

Chemical and Radiological Characterizations of the Desert Dust Coming from Northern Africa to Batman (Southeastern Turkey)

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ABSTRACT

This work investigates the chemical and radiological characterizations of the dust coming from Sahara in North Africa to Batman city in the southeastern region of Turkey on 20 May 2017. According to meteorological maps, the source region of the dust storm that took place in Batman was found to be Libya, which is supported by the NOAA HYSPLIT model's back trajectory analysis. XRD analyses show that the common minerals of the dust samples are quartz, feldspars, calcite, dolomite, hematite and rutile. Chemical patterns of some major, minor and trace elements in dust samples are generally consistent with those of Saharan Dust composition. The heavy metals in the dust follow the decreasing concentration order: Mn > Zn > Cr > Ni > Cu > Pb. The enrichment factors (EF) of these elements show anthropogenic contamination effects with regard to Zn, Cr and S elements in dust samples. The corresponding values of the radionuclides, the absorbed dose rates in the air and the annual effective doses in the samples were also evaluated and compared to the internationally recommended values. The findings are supposed to be beneficial for tracking and evaluating any environmental pollution inventory in this area.

Keywords: Dust, Chemical analysis, Radioactivity, Enrichment factor, Trajectory analysis.

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Introduction

Dust storms are important source of dispersal of suspended dust. Mineral-containing dusts are the most common type of aerosol having a wide range of effects on human health [1]. The Sahara Desert (North Africa) is the most important source of mineral dust-containing aerosols in the world [2]. The Saharan Desert is a 9.000.000 km² desert located in the north of Africa, separating the middle and the north of the continent (Figure 1).

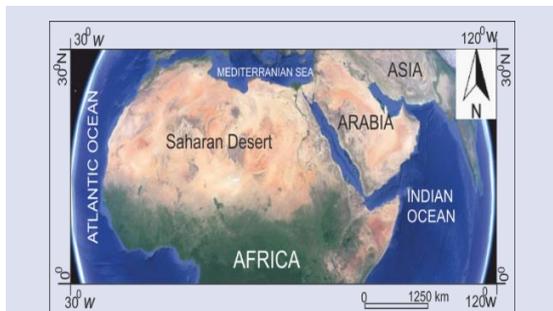


Figure 1. The Location of Sahara Desert.

Turkey faces dust events originating from the African desert frequently. Every year, dust from the neighbouring and even far away countries comes to Turkey at certain

periods. Especially in spring in March, April, May. On an annual average, 20 million tons of dust as wet or dry precipitate in our country either wet or dry. This red sand is thought to have emerged as a result of the erosion in the Great Sahara, Arabia, Iran and Syria around Turkey. The transported desert dust from different countries has significant effects on both human health and the flourishing parts of plants such as branches, leaves and flowers. The transport of dust aerosols from deserts (such as Sahara, Arabia) and semi-arid areas into and around Turkey is of great importance in terms of climate, land and marine ecosystems, and human activities and health. The main reason for dust transport is stated to be drought and desertification.

Dust storms are generally occur in dry and arid areas. Dust particles transfer into the atmosphere due to vertical winds; and through these winds, they can be transported thousands of kilometers away. Most of these mineral-containing dusts cause a great deal of damage to the environment and human health. On the other hand, these dusts cause a decrease in soil fertility and harm plants. These dust storms have an impact on human health because fine dust particles reach the airways and lungs, increasing the risk of chronic respiratory and lung diseases [3-5].

The effect of the Saharan dust storms on chemistry has been observed in the literature [6, 7-8]. In the literature, the dust has also been investigated for its radioactive content, which may effect human health [9]. However, Earth's radiation balance, which comes from the Saharan dust storms has been difficult to assess, due to limited observations from the surface in literature. No attempt about chemistry and radiological characterizations has been made yet to deal with dust storms in Turkey. In this study, the first observations were presented about the effect of a major dust storm having occurred on 20 May 2017 on the chemistry and radiation balance in Batman city (southeastern Turkey) (Figure 2). This study aims to provide information about the origins, the behaviors and the distributions of chemical and radiological

characterizations in dust samples, which can be useful for epidemiological, geological and environmental management studies. In addition, soil samples from the same region were analyzed for comparison purposes.

Materials and Methods

The dust samples were collected from different locations on the roofs of the houses from the urban area of Batman (Figure 2). X-ray diffraction (XRD) analyses of three dust samples were carried out with Rigaku D/Max-III C X-ray diffractometer. The Cu K α radiation over the range was 10°–70°.

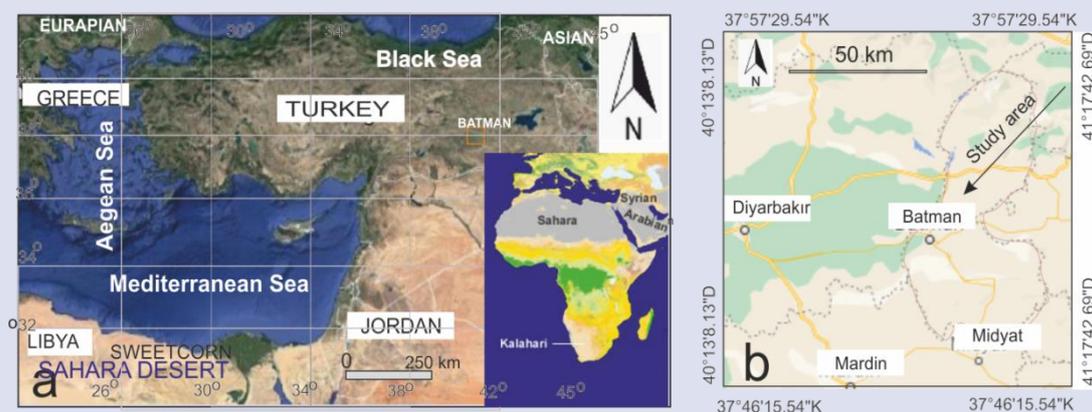


Figure 2. a) The location of the study area in Turkey. b) Sampled Batman city.

Five dust samples were made ready in pressed pellet forms for energy-dispersive x-ray fluorescence (EDXRF) analysis (Epsilon 5, PANalytical, Almelo, The Netherlands). The powder was dried at 105 °C for 4 hours. The dried pellets, which had a diameter of 40 mm and a uniform mass of 400 ± 2 mg, were prepared.

The soil samples were collected from the locations close to where the dust samples were taken. The samples were powdered and dried for a full day at 110 °C so that the moisture they had could be removed and a uniform weight could be attained. Approximately 160 g of sample was transferred in gas-tight plastic polyethylene containers. Afterward, the containers were fully sealed for 28 days to attain a secular equilibrium between ^{226}Ra and ^{222}Rn with their daughter nuclei.

The activities of ^{238}U , ^{232}Th , ^{40}K and ^{137}Cs in the samples were employed utilizing a coaxial germanium detector (HPGe) supplied by Canberra, USA. The energy resolution was 1.9 keV for 1332 keV gamma-ray peaks of ^{60}Co with a relative efficiency of 15%. The detector was shielded in a 10 cm lead shield to lessen the background radiation and was concentric with a thin layer of copper. An empty container was counted in the same manner and geometry as the samples in order to determine the background distribution around the detector. The background spectra were utilized so as to correct the net peak area of the gamma rays of the measured natural radionuclides [10,

11-12]. The calibrations of the detector were described in detail in earlier works [13-14].

The activities of ^{238}U and ^{232}Th were determined using the characteristic γ -lines of 351.9 keV from ^{214}Pb and 609.3 keV from ^{214}Bi and γ -lines of 583.1 keV from ^{208}Tl and 911.1 keV from ^{228}Ac , respectively. The contents of ^{40}K and ^{137}Cs were estimated via its characteristic gamma-ray emission line at 1460.8 keV and 661.6 keV, respectively.

The activity concentration of radionuclides in the sample units in Becquerel per kilograms (Bq.kg $^{-1}$) were calculated by the Equation below;

$$A=C/(\epsilon \times P \times W \times t) \quad (1)$$

where A is the activity of a radionuclide, C is the net count of a peak at energy E, ϵ is the measured photo-peak efficiency, P is the probability of the gamma-ray line in a radionuclide, W is the weight of the sample in kilograms and t is the counting live time

Results and Discussion

Meteorological Conditions and Trajectory Analysis

Meteorological conditions on the Mediterranean Basin and surrounding continents vary seasonally and often cause the transport of air masses through different

regions. The Mediterranean region is known as the region where cyclonic activities occur frequently all year round. Figure 3 presents 850 Mb geopotential height maps to demonstrate atmospheric circulation in the region and the transport of the air mass between 17-20 May 2017. The meteorological condition, which caused dust transport to Turkey, is associated with a deep low-pressure center located between the northeast of Libya and the southwest of Turkey on 17 and 18 May 2017. This

low-pressure center moved towards the interior of Turkey on 19 May 2017 and reached northeast of Turkey on 20 May 2017. The high-pressure center located over Algeria and Libya on 19 May 2017 deepened on 20 May 2017. The transport of the air mass takes place from the high-pressure center to the low-pressure center. In this case, the transport of the air mass containing dust was carried out from Libya to Turkey.

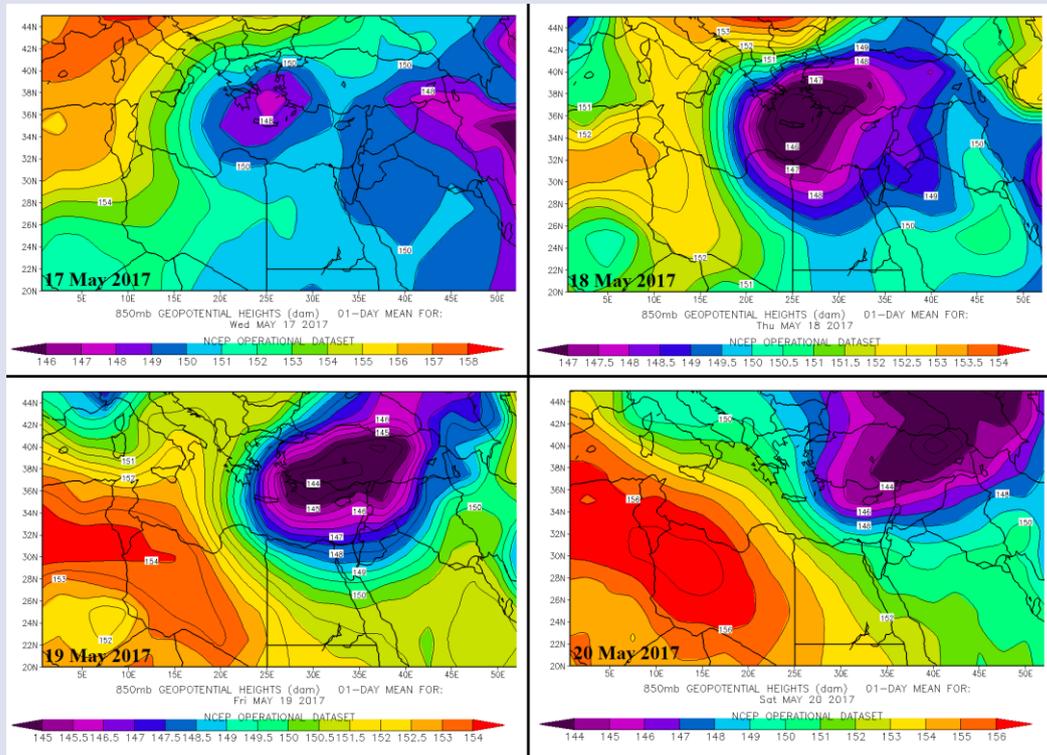


Figure 3. Atmospheric circulation in the lower (850 hPa geopotential height) troposphere on 17-20 May 2017.

To examine this movement in detail, The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model of NOAA was examined. HYSPLIT model is one of the models that is used to determine trajectories of air masses. To determine the source region of air masses reaching to Batman province (37.55 N and 41.05 E coordinates), back trajectory analysis was performed with the HYSPLIT model. HYSPLIT model was run for 96 hours duration at 12 UTC on 20 May 2017 at 10 m level (Figure 4). The red line on the map shows the source and trajectory of the air mass reaching Batman. It is clear that the source of air mass coming to Batman province is from the northern region of Libya. The air mass passed Syria and then reached the province of Batman.

Mineralogical and chemical composition of the samples

The whole-rock X-ray diffraction patterns (XRD) of D1, D5 and D9 dust samples are shown in Figure 5. In whole-rock XRD analysis, clay 4.47 Å ($2\theta = 19^\circ$), quartz 3.34 Å ($2\theta = 26^\circ$), feldspar 3.20 Å ($2\theta = 28^\circ$), dolomite 2.90 Å ($2\theta = 31^\circ$), calcite 3.03 Å ($2\theta = 30^\circ$), hematite 3.66 Å ($2\theta = 24^\circ$), rutile 3.25 Å ($2\theta = 28^\circ$) main peaks were identified (Figure 5 a-b-c). Results of XRD analysis revealed that almost all minerals observed in the samples were of feldspars, quartz, dolomite, calcite, hematite and rutile in dust samples (Figure 5). Scheuven et al. (2013) [15], Formenti et al. (2011) [16], Journet et al. (2014) [17] stated that quartz, feldspars, calcite, dolomite, hematite and rutile minerals are common to all northern African dust source areas.

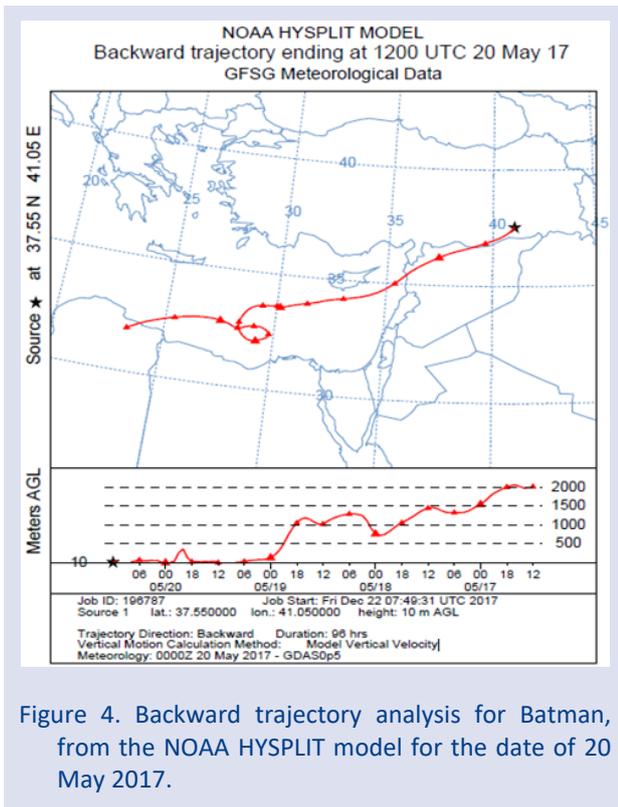


Figure 4. Backward trajectory analysis for Batman, from the NOAA HYSPLIT model for the date of 20 May 2017.

The chemical compositions of the dust samples are shown in Table 1. Silicon and aluminum are dominant in the dust samples. Average data of the desert dust from Sahara by Rodrigues-Navarro are included as a reference. The concentrations of Si, Fe, Mg, K, Ti and P, V, Mn, Zn, Cr, Ni, Pb are similar in the dust samples and Sahara dust (Table 1, Figure 6). Ca and Al have higher content in dust samples than Saharan dust, which shows higher calcite and clay contents in the investigated dust samples. Results of XRD analysis revealed that there were important amount of calcite minerals in the dust samples (Figure 5). Ca values are very high in dust samples. Scheuven et al. (2013) [15] suggested that the (Ca+Mg)/Fe ratios are between 4.29 and 8.40. This ratio is between 3.25 and 4.77, very close to this ratio in dust samples, which is consistent with north-eastern Africa (Egypt, Libya).

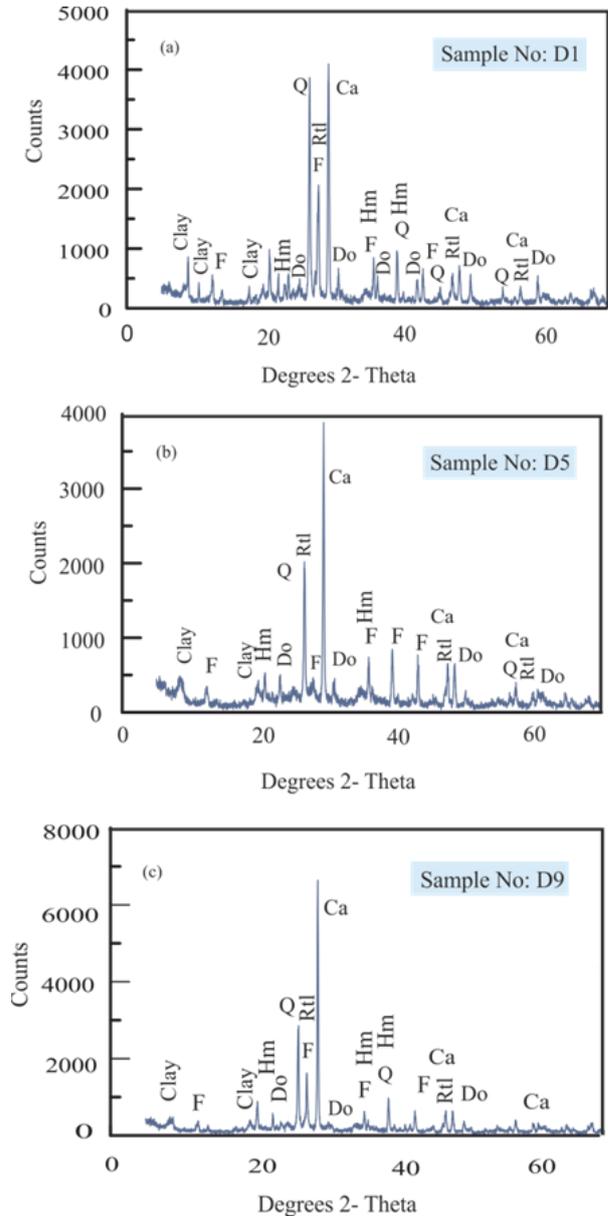


Figure 5. XRD analysis of (a) D1 (b) D5 (c) D9 dust samples showing the presence of quartz (Q), feldspar (F), calcite (Ca), dolomite (Do), rutile (Rtl), and hematite (Hm). The general reflection of clay minerals (Clay) at 4.49 Å is shown.

Table 1. The chemical composition of the dust samples S.Dust: Sahara Dust, from Rodrigues-Navarro et al. (XRF determination, only * ICP determination).

	D1	D3	D5	D7	D9	Max	Min	Average	St Dev.	S.Dust	
Major/Minor Elements (%)	Si	24.11	24	23.78	24.26	23.87	24.26	23.78	24	0.19	24.05
	Al	17.01	11.04	11.41	11.4	10.93	17.01	10.93	12.36	2.61	6.62
	Fe	3.27	3.4	4.78	3.19	3.46	4.78	3.19	3.62	0.66	3.69
	Mg	1.23	1.23	2.06	1.25	1.22	2.06	1.22	1.4	0.37	1.24
	Ca	12.18	12.22	17.04	11.77	12.66	17.04	11.77	13.17	2.18	5.72
	K	1.78	1.83	2.11	1.76	1.84	2.11	1.76	1.86	0.14	1.53
	Ti	0.60	0.61	0.58	0.6	0.64	0.64	0.58	0.61	0.02	0.45
	(Ca+Mg)/Fe	3.35	3.36	4.77	3.25	3.47	3.25	4.77	3.46	0.63	1.74
Minor/Trace Elements (ppm)	P	0.06	2.29	0.06	0.1	0.07	2.29	0.06	0.52	0.99	0.04
	Ba	338	293.39	472.53	302.01	313.48	472.53	293.39	343.88	73.84	529*
	Sr	337	350.93	313.58	322.79	372.35	372.35	313.58	339.33	23.28	162
	V	136.33	167.77	128.5	130.76	140.79	167.77	128.5	140.83	15.81	103*
	Mn	556	582.98	539.36	540.65	597.13	597.13	539.36	563.22	25.84	400
	Zn	343.87	116.67	110.29	117.03	206.97	343.87	110.29	178.97	100.51	367
	Cr	165.85	167.77	158.09	154.75	184.63	184.63	154.75	166.22	11.61	78
	Ni	91.43	93.51	90.52	83.76	108.31	108.31	83.76	93.5	9.05	51
	Cu	40.38	40.31	34.54	38.38	54.48	54.48	34.54	41.618	7.57	...
	Pb	25.8	23.31	35.4	25.16	26.29	35.4	23.31	27.19	4.73	27*
	S	2915	3574	2931.73	1907.63	2759.04	3574	1907.63	2817.48	597.1	390

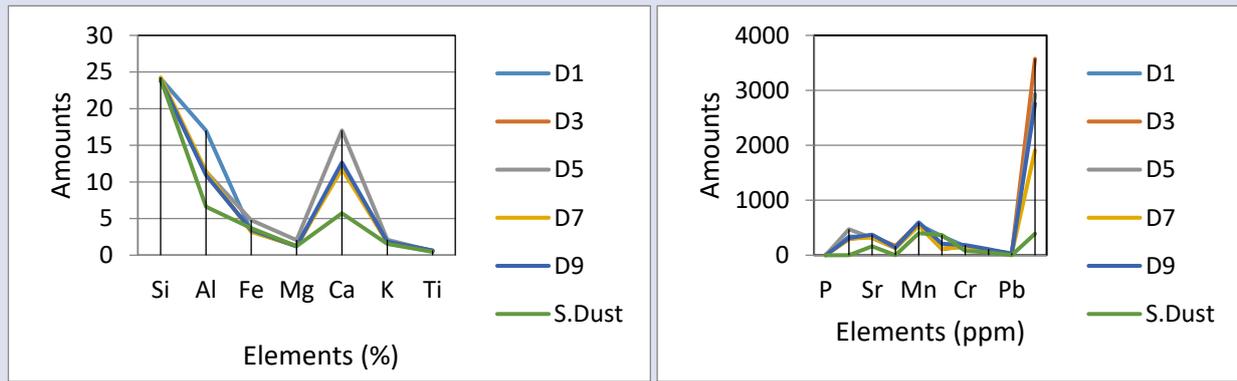


Figure 6. Element distributions relative to Sahara Dust (S.Dust) composition (data from Rodrigues Navarro) for dust samples.

Desert dust and its effects on human health have been studied in the recent years. Dust with anthropogenic pollution occurs with condensation of organic and inorganic compounds, particle-phase reactions [18]. Enrichment factor functions in its assessment and heavy metal is also very frequent in its anthropogenic contribution whose value is used. In order to decide whether heavy metals are of natural or anthropogenic origin, normalized enrichment factor (EF) is commonly used [19]. The EF is defined by Equation (2):

$$EF = \frac{\frac{C_n(\text{sample})}{C_{ref}(\text{sample})}}{\frac{B_n(\text{background})}{B_{ref}(\text{background})}} \quad (2)$$

where EF is the enrichment factor, C_n (sample) is the element content of soil sample, C_{ref} (sample) is the concentration of element in soil sample taken as reference, B_n (background) is the background value of the same element in the earth crust and B_{ref} (background) is the background value of reference element for normalization in the earth crust.

In normalization geochemical such as iron, zircon and titanium inactive elements are used. In this study, the normalization process is calculated according to Fe (Table 2). EF values of $0.5 \leq EF \leq 1.5$ indicate that the element is of lithogenic origin, whereas $EF > 1.5$ indicates there is an enrichment in the environment. $EF = 1.5-3$ is minor enrichment; $EF = 3-5$ is moderate enrichment; $5-10$ is moderately severe enrichment; $10-25$ is severe enrichment; $25-50$ is very severe enrichment; and $EF > 50$ is extremely severe enrichment. EF values do not suggest an anthropogenic effect for Cu and Mn in desert samples, however, Ni and Cr show minor, S shows moderate and Pb and Zn show highly anthropogenic effects. These results demonstrate that the rapid, intense dust advection during the incident led to a great deal of contamination of the environment. In fact, Schaule and Patterson (1981) [20] and Lyamani et al., (2005) [21], and Sholkovitz et al., (2009) [22] suggested an anthropogenic combustion of lead and Ni in Saharan soils. Garrison et al. (2014) [23] reported that in the African dust, great majority of enriched metals/metalloids could be emitted from biomass burning, oil combustion, mining activities and vehicle traffic.

Table 2. The enrichment factors (EF) for heavy metals for dust samples.

Samples	Mn	Ni	Cu	Zn	Cr	Pb	S
D1	0.89	1.86	1.12	7.51	2.52	7.89	4.68
D3	0.90	1.83	1.08	2.45	2.47	6.86	5.52
D5	0.59	1.26	0.66	1.65	1.65	7.41	3.22
D7	0.89	1.75	1.09	2.62	2.43	7.89	3.14
D9	0.91	2.09	1.43	4.27	2.67	7.60	4.18
Average	0.84	1.76	1.08	3.70	2.35	7.53	4.15
St Dev.	0.14	0.30	0.28	2.33	0.40	0.43	1.00

Radiological Characterization of the Dust Samples

The activities of ^{40}K , ^{137}Cs , ^{238}U and ^{232}Th were estimated to be 375, below detection limit (BDL), 72 and 17 Bq.kg^{-1} , respectively in the soil sample and 240, 9, 84 and 10 Bq.kg^{-1} respectively in the dust sample. The absorbed dose rate in the air (D) depends on the activities

of these radionuclides in the samples. D was computed in units of nano gray per hour (nGy.h^{-1}) utilizing Equation (3) [24]:

$$D = 0.462x A_U + 0.621x A_{Th} + 0.0417x A_K \quad (3)$$

where A_K , A_{Th} and A_U are the activities of ^{40}K , ^{232}Th and ^{238}U (in $Bq.kg^{-1}$), respectively. The calculated absorbed dose rates in the air were found to be $59 nGy.h^{-1}$ for soil sample and $55 nGy.h^{-1}$ for dust sample, respectively, which is lower than the world mean ($60 nGy.h^{-1}$). In order to assess the annual effective dose rate (AEDR); the conversion coefficient 0.7 sievert per gray ($Sv.Gy^{-1}$) from the absorbed dose in the air to the effective dose and the outdoor occupancy factor (0.2) recommended by UNSCEAR was utilized [24]. Accordingly, AEDR was computed in units of mili sievert per year ($mSv.y^{-1}$) utilizing Equation (4):

$$AEDR = D \times T \times F \quad (4)$$

where D is the computed dose rate (in $nGy.h^{-1}$), T is the outdoor occupancy time ($0.2 \times 24 h \times 365.25 d = 1753.2 h.y^{-1}$), and F is the conversion factor ($0.7 \times 10^{-6} Sv.Gy^{-1}$). The computed value of the annual effective dose is $0.073 mSv.y^{-1}$ in the soil sample and it is $0.068 mSv.y^{-1}$ in the dust sample. These values are compatible with the world mean of $0.070 mSv.y^{-1}$ [24].

Conclusions

In this study, the dust storm occurred on 20 May 2017 in Batman city was investigated in terms of mineralogical, chemical and radiological characterizations. The results were assessed for compliance with the international values. Meteorological maps showed that there was a high-pressure center over Algeria and Libya, but a low-pressure center over Turkey on 20 May 2017. Therefore, dust transportation occurred from Libya towards Turkey. XRD analysis showed that quartz, feldspars, calcite, dolomite, hematite and rutile minerals were present in dust samples. Si, Fe, Mg, K, Ti and P, V, Mn, Zn, Cr, Ni, Pb contents are similar in the investigated samples and Sahara dust. The computed value of the annual effective dose rate is in line with the world mean content. The results are anticipated to contribute to the improvement of monitoring of the environment and estimations of today's climate models related to the dust impact on climate.

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Conflicts of interest

There are no conflicts of interest in this work.

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