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How different source regions across the Middle East change aerosol and dust particle characteristics

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Abstract

A major question is whether different source regions across the Middle East account for changes in aerosol and dust particle characteristics, which impact Western Iran. Therefore, over a period of sampling from April 2017 to April 2018, dust particles were collected in Western Iran from different cities including Urmia, Sanandaj, Sare-Pole-Zahab, Dehloran and Abadan. The research aim is to compare the chemical compositions of dust and aerosol samples collected during the dust events from the different regions. Results of the analysis of components indicate that during dust events, the concentrations of major and trace elements change. The variability of chemical species during dust events, noted by tracking the dust plumes in satellite images, was also assessed and the results related to the different source areas, namely the dry lands of North-Western Iraq and the desert areas of South-Eastern Syria, some parts of Kuwait and KSA (around the Persian Gulf). Generally, the results show, different source regions across the Middle East have individual chemical compositions with different abundances.

Keywords: Dust-Prone Regions; Dust Particles; Sediment Source Fingerprinting; The Middle East

1. Introduction

Although wind erosion processes impact deeply the Earth systems and all components of the atmosphere (Ravi *et al.*, 2011), due to the potential impact of which, the dust events in the different kinds and various magnitudes are appeared. Some parameters such as soil productivity, air quality, hygienic and health affairs undergo change due to dust events (Webb *et al.*, 2017; Pi *et al.*, 2017). Generally, mineral dust as a main component of the atmospheric particulates emitted to the atmosphere is a critical component of Earth surface processes; it influences the present-day climate through a variety of direct and indirect means (Mahowald, 2011).

The spatially chemical distribution of dust particles has been considered and separated according to the world hemisphere (Goudie and

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Middleton., 2006; Prospero et al., 2002), geographical latitudes (Bullard et al., 2016), global scale (Ginoux et al., 2012) and region by region (Ahmady-Birgani et al., 2018, 2015; Zarasvandi et al., 2011; Wu et al., 2009). The gained results show that the most prone regions of the globe to dust events are in the 'dust belt' confines comprise low, middle and high geographical latitudes (i.e. central Asia, the Middle East, North Africa, Alaska, Canada, Greenland, Iceland, Antarctica, New Zealand, and Patagonia). Regarding elemental ratios (e.g. Ca/Al) or anomalies in elemental concentration due to the various geological, geomorphological and topographical settings, the sources of dust particles emission have been rather precisely reported, which indicates to the given source areas of each dust event.

The various sources generating aerosols and dust to the atmosphere include different environments. Even saline lakes desiccated could have been the main source of dust particles (Mardi *et al.*, 2018; Indoitu *et al.*, 2015; Singer *et al.*, 2003). These particles are typically

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composed of 0.001 to 50 μ m sized mineral and organic particles, as well as similar size particulates of liquid phases. The surfaces of dust particles provide suitable interfaces for reactions with gases, liquids and other solids in the environment. Dentener *et al.* (1996) found that oxidation of gases such as SOx and NOx occurs on the surfaces of mineral dust particles. Also dust particles can mix with sulphate and anthropogenic contaminants by coagulating with aerosols (Roth and Okada, 1998; Wurzler *et al.*, 2000).

Dust events are a natural phenomenon occurring around the globe, but recently (from 1996 to present), according to the World Meteorological Organization, dust events are occurring more frequently (for example, the dust event frequency in the current decade over Iran is 50% greater than last decade). In some seasons in certain Middle East regions, such as Iran, Jordan, Iraq and Syria (the Tigris and Euphrates River Valleys), the Persian Gulf coasts, Sea of Makran coasts and the Southern Arabian Peninsula (the Ad Dahna and the Rub Al Khali deserts), dust events are immense and occur about 30% of the time, on average being more frequent in summer (Kutiel and Furman, 2003). In recent years, statistics demonstrate that some cities in Iran rank first to third in the world in terms of dust pollution, measured as the annual average of PM₁₀ particle size (e.g. Ahvaz city beside the Abadan, Zabol city on the northern Sea of Makran and Bushehr city on the northern the Persian Gulf) (WHO Report, 2016). This data suggest the need for more research on this dust and its source areas, as the dust source fingerprinting has been a key point in the research (Ahmady-Birgani et al., 2018, 2015). Some of the increase in dust activity has been ascribed to climate change, but major factors are desertification (both human induced and climate related), wind erosion (Rashki et al., 2013), dam construction on rivers, civil wars, wetland desiccation and excessive ground water withdrawal (Ahmady-Birgani et al., 2017, 2015). Much dust is derived from near-surface Quaternary regolith and soil, which can be easily contaminated by pollutants from agricultural, industrial and military activities in the source regions.

Based on previous studies around the world regarding the dust source identification, various approaches such as mineralogical identification (Ahmady-Birgani *et al.*, 2015; Friese *et al.*, 2017), geochemical methods (Ahmady-Birgani *et al.*, 2018; Bozlaker *et al.*, 2018; Scheuvens *et al.*, 2013) and isotope analysis (Sharifi *et al.*,

2018; Pourmand *et al.*, 2014) have been applied. To differentiate dust event source areas, focusing on physical properties and chemical composition of each dust event is mandatory. It should be highlighted, that due to differences in geological, geomorphological and topographical settings of each individual source area, by inference, different compounds of atmospheric particulates are reasonably expected. Therefore, the aim of this study is to investigate the characteristics of mineral dust collected in Western Iran, where there is significant dust depositions related to dust events originating throughout the Middle East region.

2. Materials and Methods

Samples of dust particles were collected in Western Iran, in different cities including Urmia, Sanandaj, Sare-pole-Zahab, Dehloran and Abadan during severe dust events using a Volume (MVS) Microcomputer Medium Controlled Air Sampler and Low Volume Samplers, purchased by Urmia University (Figure 1). A total of 5 pure samples were exactly collected during the severe dust events, once the dust event had broke out and finished. Following collection, each sample including the filter, was weighed using a precision weighing balance and the weight of the filter subtracted to obtain an estimate of the mass and concentration of the particulates.

Sample preparation and chemical analysis were performed with an ICP-AES instrument. For this study, we were interested in the acid soluble component of the dust rather than the total composition, which includes insoluble minerals. Half of each quartz fiber filter with collected particulates was digested with aqua regia in a closed Teflon microwave vessel at a temperature of 140°C for 65 min. This digestion procedure was chosen to select for the organic and more soluble inorganic components (e.g. carbonates, sulfates, iron and manganese oxides, chlorides and clay minerals) as well as adsorbed ions, in the dust samples, and to avoid the highly insoluble components and chemically inert phases such as quartz, other rock-forming silicates and resistant minerals (e.g. zircon, rutile and chromite). The procedure also allowed digestion of the dust particles embedded in the filters, without dissolving the quartz in the filters. Prior to digestion, each filter half was weighed using a precision weighing balance and an approximate sample mass calculated bv subtracting the weight of unused half filters.



Fig. 1. Location of sampling site across the western Iran (black circles) and the Medium Volume (MVS) Microcomputer Controlled Air Sampler and Low Volume Samplers are seen.

Digests were cooled to room temperature, quantitatively transferred to 50 ml centrifuge tubes and diluted to 30 ml with Ultrapure water). The tubes were then centrifuged at 4000 rpm for 10 min. 1 ml of the digest was transferred into a 10 ml centrifuge tube and then diluted to 10 ml with ICP-AES internal standard. Solutions from the digest were analyzed for major and trace elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES Elan DRC-e with oxygen and methane reaction gases to reduce poly-atomic interferences). Calibration was performed using a complex external standard) AccuStandards 1-5), covering the full mass range, with correction for blanks including, blank acid and blank filter solutions. International Reference Material (MRM) was used as an external cross-check for calibration

and for assessing accuracy of extraction efficiency. Uncertainties of the analytical procedures at the median levels in the general population were below 5% for all the elements. Element concentrations from the analyses were calculated in ppm.

In addition, the dust plume trails for each event were detected by the MODIS satellite images. In this regards, each dust event reported by synoptic meteorological stations observer was collected and its satellite image was downloaded. For some mixed dust events originating from different regions, no analysis was done. In this study, region-by-region sample collection was considered and each dust sample collected had individual properties of the region originated. Moreover, in Figure 2 conceptual diagram of research procedure is seen.



Fig. 2. Conceptual diagram of the research procedure.

3. Results and Discussion

Geochemical analyses for the major and trace elements in the samples as the concentration measurements according to ppm (part per million) are shown in Fig. 3. The variabilities of each element in each dust event episode give a good indication of the various source areas impacting Iran.

The Middle East region as a main source of dust emitting to atmosphere has an area of approximately more than 7 million km² and is inhabited by a little less than 400 million population. The vast lands with various geographical landforms are known as the main sources of dust events now, which have been spread across the Middle East. Therefore, categorizing dust events source areas across the region is vital according to their frequency,

intensity, abundance, physical properties and chemical compositions.

As the results show, the major elements show the highest abundance in samples and trace elements were low. Although these variabilities differ from region to another, they indicate the key roles of any dust source areas. Generally, 18 chemical elements were analyzed by ICP-MS, including sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), titanium (Ti), potassium (K), iron (Fe), calcium (Ca), nickel (Ni), copper (Cu), vanadium (V), lead (Pb), arsenic (As), zinc (Zn), cobalt (Co), selenium (Se), cadmium (Cd) and chromium (Cr). According to where they are being emitted to the atmosphere, those elements are associated with a specific source. In Table 1, possible and potential source areas of each element have been illustrated. As Table 1 shows, possible source areas could be categorized into two groups, including natural and anthropogenic agents.



Fig. 3. Concentration of the major and trace elements in different receiver regions. Each bar color shows one severe dust event of one individual region, which could be precisely distinguished by satellite images



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Table 1. Pos	sible both anthropogenic and natural sources for dust particles with different elem	nental compositions (provided by authors)
Elements	Natural (geogenic) sources	Anthropogenic sources

Na	Detrital feldspar and clay minerals, fine-grained unweathered plagioclase, the most abundant of the alkali metals, the principal cation in sea water, in brines and evaporate deposits salty lakes and playas	NA
Mg	The most abundant cation in sea, the major constituent of many mineral groups, including silicates, carbonates, sulphates, phosphates and borates, including magnesite and dolomite, the major component of many mafic rock-forming minerals, including olivine, pyroxene, amphibole, biotite mica and clay minerals and calcareous rocks	fertilizers and liming
Al	The major constituent in many rock forming minerals, such as feldspar, mica, amphibole, pyroxene and garnet, the secondary clay minerals, e.g., kaolinite and smectite, With the exception of shale, sedimentary rock types commonly contain very little Al ₂ O ₃ , high in mafic rocks such as basalt, Abundance of clay and mica minerals in the sediment explains the relatively high Al content	Aluminum smelters, cement plants, sewage and dust
Si	The most common source of Si is plagioclase feldspar, Common source minerals include quartz and feldspar, Sandstone and conglomerate contain between 65 and 95% silica, the major constituent of nearly all rocks except for limestone and evaporates, an important component of detrital sedimentary rocks, and felsic and intermediate igneous rocks	Some quartz may be released into the atmosphere during coal combustion
Ti	Titanium forms several minerals, including ilmenite, rutile and sphene CaTiSiO, it also occurs as an accessory element in pyroxene, amphibole, mica and garnet, Ti may also substitute for Mg or Fe in silicate minerals, leading to enrichment of Ti in amphibole and mica, elevated Ti values are indicative of mafic and ultramafic rocks, the TiO ₂ contents of carbonate rocks and quartzite are generally lower than those of shale	paint pigments, its alloys with Al, Mo, Mn and Fe are used extensively in aircraft, ship and missile manufacture
K	Potasium is found out in sea waters, river particulate matters, It forms several minerals, including sylvite KCl in evaporite deposits, is a major constituent in many igneous rocks and enriched in felsic relative to mafic igneous rocks, Elevated values of K indicate the presence of felsic rocks, especially kaolinised intrusives, K is a major constituent of many rock-forming minerals, including important silicate minerals such as alkali feldspar, leucite, biotite, muscovite, phlogopite and some amphiboles, a component of many phosphate, halide and sulphate minerals, releasing through the weathering of feldspar minerals	K-Fertilizers
Fe	Forming several common minerals, including pyrite, magnetite, haematite and siderite and many rock-forming minerals, including mica, garnet, amphibole, pyroxene and olivine, is generally enriched in mafic rocks relative to felsic, Iron is a major element in soil with a median value of 2.1% (Rose et al. 1979). Iron in soils is mostly as Fe^{2+} in ferro-magnesian silicates, such as olivine, pyroxene, amphibole and biotite, and as Fe^{3+} in iron oxides and hydroxides, as the result of weathering common minerale including exolution graphic approximate the product of the second sec	Anthropogenic sources of iron include the iron and steel industry, sewage and dust from iron mining. Iron sulphate is also used as a fertiliser and herbicide
Ca	calcult is following several common initials including calcule, gypsuin, dolonite, anhydrite, feldspar, amphibole and pyroxene, is often associated with clay minerals such as illite, chlorite and Ca–montmorillonite, rocks such as granite and sandstone have relatively low total CaO contents, limestone and dolomite are carbonate sediments, Plagioclase is the principal host for Ca in some detrital sediments, sulphate minerals such as gypsum and anhydrite are particularly in sandstone and evaporates	Liming land to correct soil acidity, cement factories, fertilizers and dust
Ni	It is substituted during fractionation between Fe and Mg, it is partitioned into ferromagnesian minerals such as olivine, orthopyroxene, It is strongly enriched in ultramafic and mafic lithologies relative to felsic igneous rocks, Ni in igneous rocks generally correlates with Mg, Cr and Co. Ni is present in sulphide minerals, such as pyrite and chalcopyrite, and often correlates well with Cu in sulphide-rich rocks, In sedimentary rocks, Ni is mostly held in detrital ferromagnesian silicate minerals, detrital primary Fe oxides, hydrous Fe and Mn oxides, and clay minerals, organic matter and coal can contain Ni concentrations.	Fertilizers, steel works, metal plating and coinage, fuel combustion and detergents, waste tips
Cu	Elevated Cu values are more likely to indicate the presence of mafic rocks, forming several minerals, including chalcopyrite, covellite and malachite and trace levels in	Copper mining and smelting, the electrical industry, agriculture, sewage

mica (biotite), pyroxene and amphibole, greater affinity for mafic than for felsic igneous rocks, Cu is strongly concentrated into sulphide minerals during hydrothermal mineralisation. In unmineralised sediments, Cu concentrations are principally determined by mafic detritus, secondary Fe and Mn oxides, clay minerals and organic matter. Fine-grained clastic rocks, particularly black shale, are typically enriched in Cu

It forms several minerals including magnetite, vanadinite and carnotite, It is present as a trace element in mica, apatite, pyroxene and amphibole, V is frequently found as a substitute for Fe in magnetite and in the ferromagnesian silicate minerals, mafic rocks are typically enriched in V relative to most intermediate and felsic rocks, Elevated V values are indicative of mafic rocks, The V content of sedimentary rocks reflects the abundance of detrital Fe oxides, clay minerals, hydrous oxides of Fe and Mn, and organic matter, The average V content of quartitic sandstone and pure carbonate sediments is low, Coal may also contain appreciable amounts of V, The most V-rich sedimentary rock is black shale

Forming several important minerals including galena, anglesite and minium, at trace levels of other minerals, including K–feldspar, plagioclase, mica, zircon and magnetite, The sedimentary rocks with the highest concentrations are black shale due to organic matter, pure limestone and quartzitic sandstone are typically depleted of Pb, it is mainly associated with clay minerals, Mn oxides, Fe and Al hydroxides and organic matter, it is enriched in felsic igneous rocks relative to mafic rocks

Arsenic is partitioned into a variety of sulphide and sulpharsenide minerals, arsenopyrite, realgar and orpiment, it is widely present as an accessory element in other sulphide minerals and phosphate minerals such as galena, apatite, pyrite and sphalerite, As is not preferentially enriched in felsic or mafic igneous rocks. In

sedimentary rocks, As is concentrated in clays, hydrous Fe and Mn oxides, sulphides and phosphates, coal and ironstone, particularly phosphatic ones, can contain appreciable amounts of As

Zinc forms several minerals, including sphalerite, smithsonite and zincite, a trace element in pyroxene, amphibole, mica, garnet and magnetite, Zn is enriched in mafic relative to felsic rocks, Zinc is partitioned into oxide and silicate minerals by substitution for Fe and Mg, Zinc is readily adsorbed onto ferric oxides, Zn in

Zn sedimentary rocks is controlled by the abundance of ferromagnesian silicates, detrital oxides, magnetite, and clay minerals, Carbonate rocks and quartzofeldspathic sand are depleted in Zn compared with greywacke and shale, Zn is easily adsorbed by mineral and organic components in most soil types, accumulates in the soil surface horizons, Elevated Zn values more likely indicate mafic rocks, or Fe/Mn coprecipitation

Cobalt forms several rather rare minerals including smaltite, cobaltite and linnaeite, as an accessory element in olivine, pyroxene, amphibole, mica, garnet and sphalerite, is associated with the iron sulphides pyrite, arsenopyrite and pyrrhotite, and in oxide accessory minerals, such as magnetite, Co is generally enriched in mafic relative to

Co felsic igneous rocks, Cobalt, together with Cr and Ni is indicative of mafic rocks, quartz, feldspar and pure calcium carbonate contain very little Co, pure sandstone and limestone are very low in Co, in sedimentary rocks, Co vary with the Fe and Mn content and is concentrated in the fine-grained fractions Selenium forms several rare minerals, including crookesite, berzelianite and

tiemannite, is more widely present as an accessory element replacing sulphur in more common sulphide minerals, such as pyrite, chalcopyrite, pyrrhotite and sphalerite, its concentrations in volcanic rocks are low, Because of similarities in the chemistry of Se and S, Se is concentrated in sulphide ore deposits, uranium deposits in sandstone and the diagenetic pyrite of fine-grained sediments, Organic-rich sediments are enriched in Se, e.g., black shale and phosphate rocks

Cadmium occurs as a substitute for Hg, Cu, Pb and Zn in sulphide minerals, especially sphalerite and smithsonite, it is found in trace amounts in some silicate minerals, such as biotite and amphibole, some types of coal, peat and crude oil contain relatively high Cd levels, lower concentrations occur in igneous and

Cd contain relatively high Cd levels, lower concentrations occur in igneous and metamorphic rocks, sandstone and limestone, but higher levels are found in shale, Clay minerals and iron oxyhydroxide coatings adsorb Cd, and the metal also co-precipitates with manganese oxide

Chromium is forming several minerals, including chromite and crocoite and is present as an accessory element in several others, such as spinel, amphibole, mica, pyroxene and garnet, Cr readily substitutes for Fe and Mg, Cr is enriched in ultramafic rocks along with elements such as Ni. While the principal Cr ore mineral, olivine is generally poor in Cr, but pyroxene, amphibole and mica may be enriched, Elevated Cr values are indicative of mafic or ultramafic rocks, Very low Cr contents in association with elevated values of K, Th, U and REEs may indicate the presence of felsic rocks sludge and steel works. Copper compounds are widely used in agriculture and are a possible source of drainage anomalies, copper sulphate as a fungicide in fruit cultivation and vineyards, liquid manure from pigs and chicken farms

Oil and coal combustion, steel alloy tool production and traffic pollution. Vanadium has a variety of industrial uses in metallurgy, electronics and dyeing, airborne anthropogenic V

From vehicle exhausts, road dusts, using leaded petrol and gasoline, metalliferous mining (especially sulphide ores), metallic detritus, Pbbearing glass and pottery glazes, batteries, old lead-based paints, the corrosion of lead pipes in areas of soft water and sewage sludge,

Coal combustion, geothermal power plants, sulphidic ore roasting and smelting, and pig and poultry sewage, herbicides, insecticides and fungicides containing arsenic compounds

Industrial activities such as mining, coal and waste combustion, and steel processing, an anticorrosion coating, a constituent of brass, white pigment (ZnO) in paint and rubber products, in the manufacture of dry batteries, liquid manure spreading

Coal combustion, special steels, fertilizers and lead, iron and silver mining and processing, metallurgical work

The burning of fossil fuels, combustion of coal in electricity generation, smelters, vulcanised rubber, wastewater and some phosphate fertilizers

Sewage sludge, electroplating and battery, paint, ink and plastic manufacture, the increasing use of Zn in fertilizers may lead to Cd contamination, Phosphate fertilizers, mining, chemical industries, fertilizer use in agriculture, brass metallurgy, textile and paper industries

Leather tanning industry, electroplating operations, paints/pigments, cement, airborne emissions from chemical plants and incineration facilities, stationary fuel combustion, metal industry

According to previous studies on the chemical composition of dust particles spread over the Middle East region (e.g. Engelbrecht *et al.*, 2013,

2009_a, 2009_b; Ahmady-Birgani 2018) the possible sources of dust particles are categorized into five groups, including (i) evaporate deposits,

v

Pb

As

Cr

(ii) dust-gypsum, (iii) dust-calcic, (iv) dustsiliceous and (v) vehicles/ smelting. These groups are well associated by correlation coefficients, which are a measure of similarity or non-similarity among the sources. For example, high concentration of sodium (Na) and chlorine (Cl) represents the halite minerals, which are abundant in salty lakes, saline soils and playas. High magnesium (Mg) values indicate mafic or ultramafic rocks or calcareous rocks (Table 1).

Based on when the dust events have happened in this study, dust events could be traced back to April 2017 (dust event 1), May 2017 (dust event 2), May 2017 (dust event 3), September 2017 (dust event 4) and October 2017 (dust event 5), respectively. From satellite imagery (i.e. MODIS), it is possible to determine the trajectory of dust event episodes that occurred during the sampling periods. During the image processing and classification, the radiometric calibration, atmospheric correction (using FLAASH module) and bow-tie effect correction using ENVI 5.2 software were applied. As satellite images show, the dry lands of the North-West and central Iraq and the desert areas of South-Eastern Syria, some parts of Kuwait and KSA have significant contributions in the dust events taking place. These dust source areas have been impacting Iran for a long time, without any considerations by their authorities and with no one bearing responsibility (Figure 4).

In total, variabilities of elements analysed plus satellite images monitoring of each dust event episode could give the authorities and end-users to rank the dust events source areas according to the frequency, abundance, intensity, and concentration, which is related to the different kinds of elements (i.e. Radioactive, Toxic ones). So, apart from analyzing the dust samples collected, knowing about where they originating from is very impressive and important, and can assist researchers to model such natural hazards based on physical properties and chemical composition.



Fig. 4. The main source dust-prone regions across the Middle East affecting the western Iran and the Persian Gulf



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4. Conclusion

This study shows that there are systematic differences in the chemical composition of fine dust particles collected at some sites in Western Iran (i.e. Urmia, Sanandaj, Sare-pole-Zahab, Dehloran and Abadan cities), during periods of dust events. Major and trace element variability observed in samples from different dust event episodes appears to reflect different source areas and dust plume trajectories as indicated by satellite imagery. This highlights the importance of tracking and locating dust sources for major dust events and understanding the compositions of these source areas in order to predict the chemical characteristics of particulates in a dust event.

As results show, the most dangerous source areas to dust storms are located near residential and agricultural land, contaminated by Sewage sludge, industrial activities and combustion of fuels. During the severe dust events 1 and 2 (April 2017 and May 2017), which are located in South-Eastern Syria (downstream of the Al-Asad dam) and North-Western Iraq (along the Euphrates River), the highest concentration of toxic trace elements such as Se, Cd, Pb, Ni, Zn, Cu, As and V accompanied by low major elements are readily seen. Therefore, the vicinity of dust source areas to the potentially contaminated land is more dangerous and more harmful for human beings exposure. In addition, the dust storms carried over long distances, because of smaller dust and higher adsorbent capacity, convey more microorganism and trace elements, which are more harmful.

Recent drought conditions in Iraq (e.g. a decrease in mean annual precipitation from 136 mm to about 36 mm) as well as general land degradation appear to have exacerbated the problem (Al-Dabbas *et al.*, 2012). Additional dust is contributed from the desiccation of natural wetlands, particularly at the head of the Persian Gulf, including the Hawizeh Marshes, a result of reduced water flow due to the damming of the Tigris and Euphrates Rivers (Ahmady-Birgani *et al.*, 2015). All these mismanagements and its consequent damages make the Middle East region prone to dust events.

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