP-100. Each point represents an average of 30 s and the range of measurements in each size bin was generally less than 5% of the average value, with some exceptions at the large sizes where the range was larger (~10%) due to the lower particle counts. The figure also shows the corresponding size distribution of the particles at 1100 m above Tel Aviv. Since the measurements were conducted in April, the morning inversion in Tel Aviv was still below the flight level; therefore, at a height of 1100 m the particle concentration was still very low. In contrast, the particle concentrations in both haze layers over the Dead Sea are much higher, with a large fraction of giant particles (particles larger than 1–2 μm). The figure shows that the size distributions in both haze layers 1 and 2 are somewhat similar, with slightly larger concentration of giant particles in layer 1. The size distributions of the

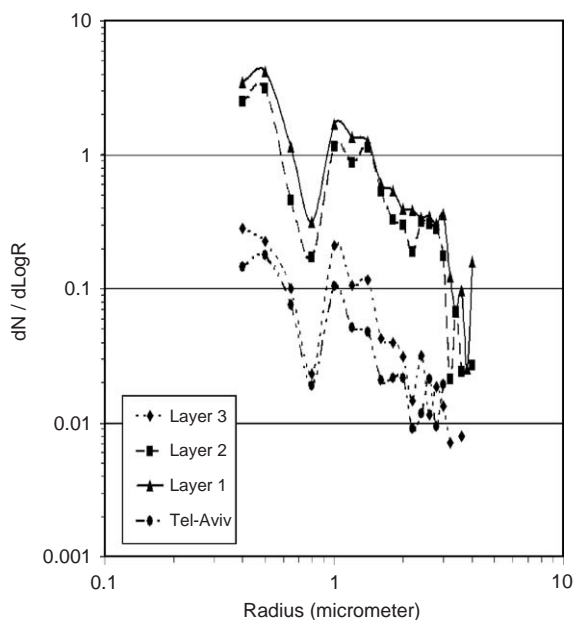


Fig. 5. Averaged size distributions in haze layer 3 (1000 m ASL), haze layer 2 (300 m ASL) and haze layer 1 (–100 m ASL) around 10:00 LT. The size distribution was measured by FSSP-100 over Tel Aviv (at 1160 m and at 9:30 LT) on 29 April 1998 is also shown.

particles over Tel Aviv and in layer 3 are very similar, indicating that the pollution in layer 3 and over Tel Aviv is from similar sources.

3.1.2. The measurements at the ground station

The ground-based measurements were carried out at Metzukey Dragot from 31st October until 2nd November 1999.

The objective of these measurements was to monitor the diurnal variations of the haze. Metzukey Dragot was chosen because, it is close to the shores of the Dead Sea and its elevation (about 500 m above the sea surface or 100 ASL) puts it at about the same height as haze layer 2, at least for part of the day.

The aerosol size measurements were conducted almost continuously, while the aerosol mass was collected on filters a number of times each day. Fig. 6 shows the variations in aerosol concentrations, as was measured by the CN counter. One can clearly see the sharp increase in particle concentrations at the measuring site, from around 7:00 LT to about 14:00 LT and the decrease that continues until the next morning. Although CN measurements were performed only during days and evenings, the general trend is apparent. This cycle agrees

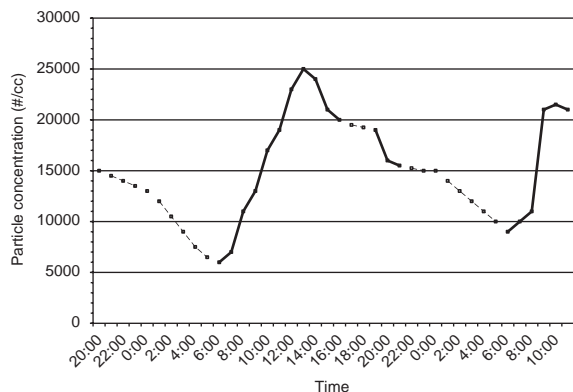


Fig. 6. Average particle concentrations (cm^{-3}) measured at Metzukey Dragot ground station as a function of time (31st October–2nd November 1999). The black line represents actual measurements, whereas the dashed ones represent interpolation.

with our conclusion that haze layer 2, which in the morning hours is below the level of Metzukey Dragot, begins to lift as the sun heats the land around the lake. This increase in concentration at the measuring site continues until the input of particles from below just balances the mixing and dilution with the air above. In the afternoon, around 14:00 to 18:00, the effects of the Mediterranean sea breeze, with first light easterly and then stronger northerly winds, is felt at the site, leading

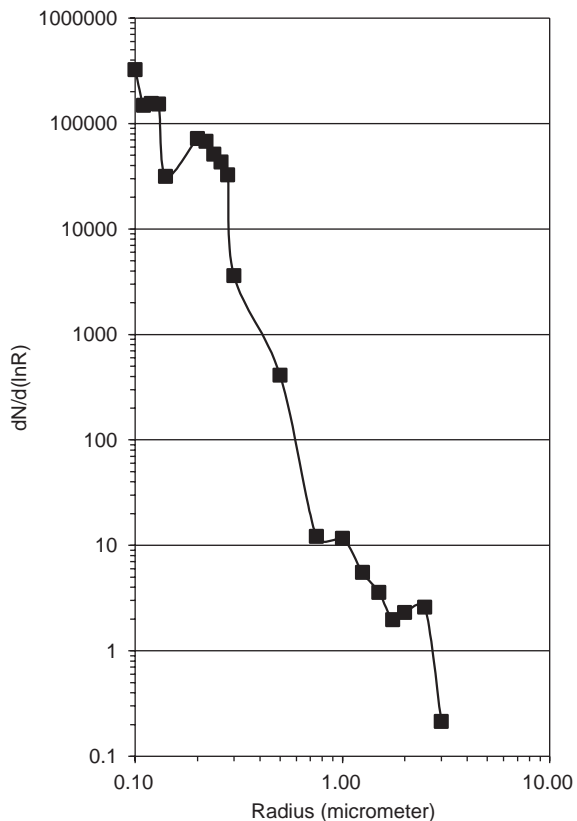


Fig. 7. Average aerosol size distributions at the ground station of Metzukey Dragot collected at 18:00 on 1 November 1999. The measurements were carried out using the optical sampler SPP-200 (PCASP, 0.1–3.0 μm). Each point represents an average of 300 measurements.

Table 1
Meteorological parameters measured during the field campaign at Metzukey Dragot 31 October–2 November 1999

Time	21:00 Oct. 31	24:00 Nov. 1	06:00	09:00	12:00	15:00	18:00	21:00	24:00 Nov.2	06:00	09:00	12:00
Wind direction (deg)	270	270	360	60	80	40	360	320	270	290	30	90
Wind speed (m s^{-1})	10	9	0.5	2	0.5	1	5	5	5	4	6	0.5
Temperature ($^{\circ}\text{C}$)	21.6	21.6	19.5	23.5	25.4	24.8	24	22.8	20.5	17.2	21	28.2

to a partial clearing of the valley from its pollution (see Table 1).

One would expect the night concentrations to drop rapidly, but catabatic winds from the west bring new fine particles from pollution sources near the ridge top, including from regions close to Jerusalem to the North West of the measuring site. In spite of the transport of pollution from these sources, the net effect is a decrease in particle concentration at night at the ground station.

The aerosol size distributions that were measured during the evening hours (around 18:00 LT), after most of the haze dissipated, show a different size distribution from that measured in the haze (compare Fig. 7 and 5). The presence of high concentrations of fine particles in Fig. 7 implies the presence of newly arrived pollution particles.

4. The chemical composition of the haze layer

A special flight to sample particles for chemical analysis was performed on 18 September, 1998. The flight was carried out in a different pattern than the usual flights, because we spent more time at each level, in order to collect enough material for analysis.

Bulk analyses of samples collected at different elevations on this flight were carried out using an ion chromatograph (IC) and are shown in Tables 2 and 3.

Table 2 shows that concentrations of nitrate in the afternoon are similar at -150 and 500 m, while the concentrations of sulfate are significantly different. Almost twice the amount of sulfate is found in layer 2 as compared to layer 1. Similar concentrations of nitrate at both elevations suggest that the mixing of air in the afternoon originates from the lower levels (convection), bringing nitrate particles from layer 1 up to layer 2. On the other hand, sulfate particles, which are transported from distant sources, are present in high concentrations in layers 2 and 3, and convection from below prevents their mixing with the lower levels.

The results of the bulk mass measurements of different elements at different times during the day are shown in Table 3.

Table 3 shows that

1. Vanadium (V), which is emitted from industrial pollution, is present in both layers 2 and 3.
2. Calcium (Ca) was found in high concentrations in layer 1 during the noon measurements (around $80 \mu\text{g m}^{-3}$). As the convection started to transport particles upward, concentrations decreased near the surface but increased above. The source of these particles could have been from mineral dust always found in the region.
3. Iron (Fe) was found in small amounts during the noon measurements, somewhat correlated with the presence of Calcium. As the convection started, the concentration of iron diminished.

Table 2

Concentrations of nitrate and sulfate ions at different altitudes and times, obtained from bulk chemical analysis

Sample	Sampling time	Elevations (m)	Nitrate ion ($\mu\text{g m}^{-3}$)	Sulfate ion ($\mu\text{g m}^{-3}$)
1	Before noon	Variable*	10.55	6.66
2	Noon	-150	8.33	~ 0
3	Afternoon	500	16.67	44.17
4	Afternoon	-150	15.32	18.55

The samples were collected on 18 September 1998. The altitudes of -150 m and 500 m represent the middle of haze layers 1 and 2.

*The collected sample in this case is an integral of the whole haze layer from a height of 1300 m to -260 m ASL.

Table 3

Concentrations of a number of elements obtained from bulk chemical analysis of samples taken during a flight in the haze layers above the Dead Sea on 18 September 1998

Sample	Measurement time	Elevation (m)	V ($\mu\text{g m}^{-3}$)	Fe ($\mu\text{g m}^{-3}$)	Ca ($\mu\text{g m}^{-3}$)	Na ($\mu\text{g m}^{-3}$)
1	Before noon	Variable (**)	0.33	~ 0	50	4.17
2	Noon	-150	1.85	1.37	80.65	12.1
3	After noon	500	1.33	~ 0	16.67	8.33
4	After noon	-150	~ 0	~ 0	19.23	~ 0

The concentrations were measured by inductively coupled plasma-MS (ICP-MS).

**The average measurement from a sample collected from a height of 1300 m to -260 m ASL.

4. The sodium concentration of the lower haze layer was found to be high at noon but decreased as the convection set in. These particles at the lower layer are probably from industrial sources, as will be discussed below.

The chemical analysis of haze layers 1 and 2 shows that they are of a distinct composition. Both layers are composed of pollution particles; however, their sources are different. Our results show that the upper layer is composed of sulfate particles that most probably originate from industrial pollution near the Israeli coast or even farther away. The lowest haze layer must originate from particles emitted from sources in the Dead Sea region. We have used RAMS and HYPACT models to simulate the transport of particles over the Israeli terrain; a discussion of the model is beyond the scope of this work, but model results show that the source of particles in the lowest layer could be the Rotem Plato industrial region to the southwest of the Dead Sea. Pollution from this region could be transported at night to the lake. This point was confirmed by examination of particles having the same composition, collected during a flight over this industrial region.

Analysis of the samples collected on the ground was carried out in the same way as the airborne samples. Some of the samples were collected for 8 h on 47 mm, 0.2 μm pore size teflon filters at a flow rate of 17.5 L min^{-1} , while others were collected for 24 h with a high volume sampler (HVS) at 1 $\text{m}^3 \text{min}^{-1}$. The results from the 8 h filters are shown in Table 4.

The results indicate that most of the ions that were measured (sulfate and nitrate) are byproducts of air pollution. Temporal trends during the time of collection, from when the haze appeared in the morning until it disappeared in the afternoon, could not be discerned. However, the steady concentration of the nitrate ion ($\sim 20 \mu\text{g m}^{-3}$) over the whole measuring period suggests that the nitrate source for the lower haze layer is steady.

In addition to bulk analysis, we collected aerosols samples for elemental analysis of individual particles. The results complemented out bulk analysis and showed that the particles in layers 2 and 3 were mostly fine (diameters $< 1.0 \mu\text{m}$), composed of sulfur, probably

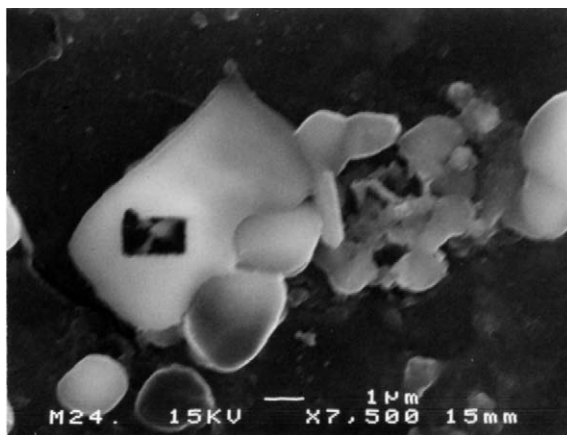


Fig. 8. An electron micrograph of particles, collected in haze layer 1, at 11:30 LT on 18 September 1998. Note the large particles and the fact that all the edges are round, suggesting that the particles were soluble and were wet. The black mark on the large particle is a hole created by the electron beam of the microscope due to the volatility of sodium nitrate.

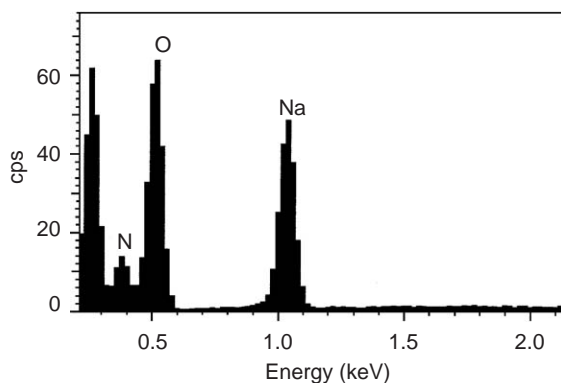


Fig. 9. Spectra of elemental analysis carried out on the largest particle shown in Fig. 8.

sulfate. Both medium and large particles (even particles $> 2 \mu\text{m}$) were found in the lower haze layer. The majority of these particles contained sodium (Na) and Calcium (Ca).

From Fig. 8 one can see that the particles in layer 1 are different in size from those in the upper layers (2 and 3). The largest particle in this figure (with the black hole inside) had diameter of about 4–5 μm , in contrast to the small (0.5 μm) sulfur particle in layer 2. The elemental spectra (see Fig. 9) of the particles from Fig. 8 reveal the presence of sodium as a major element and of nitrogen as a minor one.

The large sodium and oxygen peaks and the total absence of other metals suggest that these particles must contain oxidative components of nitrogen and sodium, exclusively. The most probable composition of these

Table 4
Concentrations ($\mu\text{g m}^{-3}$) of the main anions from samples collected on the ground at Metzukev Dragot

Date	Sulfate (SO_4^{2-})	Nitrate (NO_3^-)	Chloride (Cl^-)
1-November	23.93	19.64	6.91
2-November	40.00	22.74	4.64

Each measurement represents 8 h of continuous sampling, from 07:00 to 15:00 (LT).

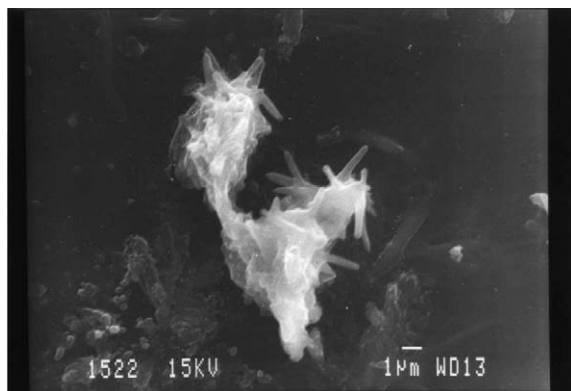


Fig. 10. A SEM photomicrograph of a sodium nitrate particle, following its reaction with Nitron reagent.

particles could be sodium nitrate (NaNO_3). In order to validate that the particles contain sodium nitrate, we used the method proposed by Mamane and Pueschel (1980) in which Nitron is used to identify the presence of nitrate ions by the reaction spot technique. In this method, the sample is postcoated with Nitron and is placed in a humidity chamber at 95% for two hours. A reaction between Nitron and nitrate in the particles produces the features seen in Fig. 10. These features clearly identified the presence of nitrate in the lower haze layer of the Dead Sea.

5. Summary and conclusions

The haze particles over the Dead Sea can originate from the sea water itself or from natural or anthropogenic sources that are located away from the Dead Sea. However, based on the fact that the haze only appears when the atmosphere is stable, the Dead Sea as a source has to be ruled out. This is because, the Dead Sea has no biological activity to speak of (Oren, 1981), therefore, bursting of air bubbles at the water surface cannot be a major source of particles. Some of the mountains surrounding the sea are made of salt, but the haze appears only when the wind is very weak, making suspension of particles from the surface very difficult.

The results from our airborne and ground measurements indicate that the haze is composed of two main layers (1 and 2, at -100 and about 300 m ASL) and a third layer at a much higher elevation around 1000 m ASL. The two lower haze layers are distinct in their composition. In the morning hours the lowest layer (layer 1) is composed principally of sodium nitrate particles originating from an industrial source to the southwest of the Dead Sea. These particles are

transported at night to the lowest levels of the atmosphere above the Dead Sea due to the land breeze around the lake. In the morning these particles constitute the major component of the lowest haze layer. The morning haze that appears at around 300 m ASL is composed of many sulfate particles but some sodium nitrate as well. These particles must be a mixture of particles similar to those found at the lower layer and pollution particles that were brought down the slopes of the valley at night by the catabatic winds. Layer 3 is located below the marine inversion and is composed mostly of sulfate particles that are brought from distant sources. As the day progresses, convection starts due to the heating of the land around the lake. This convection helps to mix the two lower layers and produce one thicker layer of relatively uniform composition.

The haze layers become weaker or disappear all together in the late afternoon when the bulk of the Mediterranean sea breeze reaches the valley.

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