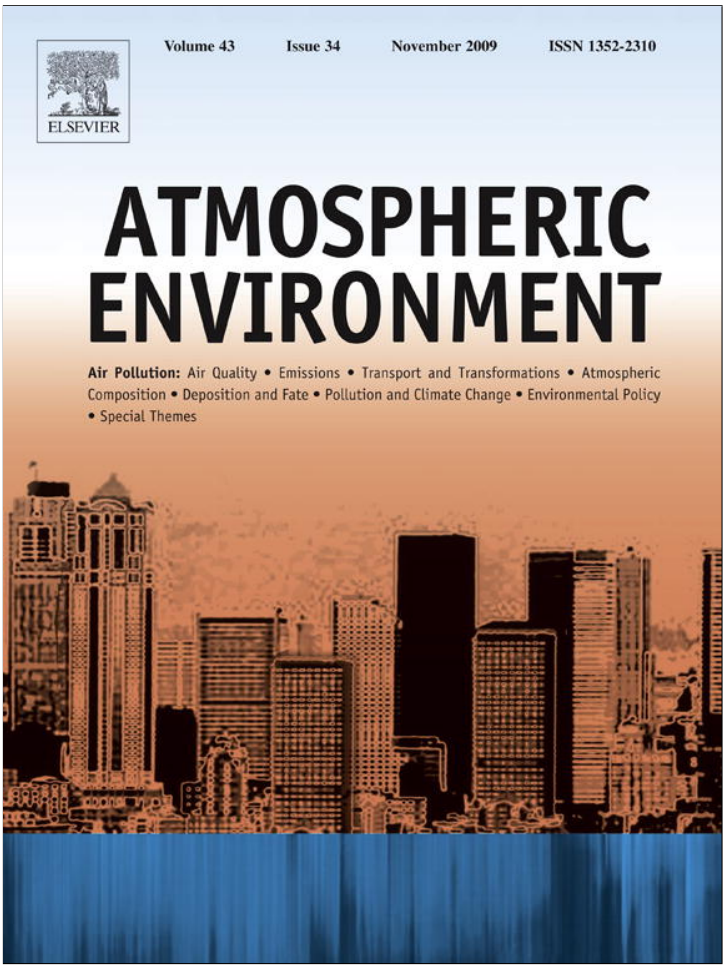

Atmospheric Environment 43 (2009) 5463–5468

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

A method to determine the effect of mineral dust aerosols on air quality

Eliezer Ganor, Amnon Stupp*, Pinhas Alpert

Department of Geophysics and Planetary Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel

ARTICLE INFO

Article history:
Received 6 May 2009
Received in revised form
14 July 2009
Accepted 16 July 2009

Keywords:
PM10
PM2.5
Pollution level
Dust increase
Chemical and mineralogical composition
Tel-Aviv Israel

ABSTRACT

Natural mineral dust storms (DS) from the Arabo-African region blow over the Mediterranean, reach Israel, and add to the anthropogenic particulate pollution. The effects of mineral dust on air quality in Israel were investigated using only PM10 and PM2.5 automatic measurements. The method does not require any other inputs such as satellite observations, model back-trajectories, dust forecast models, or mineralogical analyses. The method employs an automatic algorithm with three thresholds: the half-hour PM10 average must be above 100, this level is maintained for at least 3 h, and the maximum concentration recorded is above 180 $\mu g\,m^{-3}$. The algorithm was designed for Israel, but can be adapted for other locations.

The contribution of DS caused PM10 values to exceed the Israeli annual standard of 60 $\mu g\,m^{-3}\,year^{-1}$ in 6 of the 12 years examined. The DS contribution to PM10 annual average ranged from 9.4% to 29.5%. The level recommended by WHO, 20 $\mu g\,m^{-3}\,year^{-1}$, was exceeded every year even without the DS contribution. The number of days in which the daily Israeli standard (150 $\mu g\,m^{-3}$) was exceeded during the 12 years was 6–20 days per year. The number of days in which the daily standard was exceeded shows an increasing trend of 7 days per decade.

PM2.5 in Israel is in the range 40–56% of PM10. PM2.5 values were over the recommended standard with and without DS. The contribution of DS to annual average of PM2.5 ranged from 3.6% to 19.1%.

The automatic algorithm was calibrated with a list of Dust Storms identified by visual means supported by mineralogical analysis. Mineralogical analyses of single particles were performed using Environmental Scanning Electron Microscope (ESEM). Two representative samples are given. The main difference is that the particles of the Saudi-Arabian storm had much more palygorskite, while the North-African storm had more sea-salt and organic particles. The mineral composition differences indicate that analysis can differentiate between sources.

1. Introduction

Particulate air pollution has increased over the past decades in many cities of the world. Particles with aerodynamic diameter less than 10 μm (PM10) are considered inhalable particles, which can reach the lungs. Particles above 2.5 μm and below 10 μm penetrate to the bronchi, while particles below 2.5 μm (PM2.5) are respirable particles and penetrate to the alveoli (Heyder, 1986). Inhalable particles are considered a major health hazard (Dockery et al., 1993; Schwartz, 1994; Prospero, 1999; Annesi-Maesano et al., 2007). The health standard for airborne particles is given in weight in micrograms per cubic meter. The Israeli PM10 standard is 60 $\mu g\,m^{-3}\,year^{-1}$ and 150 $\mu g\,m^{-3}$/24-h. The Israeli recommended PM2.5 standard is 15 $\mu g\,m^{-3}\,year^{-1}$ and 65 $\mu g\,m^{-3}$/24-h. The European Commission goal for 2010 (EC Directive, 1999) is PM10 of 20 $\mu g\,m^{-3}$ annual mean with natural sources excluded. The level recommended by WHO for PM10 is 20 $\mu g\,m^{-3}\,year^{-1}$ (WHO, 2006). Previous studies have shown annual PM10 concentrations of 44–53 $\mu g\,m^{-3}$ for major Italian cities (Galassi et al., 2000), 18–41 $\mu g\,m^{-3}$ depending on station in Berlin (Lenschow et al., 2001), 51 $\mu g\,m^{-3}$ at Heraklion, Crete and only 28 $\mu g\,m^{-3}$ at Finokalia, Crete (Gerasopoulos et al., 2006), and upto 75 $\mu g\,m^{-3}$ at Athens (Chaloulakou et al., 2003). In Beirut, Lebanon, monthly average of 76 $\mu g\,m^{-3}$ was measured (Shaka and Saliba, 2004). In this study we find PM10 annual averages of 47–68 $\mu g\,m^{-3}$ for the years 1995–2006 for Tel-Aviv, Israel, in the same range as that found for other cities in the region.

Natural mineral dust storms (DS) from the Arabo-African region blow over the Mediterranean and reach Israel, Lebanon, Syria, Turkey, Cyprus, Greece, Italy, Malta, France, Spain, can reach England and have even been reported in satellite images over Norway and Odessa (Barkan, 2009). DS reach Israel mostly during the transition and winter seasons (Mamane et al., 1980). The mineral dust adds directly to the anthropogenic particulate pollution, and the mineral

* Corresponding author. Tel./fax: +972 3 6405205.
E-mail addresses: ganor@post.tau.ac.il (E. Ganor), amnons@post.tau.ac.il (A. Stupp).

1352-2310/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2009.07.028

dust particles can also adsorb and become coated by anthropogenic pollutants such as sulfates, nitrates, pesticides, PAH and heavy metals (Levin et al., 1996; Falkovich et al., 2001, 2004).

The Israeli standard does not allow subtraction of the natural contribution, as does the EU standard. However, it is important to differentiate between the natural and anthropogenic contributions, for health considerations, and in order to determine the reduction needed in the anthropogenic emissions.

The usual way of determining the natural contribution is via chemical analysis of the aerosols, where particles with large fractions of Al, Ca and other crustal components are attributed to natural mineral dust. This method requires collection of aerosols on filters, frequent replacement of the filters, at best daily, and costly analysis of tens or hundreds of filters. Other methods involve back-trajectories and satellite images to track dust plumes from the sources. Recently Escudero et al. (2007) and Mitsakou et al. (2008) have quantified the contribution of mineral dust to air quality in Spain and in Greece, using a methodology different from the one presented here. Escudero's method relies on back-trajectories and other data (satellites, synoptic) to identify DS, and also chemical analysis to verify this identification. Then the measured daily average PM10 for the days without DS is used to estimate PM10 background, and from that the contribution of DS is calculated. Mitsakou's method is model based, using the SKIRON (DREAM) model to estimate contribution of DS to daily average PM10 measurements.

We present a method for identification of DS using only PM10 measurements from automatic stations. Once calibrated, the method does not require any other input, either data or analysis. The method produces a list of DS with beginning and ending times at a half-hourly temporal resolution.

The usefulness of the method is demonstrated through the investigation of the period 1995–2006, with 384 DS identified in Tel-Aviv, and the implications of DS to air quality in Israel analyzed.

2. Methodology and measurements

Table 1 shows a qualitative division of levels and sources of particulate pollution in Tel-Aviv, Israel. The table is based on daily observations of visibility and weather conditions, and on measurements at the Tel-Aviv university Israel Ministry of Environment station, including chemical and mineralogical analyses (Ganor et al., 2000). The table shows that during DS pollution increases to above 150 $\mu g\,m^{-3}$ while the background is about 50 $\mu g\,m^{-3}$, and therefore distinguishing between DS and other sources of PM is possible.

DS were identified manually at Tel-Aviv, and a list of DS for the years 1958–2006 was prepared (Ganor et al., 2007). Our decades-long knowledge of DS in Israel and the region enabled us to identify DS from visual indicators – visibility, sky color, sample color, and dry and wet deposition. Our confidence in this ability relies on electron microscope analyses and mineralogical analyses which were performed over decades, and which showed that indeed the majority of PM10 during such episodes is from natural dust.

An automatic algorithm was developed, which for the first time makes it possible to distinguish the contribution to PM due to natural mineral dust from other aerosol sources, using only automatic PM10 concentration measurements and no other input.

The algorithm was designed based on our experience with DS in Israel for over 50 years, leading to knowledge such as that a DS is characterised by a minimal duration, large minimum concentration, and large maximum concentration (Ganor et al., 2000, 1998; Ganor and Foner, 2001; Falkovich et al., 2001, 2004; Ganor, 1999; Pardess et al., 1992; Levin et al., 1990). The algorithm was calibrated using the list of manually identified DS for one particular year. After calibration the algorithm was used on a different year and the results were compared with the manual identification for that year, with very good agreement. All DS on the manual list appeared on the automatic list, with some additional DS identified with the automatic algorithm.

The automatic algorithm uses three thresholds. An episode is identified as DS only if: the half-hour PM10 average is above 100, this level is maintained for at least 3 h, and the maximum concentration recorded is above 180 $\mu g\,m^{-3}$.

PM10 was measured from 1995 to 2006 by the TEOM series 1400 in the Tel-Aviv automatic stations of the Israel Electric Company. The record of the measurements is of half-hourly averages. Using the algorithm on the record produces a list of DS with a half-hour resolution of the beginning and end of each DS. The list of DS produced by the algorithm makes it possible to analyze the contribution of DS to air quality in Tel-Aviv over this period.

The contribution of DS to PM10 for any time period is calculated as follows:

A time period is defined by the number of half-hour records within it nT.

For every half-hour i there is a PM10 concentration

$PM10_i$

The total PM10 during a time period is therefore

$$T = \sum_{i=1}^{nT} PM10_i$$

The average PM10 for a time period is

$$avg = T/nT$$

During a time period one or more DS might be identified. The number of records during the DS or DS-s in a time period is nDS.

The total PM10 during DS which occurred during a time period is therefore

$$TDS = \sum_{i=1}^{n\mathrm{DS}} PM10_i$$

The average PM10 without DS is

$$avgWithoutDS = \frac{T - TDS}{nT - n\mathrm{DS}}$$

Therefore the contribution of DS to the average PM10 during this time period is

$$DS\ contribution = avg - avgWithoutDS$$

The automatic method makes it possible to analyze a large number of DS over a long measurement period, but the method also

Table 1
Daily average concentration ($\mu g\,m^{-3}$), annual frequency, weather conditions, and composition of inhalable particles, PM10, in Tel-Aviv (Ganor et al., 2000).

Pollution level	Concentration [$\mu g\,m^{-3}$]	Frequency	Weather condition	Composition
Low pollution	5–40	28%	During and after Rain, and on Yom-Kipur	Black carbon, Minerals
Medium pollution	35–65	45%	Summer smog, high inversion	Sulphates, Black Carbon, Sea Spray, Nitrates, Minerals
High pollution	65–150	24%	Winter smog, low inversion	Black Carbon, Salts of Sulphates and Nitrates, Heavy Metals, Minerals
Very high pollution	100–3000	3%	Dust Storms	Pollen, Minerals, Sea Spray

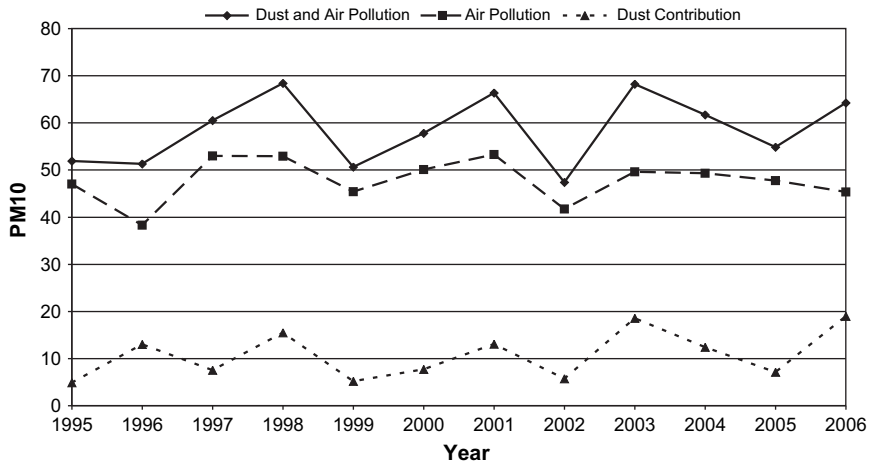

Fig. 1. Annual contribution of mineral dust to Tel-Aviv ambient air (PM10) 1995–2006. Continuous line – dust and air pollution, dashed – pollution only, dotted – Dust.

has limitations. In the above derivation the contribution of non-DS pollution during DS to the average over the period analyzed is assumed to be negligible. This is reasonable since the PM10 during a DS typically increases to more than 3 times the background. Fig. 1 shows that the annual DS contribution is at least 5 $\mu g\,m^{-3}$. Since DS take about 3% of the year, on average the PM10 level during DS would be at least 150 $\mu g\,m^{-3}$, while the average background is about 50 $\mu g\,m^{-3}$ (Fig. 1). In fact, since DS are concentrated in certain months, the average PM10 during DS for all 12 years is 310 $\mu g\,m^{-3}$, six times the background. In particular, if the time period analyzed is an entire year, the contribution of the background during 3% of the records is certainly negligible. Therefore the calculation of *avgWithoutDS* above gives a very good approximation to the true non-DS contribution. From this it follows that the derivation of *DS contribution* is also very good.

For the contribution of mineral dust to PM2.5 levels, the Dust Storms identified from the PM10 records were used. The same derivation described above was then used on the PM2.5 records. Therefore, again it was assumed that all PM2.5 during a DS came from mineral dust. For PM2.5 it is not as clear that the background can be neglected. If it cannot this would decrease the contribution of DS to PM2.5 even below the results shown. However, mineralogical analysis shows that most mass during DS in the PM2.5 fraction is also mineral dust. Also, as for the PM10, for the annual averages *avgWithoutDS* is a very good estimate and therefore also the *DS Contribution* is correct.

3. Results

Table 1 shows that during DS pollution increases to above 150 $\mu g\,m^{-3}$ while the background is about 50 $\mu g\,m^{-3}$. The table shows that distinguishing between DS and other sources of PM is possible based on PM10 alone.

Two mineralogical and chemical analyses are given below as examples of DS from the eastern and the southern sectors. Back-trajectories show the DS on 23 April 2001 originated from Saudi-Arabia and the 21 April 2001 DS originated from North Africa. The analyses were performed using Environmental Scanning Electron Microscope (ESEM) as described by Jeong (2008), Falkovich et al. (2001), Levin et al. (1996), Ganor (1999), Ganor et al. (1998, 1993). One thousand (1000) single aerosol particles smaller than 2.1 μm were analyzed. The particles were collected with an Andersen sampler, and 500 particles were chosen from each DS.

By percent of number of particles the particles for the Saudi-Arabian DS were illite–smectite (montmorillonite) 33%, calcite 30%, gypsum 10%, palygorskite 6.8%, quartz 3.7%, dolomite 3.4%, feldspar 3.3%, nitrate 2.1%, clay 1.3%, halite 1.2%, illite 0.6%, organic 0.5%, kaolinite 0.3%. And for the North-African DS the particles were

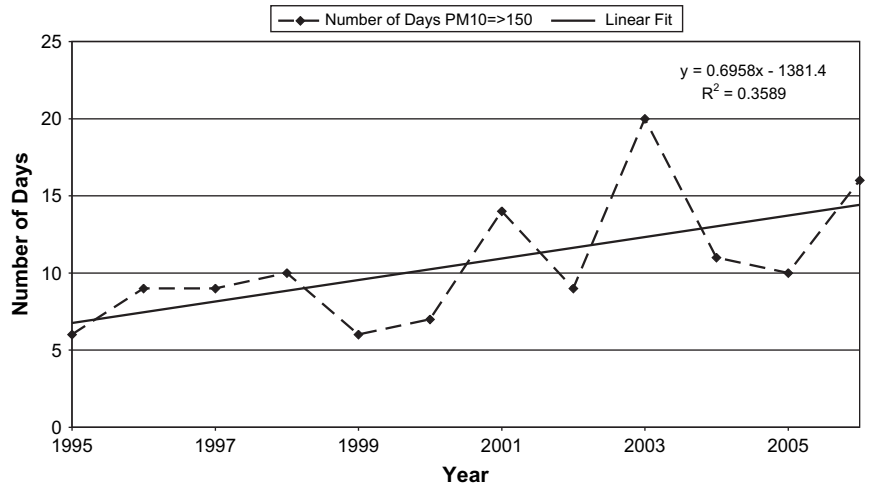

Fig. 2. Number of days in which PM10 was above the daily (00 h–24 h) standard 1995–2006.

composed of illite–smectite 22%, calcite 21%, gypsum 10%, halite 9%, hematite and magnetite 8.6%, nitrate 5%, quartz 4.9%, organic 4.9%, dolomite 3.3%, kaolinite 2.9%, illite 2.9%, clay 2%, feldspar 1.2%, palygorskite 0.8% (Fig. 3).

The automatic algorithm and DS contribution analysis show that the contribution of DS caused PM10 values to exceed the Israeli annual standard of 60 $\mu g\,m^{-3}$ $year^{-1}$ in 6 of the 12 years (Fig. 1). The level recommended by WHO for PM10, 20 $\mu g\,m^{-3}$ $year^{-1}$

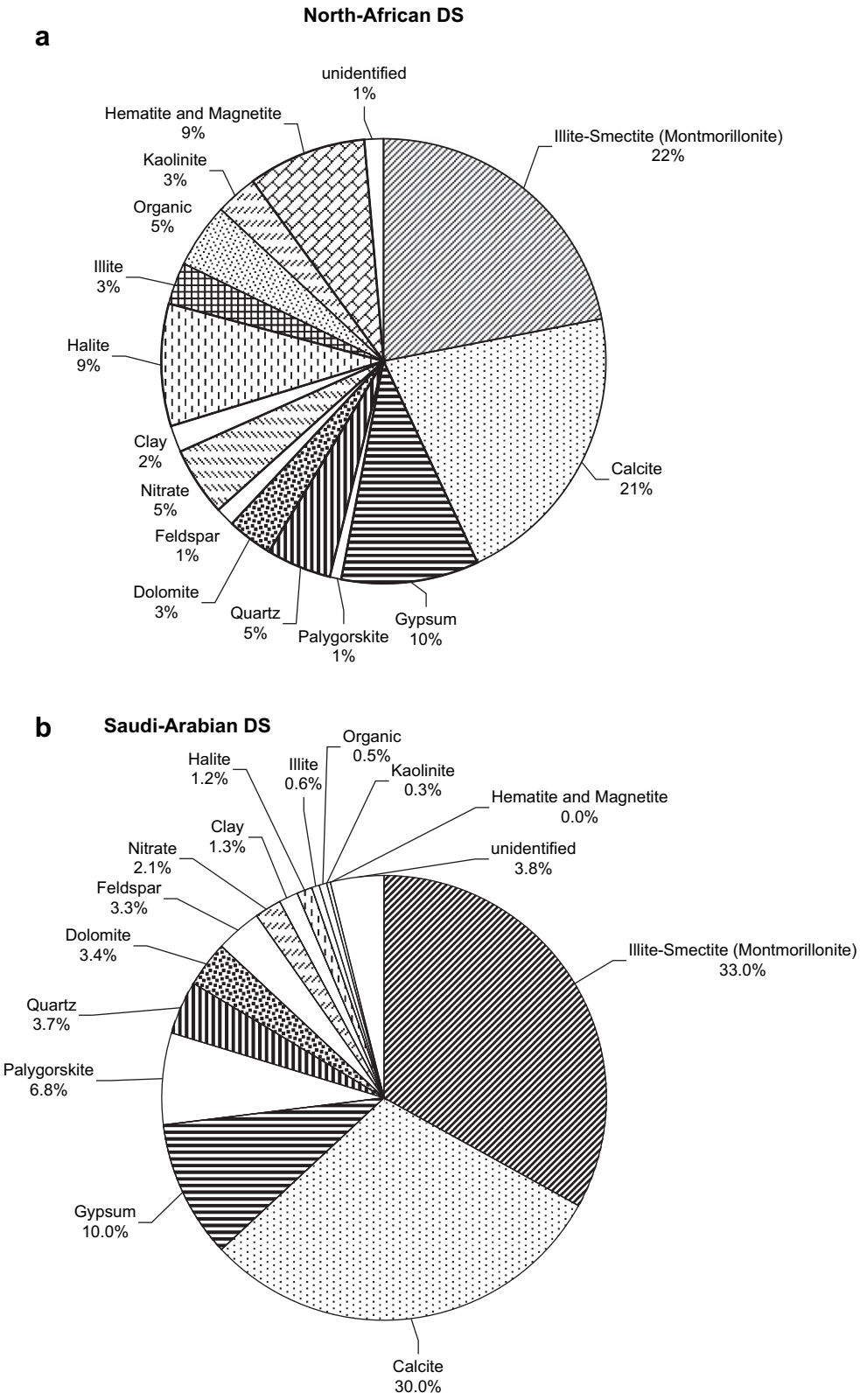

Fig. 3. Mineralogical composition of Saudi-Arabian and North-African Dust Storms.

Table 2
Annual averages of PM10 and PM2.5 in $\mu g\,m^{-3}$ at Tel-Aviv 1995–2006, with and without the contribution of DS, and the standard deviation of daily average PM10, based on half-hourly data.

Year	Mean total PM10	Mean PM10 without dust	Contribution of DS [%]	Standard deviation of daily PM10	Mean total PM2.5	Mean PM2.5 without dust	Standard deviation PM2.5	Contribution of DS [%]
1995	51.9	47	9.4	28.2				
1996	51.3	38.3	25.3	100.8				
1997	60.5	53	12.4	37.5				
1998	68.4	52.9	22.7	132.1				
1999	50.6	45.4	10.3	31.5				
2000	57.8	50.1	13.4	43	32.4	31.2	34.3	3.6
2001	66.3	53.3	19.7	74.4	28.2	25.8	14.9	8.6
2002	47.4	41.7	12	34.8	26.6	25.0	9.6	5.7
2003	68.2	49.6	27.2	78.5	27.3	23.2	17.5	15.1
2004	61.7	49.3	20	69.2	26.6	24.0	15.0	9.9
2005	54.8	47.7	12.9	36.6	25.4	23.9	10.8	6.2
2006	64.3	45.3	29.5	102	29.1	23.6	29.7	19.1

(WHO, 2006), was exceeded every year even without the DS contribution.

The standard deviation of daily average of PM10 is between half and 2.5 times the annual mean (Table 2). This shows the enormous variability introduced by DS, which can increase the daily average by a factor of ten compared to the background.

PM2.5 values (Table 2) were over the recommended standard ($15\ \mu g\,m^{-3}\,year^{-1}$) with and without DS. The standard deviation of daily averages for PM2.5 is much lower than for PM10 since the contribution of mineral dust to PM2.5 is much lower than for PM10. PM2.5 is in the range 40–56% of PM10. This is in line with previous work finding PM2.5 to be about half of PM10, and PM10 being about half of TSP (Wanger and Ganor, 1999).

The number of days in which the daily standard (daily average $150\ \mu g\,m^{-3}\,day^{-1}$) was exceeded during the 12 years was 6–20 days per year (Fig. 2). A least-squares linear fit gives a slope of 0.6958, showing an increasing trend of 7 days per decade. This is in agreement with work showing an increase in days with DS during a year since 1958 (Ganor et al., 2007). The R-squared value of the fit is 0.36, which is formally significant for 12 data points. In addition, days with average daily PM10 above $150\ \mu g\,m^{-3}\,day^{-1}$ are days with severe DS in Israel, and therefore we consider this trend important.

4. Conclusions

A method for identifying dust storms (DS) using only automatic half-hour average PM10 measurements has allowed us to construct a list of DS. For each DS in the list we have beginning time and end time, at a temporal resolution of half-hour, and average concentration every half-hour.

Using this list we could calculate the contribution of DS to PM10 and PM2.5.

In 6 of the 12 years the DS contribution raised the annual concentration above the annual Israeli standard. The contribution of DS to PM10 annual average ranged from 9.4% to 29.5%. The level recommended by WHO, $20\ \mu g\,m^{-3}\,year^{-1}$, was exceeded every year even without the DS contribution.

The number of days in which the daily Israeli standard ($150\ \mu g\,m^{-3}\,day^{-1}$) was exceeded during these 12 years was 6–20 days per year. This number shows an increasing trend of 7 days per decade.

The contribution of mineral dust to PM2.5 is much lower than for PM10. However, the PM2.5 values were over the recommended standard with and without DS. The contribution of DS to annual average of PM2.5 ranged from 3.6% to 19.1%.

The excesses of PM10 and PM2.5 over the standards lead us to conclude that since mineral dust storms are beyond our control the anthropogenic emissions must be reduced. These reductions should be close to 20% for PM10 – as seen in Table 2 for year 2003, where the annual average should be reduced by $8.2\ \mu g\,m^{-3}$ which are 16% of the $49.6\ \mu g\,m^{-3}$ we attribute to anthropogenic pollution, and close to 60% for PM2.5 (e.g. $14.1\ \mu g\,m^{-3}$ out of $23.6\ \mu g\,m^{-3}$ anthropogenic for 2006). Such reductions would also decrease the interaction of mineral dust with the anthropogenic pollutants with which it is often found to be coated.

For use in other regions than Israel the algorithm needs to be calibrated for the particular region. It could also be that for some regions, with low relative Saharan Dust contribution, this method will not be workable.

The mineral analysis shows that mineral dust composition differs by sources. Dust from Saudi-Arabia has more palygorskite, illite–smectite, calcite and dolomite. While the North-African storm has more salt, and organic particles. The increase in salt and organic particles in the dust from North Africa is probably particles added to the dust in its path which takes it over the Nile, the Mediterranean sea or the Red sea, and over urban areas in Egypt and Israel.

Acknowledgements

We thank the Israel Electric Company Environmental Unit for the PM10 and PM2.5 data

References

Annesi-Maesano, I., Forastiere, F., Kunzli, N., Brunekref, B., 2007. Particulate matter, science and EU policy. European Respiratory Journal 29, 428–431.
Barkan, J., 2009. Personal communication.
Chaloulakou, A., Kassomenos, P., Spyrellis, N., Demokritou, P., Koutrakis, P., 2003. Measurements of PM10 and PM2.5 particle concentrations in Athens, Greece. Atmospheric Environment 37, 649–660.
Dockery, D.W., Pope, A.C., Xiping, X.U., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E., 1993. An association between air pollution and mortality in six U.S. cities. The New England Journal of Medicine 329 (24).
EC Directive 1999/30/EC of the European Parliament and of the council, 29 June 1999. No. L163. Official Journal of the European Communities, 41.
Escudero, M., Querol, X., Pey, J., Alastuey, A., Pérez, N., Ferreira, F., Alonso, S., Rodrıguez, S., Cuevas, E., 2007. A methodology for the quantification of the net African dust load in air quality monitoring networks. Atmospheric Environment 41, 5516–5524.
Falkovich, A., Ganor, E., Levin, Z., Formenti, P., Rudich, Y., 2001. Chemical and mineralogical analysis of individual mineral dust particles. Journal of Geophysical Research 106 (D16), 18029.
Falkovich, A., Ganor, E., Rudich, Y., 2004. Adsorption of organic compounds pertinent to urban environments onto mineral dust particles. Journal of Geophysical Research 109, D02208.
Galassi, C., Ostro, B., Forastiere, F., Cattani, S., Martuzzi, M., Bertollini, R., 2000. Exposure to PM10 in the eight major Italian cities and quantification of the health effects. In: ISEE 2000, 10–22 August 2000
Ganor, E., Levin, Z., Pardess, D., 1993. Determining the acidity and chemistry of individual fog haze and cloud droplets in Israel. Atmospheric Environment 27A (12), 1821–1832.

Ganor, E., Levin, Z., Van Grieken, R., 1998. Composition of individual aerosol particles above the Israeli Mediterranean coast during the summer time. Atmospheric Environment 32, 1631–1642.
Ganor, E., 1999. A method for identifying sulfuric acid in single cloud and fog droplets. Atmospheric Environment 33, 4235–4242.
Ganor, E., Wanger, A., Kordova, L., Teller, A., 2000. Ministry of Environmental Protection Air Quality Report 2000 (in Hebrew).
Ganor, E., Foner, H.A., 2001. Mineral dust concentrations, deposition fluxes and deposition velocities in dust episodes over Israel. Journal of Geophysical Research 106D, 18431–18437.
Ganor, E., Stupp, A., Osetinski, I., Alpert, P., 2007. XXIV IUGG General Assembly, Perugia.
Gerasopoulos, E., Kouvarakis, G., Babasakalis, P., Vrekoussis, M., Putaud, J.-P., Mihalopoulos, N., 2006. Origin and variability of particulate matter (PM10) mass concentrations over the eastern Mediterranean. Atmospheric Environment 40, 4679–4690.
Heyder, J., 1986. Single particle deposition in human airways. In: Spurny, K.R. (Ed.), Physical and Chemical Characterization of Individual Airborne Particles, pp. 73–85.
Jeong, G.Y., 2008. The bulk and single-particle mineralogy of Asian dust and a comparison with its source soils. Journal of Geophysical Research 113, D02208.
Lenschow, P., Abraham, H.-J., Kutzner, K., Lutz, M., Preuss, J.-D., Reichenbacher, W., 2001. Some ideas about the sources of PM10. Atmospheric Environment 35 (Suppl. 1), S23–S33.
Levin, Z., Price, C., Ganor, E., 1990. The contribution of sulfate and desert aerosol to the acidification of cloud and rain in Israel. Atmospheric Environment 24A (5), 1143–1151.
Levin, Z., Ganor, E., Gladstein, V., 1996. The effects of desert particles coated with sulfate on rain formation in the eastern Mediterranean. Journal of Applied Meteorology 35 (9), 1511–1523.
Mamane, Y., Ganor, E., Donagi, A., 1980. Aerosol composition of urban and desert origin in the eastern Mediterranean. I. Individual particle analysis. Water, Air and Soil Pollution 14, 29–43.
Mitsakou, C., Kallos, G., Papantoniou, N., Spyrou, C., Solomos, S., Astitha, M., Housiadas, C., 2008. Saharan dust levels in Greece and received inhalation doses. Atmospheric Chemistry and Physics 8, 7181–7192.
Pardess, D., Levin, Z., Ganor, E., 1992. A new method for measuring the mass and concentration of sulfur in airborne particles. Atmospheric Environment 26 A (4), 675–680.
Prospero, J.M., 1999. Long-term measurements of the transport of African mineral dust to the southeastern United States: implications for regional air quality. Journal of Geophysical Research 104, D13.
Schwartz, J., 1994. Air pollution and daily mortality: a review and meta analysis. Environmental Research 64 (1), 36–52.
Shaka, H., Saliba, N.A., 2004. Concentration measurements and chemical composition of PM10–2.5 and PM2.5 at a coastal site in Beirut, Lebanon. Atmospheric Environment 38, 523–531.
Wanger, A., Ganor E., 1999. Ministry of Environmental Protection Air Quality Report 1999 (in Hebrew).
WHO site for standards, document. http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf.