

INFLUENCE OF METEOROLOGICAL PARAMETERS ON AIR QUALITY AND OTHER POLLUTANTS IN DUHOK CITY, IRAQ

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ABSTRACT

This study was aimed to investigated the relationship between the daily average of meteorological parameters (MP), and the daily average (DA) of air pollutant concentrations (PC) (including particulate matter (PM)). In this study, the DA of air PC, such as carbon monoxide (CO) and sulphur dioxide (SO₂), was measured during heavy traffic in the summer season for five different locations throughout 2017, and comparison made with results similarly obtained in 2012. The particulate matter sample has been collected for the same period. The daily average meteorological parameters (MP) such as temperature (T), atmospheric pressure (AP), wind direction (WD), wind speed (WS) and relative humidity (RH) were measured and collected from the Directorate of Meteorology and Seismology Instrument at DC during the same period. The microstructure and morphology of the particles have been investigated using scanning electron microscopy (SEM), and reflected light microscopy (RLM). The chemical composition of the particles has been studied using energy-dispersive X-ray (EDX) and atomic absorption spectrometry (AAS). The EDX analysis shows that silicon and calcium were found to be the most abundant elements in the dust particles. Mineralogical characterization was carried out using X-ray diffraction (XRD), and results of which indicate the presence of calcium carbonate (CaCO₃).

Keywords: air pollution, carbon monoxide, sulphur dioxide, regression analysis, PM, SEM, EDX

* Part of Ph.D. Dissertation of 1st author.

مهدي وآخرون

مجلة العلوم الزراعية العراقية - 2020: 51: 1172-1160

تأثير العوامل الجوية على نوعية الهواء والملوثات الأخرى في مدينة دهوك-عراق

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المستخلص

تهدف الدراسة الى استقصاء العلاقة بين المتوسط اليومي للمؤثرات الجوية والمتوسط اليومي لتراكيز ملوثات الهواء (بما في ذلك الجسيمات الملوثة). في هذه الدراسة قيست المعدل اليومي لتراكيز ملوثات الهواء مثل غاز ثاني اوكسيد الكبريتات (SO₂) وأول اوكسيد الكربون (CO) خلال حركة المرور الكثيفة في فصل الصيف لسنة 2017 لخمس مواقع وقورنت بسنة 2012. الجسيمات الملوثة جمعت لنفس الفترة. والمعدل اليومي لعوامل الرصد الجوي مثل درجة الحرارة، الضغط الجوي، الرطوبة النسبية، سرعة الرياح واتجاهها لنفس الفترة تم الحصول عليها من مديرية الأرصاد الجوية والزلازل في دهوك. وتمت دراسة التركيب الدقيق وشكل الجسيمات الملوثة بأستعمال المجهر الالكتروني الماسح (SEM) والمجهر الضوئي العاكس (RLM) ودرس التركيب الكيميائي للجسيمات الملوثة بأستعمال الأشعة السينية المشتقة للطاقة (EDX) ومطياف الامتصاص الذري (AAS). كما تم فحص الخصائص المعدنية والجسيمات الملوثة بواسطة حيود الأشعة السينية (XRD).

الكلمات المفتاحية: تلوث الهواء أول أوكسيد الكربون، ثاني أوكسيد الكبريت، تحليل الأتحدار (الاحصائي)، الجسيمات الملوثة (PM)، المجهر الالكتروني الماسح (SEM)، الأشعة السينية المشتقة للطاقة (EDX)

*Received:11/8/2019, Accepted:18/11/2019

INTRODUCTION

Air pollution (AP) is defined as the presence of contaminants or pollutant substances in the atmosphere such as toxic gases (e.g., carbon monoxide (CO), sulphur dioxide (SO₂), nitrogen oxides (NO), etc.), particulate matter (e.g., dust, fumes, mist, smoke, etc.), and radioactive materials. Gaseous pollutants interact with the human body and can harmful effects on human health, cause detrimental environmental impacts, play a significant role in environmental changes, and eventually lead to unfavourable changes in atmospheric chemistry (12). Generally, at areas with congestion and heavy traffic, high concentrations of CO are expected (16). Fuel combustion for transportation and industrial processes also produces CO and SO₂ emission (40). According to the United Nations (UN) report of 2001, it was estimated that over 6×10^8 people worldwide were exposed to dangerous levels of traffic-generated air pollution in that same year (10). Particulate matter (PM) is also a source of pollutants, containing high levels of toxic and poisonous metals, as well as organic contaminants (33). The major sources of heavy metal (HeM) pollution in dust comes from construction, traffic, industry, exploration activities and smelters.

Over the past few decades, statistical studies show that meteorology also could be a contributor to air pollution episodes. For such reasons, the combination of several meteorological parameters has been correlated with pollutant concentrations (PC), or air quality (1). There are numerous studies and investigations into AP which have been performed mainly in crowded cities across the world. In three big cities in China, Beijing, Shanghai and Guangzhou, the relationships between ambient air pollutants concentrations and meteorological parameters (MP) were investigated. From March 2013 to February 2014, an analysis of MPs such as WS, T, RH, and WD and air pollutants such SO₂, O₃, NO₂, CO, PM_{2.5} and PM₁₀ was conducted. The results show that MPs have an important role in the formation of air pollution with large variations in geological areas and different seasons (17). Also, it was found in the city of Erzurum (Turkey) that the daily traffic-related pollutant concentrations are influenced by the

daily MP and the previous day's PC (34). In Cairo (Egypt), Elminir studied the relation between meteorological parameters and air pollution, finding that WD had an impact on air pollutant concentrations and also on the correlation between pollutants (14). In Kermanshah (Iran), researchers studied the relationship between weather conditions and air pollution with the increased number of emergencies involving ward admissions of asthmatic patient in Kermanshah hospitals (30). Recently, to predict ambient air concentrations in an industrial region of Turkey (namely, the city of Kutahya) the AERMOD dispersion model was used (37). Heavy metals are considered conservative pollutants because they tend to bioaccumulate in tissues over a period of time. For these reasons, investigation is essential to find the sources of heavy metals in dust storms and also to understand their behaviours and impacts. In France, the concentration of many dust's HeM such as Pb, Cu, Cd, Zn, Ni and Os were measured for various major roads, from which it was noted that there is a high level of Pb, Cu and Zn dispersed into the air. The main source of traffic pollutant emissions is reported to be engine combustion, abrasion of brake pads and tire wear (28). The mineral dust in the atmosphere has a significant role in controlling different atmospheric processes such as precipitation, cloud characteristics, the chemistry of the atmosphere and radioactive forcing (39). Mineral dust has important effect on the environment, ecosystem and biogeochemical cycles during the sedimentation of organic materials and minerals on the earth's ecosystem (11, 20). When the dust is contaminated by pesticides, soluble and chelate metallic salts and carbonaceous materials, it can have an adverse impact on human health (29). In recent years, due to the rapid increase in building density, industrial, number of vehicles, population density and energy consumption, the outdoor air quality has deteriorated in crowded urban areas (4) (including Duhok city-DC) in northern region of Iraq. The air pollution in DC may be related to the increase in number of both people and vehicles, as can be observed from the congested roads and streets located within the DC road network. Various

studies about air pollution can be found in the literature, however, there are only a limited number that have been carried out for the DC of Iraq. The main source of air pollution is motor vehicles (8). In 2010, small vehicles such as private vehicles and taxis were found to emit around 594 tonnes of pollutant per day into DC's atmosphere (when there were about 98950 small vehicles in DC in the same year) (19). It was found that the average concentration of CO in the majority of polluted areas in DC was 11.6 ppm, (32) which was higher than required by both local and international standards. In DC, the major sources of heavy metal (HeM) contaminants are due to road vehicle emissions (22). In this study, we first investigated the relation between meteorological parameters in DC during the summer season (of 2012 and 2017), and air pollution concentrations such as SO₂ and CO in DC city. Secondly, we elucidated the concentrations of HeM such as Pb, Cu, Fe, Mn, Zn, Cd, Co and Ni in dust samples from various locations using AAS. The

microstructure and morphology of the particles have been investigated using scanning electron microscopy (SEM), and reflected light microscopy (RLM). The chemical composition of these particles has been studied using energy-dispersive X-ray diffraction (EDX) and atomic absorption spectrometry (AAS). Mineralogical characteristics were being investigated using X-ray diffraction (XRD).

MATERIALS AND METHODS

Features of study area

Duhok (DC) is located in the northwest part of Iraq (Figure 1) at latitude 36°53' 20" - 36°50'N and longitude 42°54' 10 - 43°5'. DC is surrounded by mountains on three sides; the Zawa Mountains are located to the south and southeast, the White Mountains to the north and northeast, and the Mamsen Mountains to the east. DC experiences four distinct seasons with different climates, generally cold in winter (December-February), hot in summer (June-Augus) and moderate in autumn (September-November) and spring (March-May).

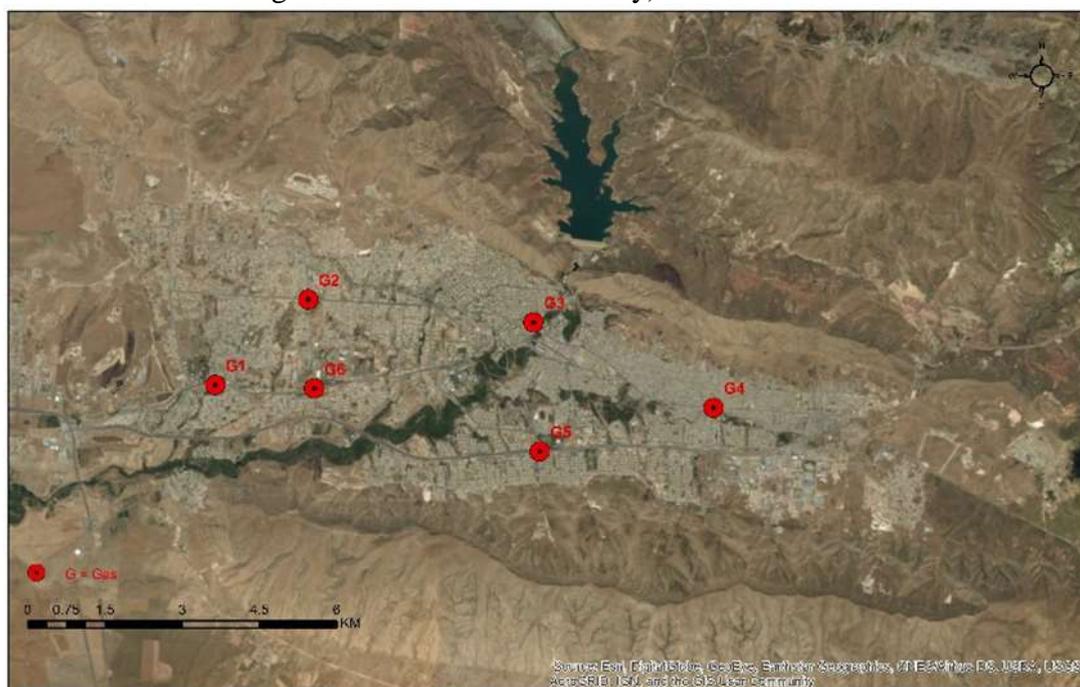


Figure 1. Aerial top view of map of Duhok city (DC) showing the areas and locations under study

Measurements of SO₂ and CO concentrations

This study was performed in the summer period from June to August 2017 for five different locations. The site location was selected as show in Figure1, in heavy traffic. The daily average pollutant concentrations of

SO₂ and CO for 2017 were measured using a Drager Multi-Gas Detector X-am 5600 at the side of the road. The results were compared with the daily average pollutant concentrations of SO₂ and CO for June to August 2012 (obtained from the Duhok Environmental Directorate (DED)).

Meteorological and atmospheric parameters

The measurements of some of the MPs such as average temperature (T) (°C), atmospheric pressure (AP) (mbar), wind direction (WD), wind speed (WS) (m/s) and relative humidity (RH) (%) were performed by ordinary apparatus. Moreover, some of the meteorological parameters such as the average T (°C), AP (mbar), RH (%), WS (m/s) and WD for the above period have been obtained from the Directorate of Meteorology and Seismology instrument at DC.

Dust samples

Dust samples were collected during the summer of 2017 by Funnel containers as show in Figure 2 at five different locations near the gas measuring locations (G₁, G₂, G₃, G₄ and G₅). To reduce the cost of this measuring

equipment, Funnel containers were hand-made locally in DC from Aluminium. The size of the top area of the funnel was 0.5 x 0.5 m². The top part of the Funnel containers was covered with mesh to form a rough area to avoid trapping and animal stand. The funnel was installed about 7-8 m above the ground on building roofs. The installation sites were chosen in such a way that neither trees nor buildings created any obstacle to obtain a more accurate measurement. Dust samples were collected carefully in very clean containers and were placed in clean plastic bags and then they were transported to the laboratory. Afterwards, the samples were dried at a temperature of 105°C overnight using a digital furnace to control the heating temperature, then their weights were measured and recorded.

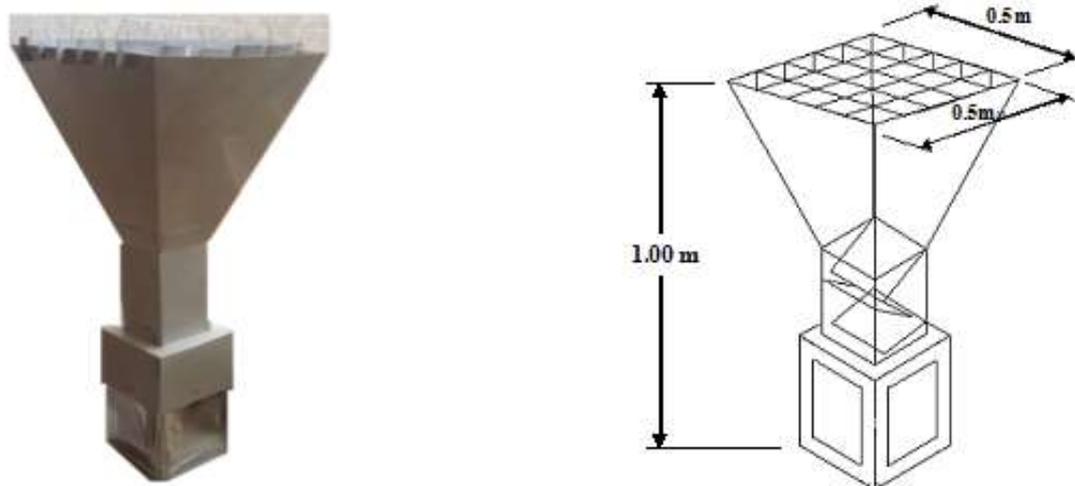


Figure 2. Funnel container for Dust samples

Statistical Analysis

A statistical package software (SPSS 16.0) has been used to analyse the data to find the relation between variables and to further find the correlation coefficients between them, applying regression analysis, linear regression. SO₂ and CO concentrations were considered the dependent variables while meteorological data (T, AP, RH, WS) were considered to be independent variables.

Chemical analysis by using AAS

Concentrations of Pb, Cu, Fe, Mn, Zn, Cd, Co and Ni were determined using an AAS (type AA240FS, Varian). This was achieved after digesting the sample (23, 35).

RLM, SEM AND EDX Microanalysis

After examination of samples using the naked eye (unaided eye), the morphology of the

particles was examined via a reflecting light microscope (RLM). The images of the samples were taken using a zoom stereo microscope (stereo 6) to observed materials that were not visible to the naked eye. The EDX spectroscopy and SEM analysis were used to obtained elemental composition and particle sizes of the PMs. The SEM system model (Nova Nanosem-450) was equipped with an EDX spectrometer. The sample images were recorded at different magnifications (between 500× and 100,000×). For SEM and EDX, an electron beam with an accelerating voltage of 10 kV was applied for the determination of the elemental chemical composition of the particles. EDX microanalysis was used for elemental analysis of dust samples.

Table 1. The minimum, maximum, means and standard deviations of SO₂ and CO concentrations and MP during the summer seasons in 2017 and 2012

	Min	Max	Mean	Standard	N
2017					
SO ₂ concentration (ppm)	0.0272	0.4984	0.066898	0.04805	92
CO concentration (ppm)	0.3857	2.632	0.853581	0.31996	92
Temperature (°C)	24.2	37.6	32.94345	2.93674	92
Atmospheric pressure (mbar)	996.0	1010.3	1003.374	2.75587	92
Relative humidity (%)	19	40	27.61821	4.28770	92
Wind speed (m/s)	0.97	2.75	1.440193	0.32910	92
2012					
SO ₂ concentration (ppm)	0.0025	0.0086	0.003992	0.00107	92
CO concentration (ppm)	0.3273	1.2929	0.762571	0.16812	92
Temperature (°C)	25.6	38.5	32.99565	2.60185	92
Atmospheric pressure (mbar)	993.6	1014	1002.091	3.10071	92
Relative humidity (%)	18	40	30.07609	4.38336	92
Wind speed (m/s)	0.04	2	0.749391	0.47279	92

To estimate the effects of MP on urban air quality the relationship between ambient air quality data and MPs for summer 2012 and 2017 was evaluated via linear regression analysis. The correlation coefficients and regression equations between daily average SO₂ and CO concentrations with daily average MPs (T, AP, RH and WS) are shown in Table 2. SO₂ and CO concentrations as a function of T are plotted in Figure 4(a,b) and Figure 5(c,d), respectively, for the summers of 2012 and 2017. From these figures and Table 2, it can be seen that both SO₂ and CO concentrations in both years have a very weak and positive correlation with T, and increase slightly with increasing T, which is in good agreement with the results of other researchers (7, 14, 24, 27, 31). The results of positive correlation of PC with average daily temperature indicates that pollutants accumulate in the atmosphere on warm days, which is caused by vehicle exhausts and emissions from diesel generators, which are spread across several places in the city. During summer, homogeneous conversion of SO₂ to particulate sulphate can be assumed to be the main oxidation mechanism under the conditions generally prevailing over the eastern Mediterranean region. It can be seen from Table 2 that both SO₂ and CO concentrations in both years have a very weak

and negative correlation with AP. These results are also in good agreement with associated studies in the literature (9, 31). The concentrations of CO in both years and SO₂ concentrations in 2017 have a barely positive correlation with RH, as shown in Table 2. Other studies (9, 14) have reported similar results to those found in this study. The positive correlation or correlation of low concentrations with low humidity can be attributed to the effect of clean free tropospheric air masses, which is in agreement with the findings of other researchers (18). The concentrations of SO₂ in 2012 were very weakly and negatively correlated with RH, which means they were inversely related to PC since this controls the rate of absorption of pollutants (24). Table 2 also show the variations of wind speed (WS) is positively correlated with SO₂ and CO concentrations in both years. Also, these results are in good agreement with the results of other researchers (6, 18). The positive correlation of concentrations of gaseous pollutants with WS might be influenced by the presence of an industrial area and power station (Kuashi) which lie in the western part of DC, and might account for the deterioration of ambient air quality. Artun (5) reported that power plants are important sources of atmospheric SO₂ and volatile organic compounds (VOCs).

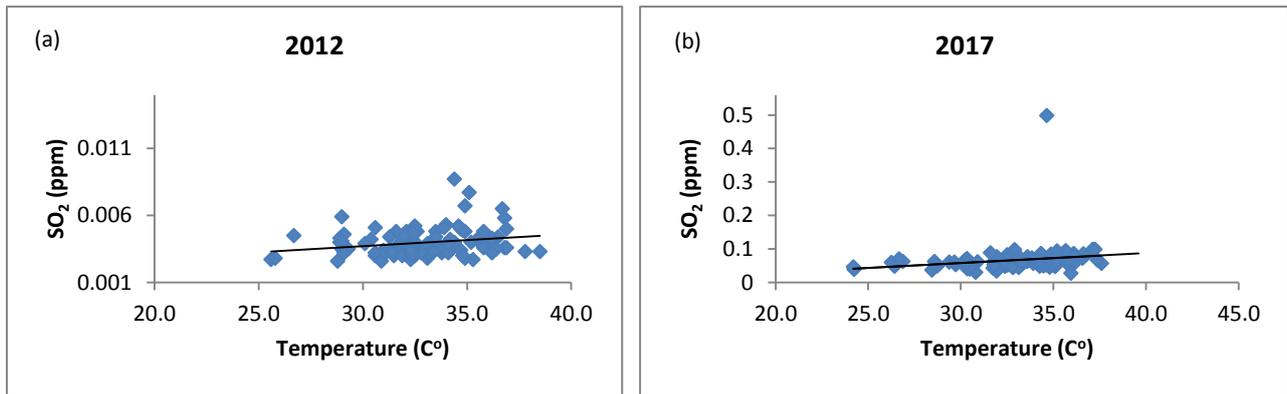


Figure 4. SO₂ concentrations versus temperature for DC in (a) 2012 and (b) 2017 for the summer seasons

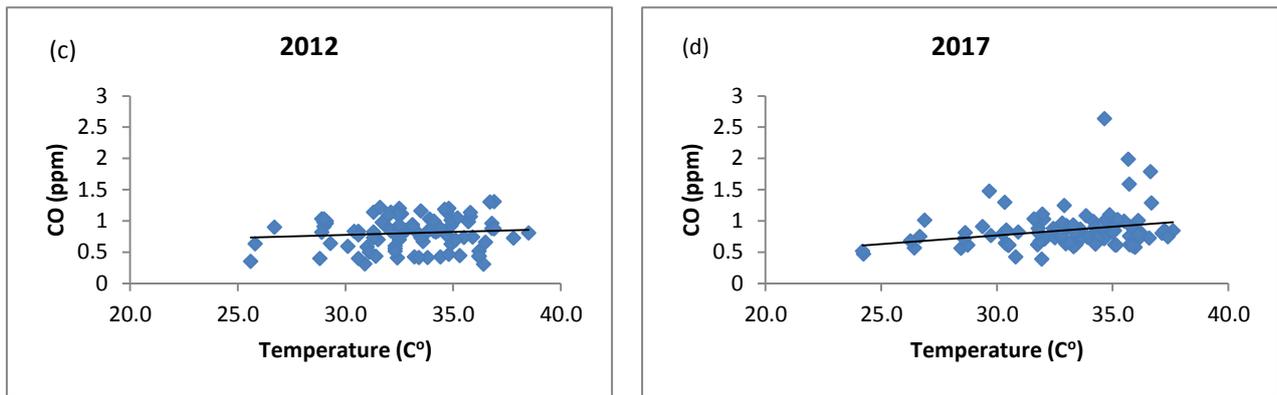


Figure 5. CO concentrations versus temperature for DC in (a) 2012 and (b) 2017 for the summer seasons

Table 2. The correlation coefficients (R) and the regression equations for MP with SO₂ and CO

Pollutants		R
	2012	
SO ₂	= 0.001015 + 0.000090*[T]	0.221
	= 0.1082 - 0.000104*[AP]	0.3
	= 0.005833 - 0.000061*[RH]	0.248
	= 0.003436 + 0.001099*[WS]	0.246
CO	= 0.4913 + 0.00951*[T]	0.1
	= 13.36 - 0.01253*[AP]	0.154
	= 0.6247 + 0.005982*[RH]	0.104
	= 0.7876 + 0.0336*[WS]	0.031
	2017	
SO ₂	= -0.03068 + 0.002962*[T]	0.181
	= 2.433 - 0.002358*[AP]	0.134
	= 0.04488 + 0.000797*[RH]	0.070
	= 0.03970 + 0.01888*[WS]	0.130
CO	= -0.0661 + 0.02792*[T]	0.256
	= 28.72 - 0.02777*[AP]	0.238
	= 0.8021 + 0.001863*[RH]	0.031
	= 0.7355 + 0.0820*[WS]	0.083

Particulate matter (PM) or dust samples (DS) :

1. Dust Characterization by RLM and SEM: Optical microscopy is a useful tool for dust characterization. Since dust can originate from different sources such as transport and emissions, from which it has a heterogeneous composition. The dust particles observed varied greatly with respect to size, morphologies, and chemical composition. Particles trapped in the 0.5 mm mesh were represented by various types of particulate matter, e.g., biological and non-biological materials. Some of these materials were large enough to be visible to the naked eye. Figure 6 (a and b) illustrates photomicrographs of dust

samples in DC at different magnifications. It displays typical particle agglomeration as seen or observed in the optical microscope. These reflected light photomicrographs show small insects, e.g., flies, small ants, or parts of insects including wings, legs and wasps, plus plant debris, ash from burning agricultural fields, wood fragments, seeds and leaves. However, dust particles showed different sizes and shapes, as shown in Figure 6 (a and b). Synthetic fibres and inorganic particles were also found. We believe that these artificial fibres could be come from the burning of agricultural fields, as well as from washed carpets which are usually dried over the roofs of buildings in DC.

**a****b**

Figure 6. Photomicrographs of dust samples in DC, using a light microscope (a-Mag.20), (b-Mag.30).

Determining the size of the dust particles can be somewhat difficult using optical microscopy but it is relatively easy with SEM. SEM images were taken without depositing a conductive layer on top the sample. The bright tiny spots observed on the SEM images could have been due to accumulated surface charging effects under the energetic electron beam as a result of the poor conductivity of the related layer. According to the SEM images shown in Figure 7, the sizes and shapes of the dust particles were different. The particles had rectangular, irregular, angular, sub-spherical to oval-like aggregate shapes. It is believed that the erosion of soil structures can change with changing wind velocity and can affect the size of the dust particles. Furthermore, the clay becomes dry and loses its moisture content at high air temperatures and an increase in breaking that causes changes to the van der Waals bonds that exist in clay mineral structures, which leads to the production of

dust particles (13). In the dust samples, the different shapes of the particles might originate from different sources such as traffic flow, geological characteristics, meteorological parameters and land use. It has been reported that WD and regional geology control the morphology and mineralogy of airborne dust (2). Other research has reported that spherical and irregular shapes are due to biological particles (36). In a close look at the SEM images at two magnifications (Figure 8 and Figure 9), it can observe that the particles have gone through a condensation or nucleation step, especially between the minimal size (of dimension 2.5 μm), which end up forming aggregate particles.

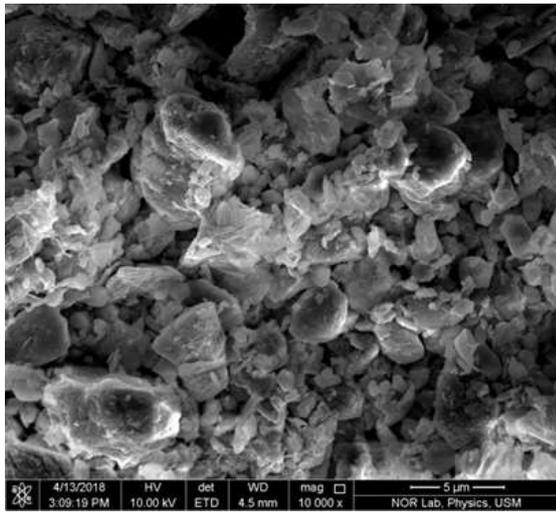


Figure 7. SEM image of the dust particles

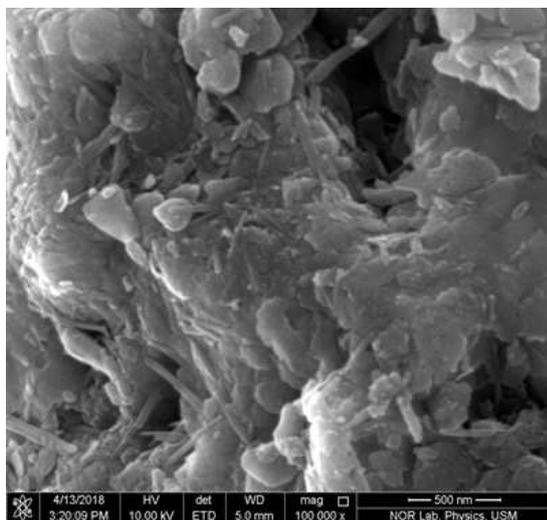
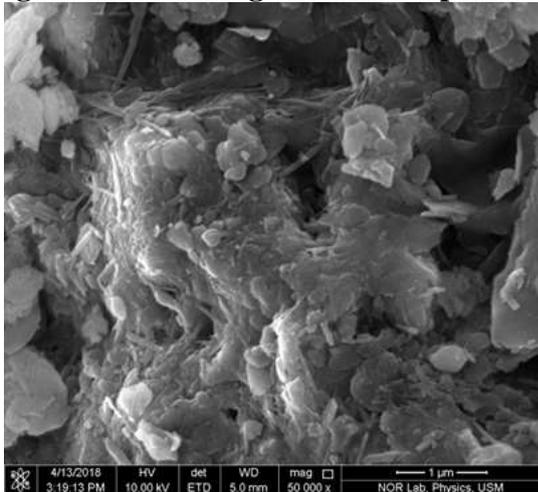


Figure 9. SEM image of the dust particles. (higher Mag. 100,000x)

2. Chemical analysis by EDX

Numerous microspheres and spheroids were observed. Many of these were analysed using a qualitative X-ray energy-dispersive spectroscopy (XEDS) or EDX analysis, where it was found that the sample was silicon-rich and Ca-rich, which appear to be shiny and

silvery in colour under the optical microscope. The qualitative EDX analysis of the dust is shown in Figure 10. The EDX spectra show the presence of Si, Ca, C, Mg, Al, K, and a significant amount of oxygen (O) as a peak value among other elements. The quantitative and composition analysis of the dust sample extracted using EDX tools is listed in Table 3. Silicon and calcium were found to be the most abundant elements in the dust particles with a significant oxygen presence. The predominant elements are O (45.67Wt%), Ca (25.76 Wt%) and Si (13.37 Wt%). The soil in DC constituted mostly of silicates and clay minerals which could be classified as a semi-desert in nature. The collected dust contained clay minerals and some sort of silicates, and showed a more complex composition. Most of the observed mineral particles have diameters in the range of 1 μm to 2.8 μm . EDX analysis revealed peaks related to Si and Al. These elements come from road dust, erosion of building products, etc., and mainly originated from crustal sources.

3. Chemical analysis by AAS

The heavy metal concentrations (Pb, Cu, Fe, Mn, Zn, Cd, Co and Ni) for the dust samples were measured using AAS at five different locations in DC in the summer of 2017. The results are shown in Figure 11. For samples taken at G₁ and G₄, both Zn and Cd were detected, whilst in other locations no trace of Zn and Cd was found. Also, Co and Ni were not detected in any of the locations due to the very low concentrations of these two elements going beyond the sensitivity of the AAS tool used. The Pb concentration varied from 14.2-45 ppm with an average of 28.14 ppm. The concentration of Pb in the dust of the study area comes from the motorized vehicles burning leaded fuel (containing tetraethyl lead used as an anti-knock agent) (26,38). Because the number of vehicles in DC have increased over the past few decades (e.g., the number of vehicles in DC in 2002 was about 20,000, which had increased to 130,277 vehicles in 2010) (22), this study shows that the increased road traffic has boosted the emission of airborne metals into DC's air through different pathways, e.g., wear products from tires, brake linings, or from combustion products of fossil fuels, and road construction materials, as well

as resuspension of road dust. Other studies (15, 22, 25) also reached similar conclusions. The concentration of Cu ranged between 1.1 to 27.1 ppm with a mean value of 13.12 ppm. We believe that Cu may have originated from car lubricants, or it can be released into the urban environment as a result of wear of the automobile oil pumps. Another possible source of Cu in dust samples is thought to be

corrosion of metallic parts of cars and engine wear (3). While the concentration of Fe varied between 9 and 21.9 ppm with a mean value of 14.86 ppm, and the concentration of manganese ranged from 2.1 to 37 ppm with a mean value of 12.8 ppm. The origins of Mn and Fe are mainly from natural sources with only traces of anthropogenic influence.

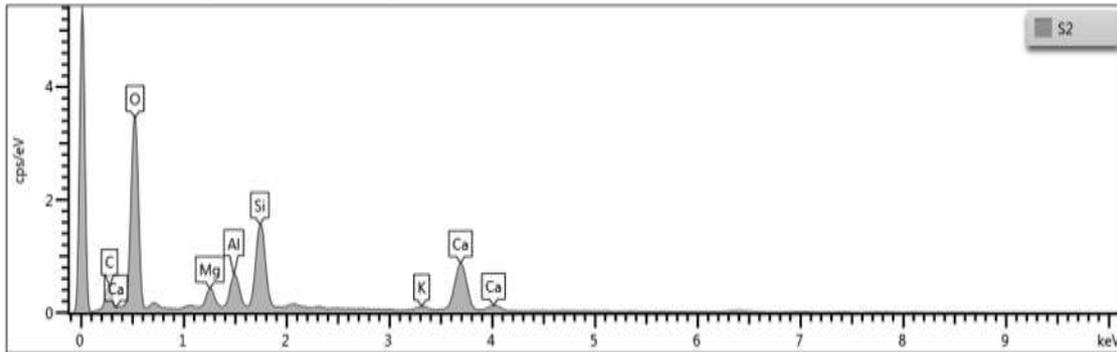


Figure 10. Typical EDX Analysis for the dust collected from DC

Table 3. Compositional analysis of EDX results

Element	C	O	Mg	Al	Si	K	Ca	Total
Wt%	6.69	45.67	2.24	4.56	13.37	1.71	25.76	100

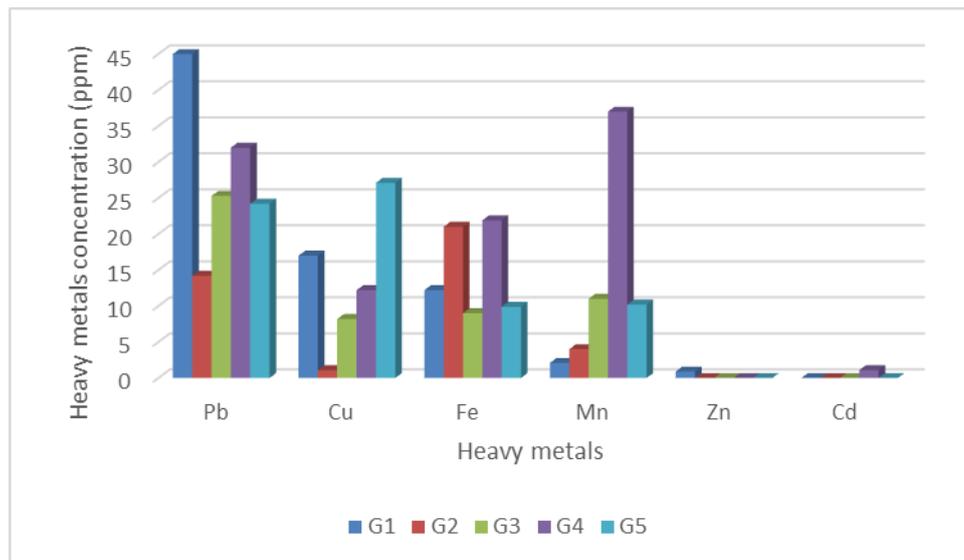


Figure 11. Concentrations of heavy metal in all locations, as found using AA

4. Mineralogical analysis of dust by XRD

X-ray diffraction analysis was used to obtain the mineralogical characteristics of the dust samples. Figure12 shows a typical XRD pattern of dust samples. The main minerals observed in the dust samples were calcite (Calcium Carbonate) (CaCO₃), quartz high (SiO₂), dolomite (CaMg(CO₃)₂), quartz low (SiO₂), wulfenite (PbMoO₄) and almandine Fe₃Al₂(SiO₄)₃. It was also noted that the most intense peaks in the XRD belonged to calcium

carbonate (CaCO₃), wulfenite (PbMoO₄) and quartz high (SiO₂). The mineralogical composition of dust could be due to land use and land cover patterns, geographical characteristics of dust, road length, and vehicular flow, as well as from building construction processes. Dusts rich in quartz, carbonates, and feldspar are usually continental and originate mainly from local sources (21, 41).

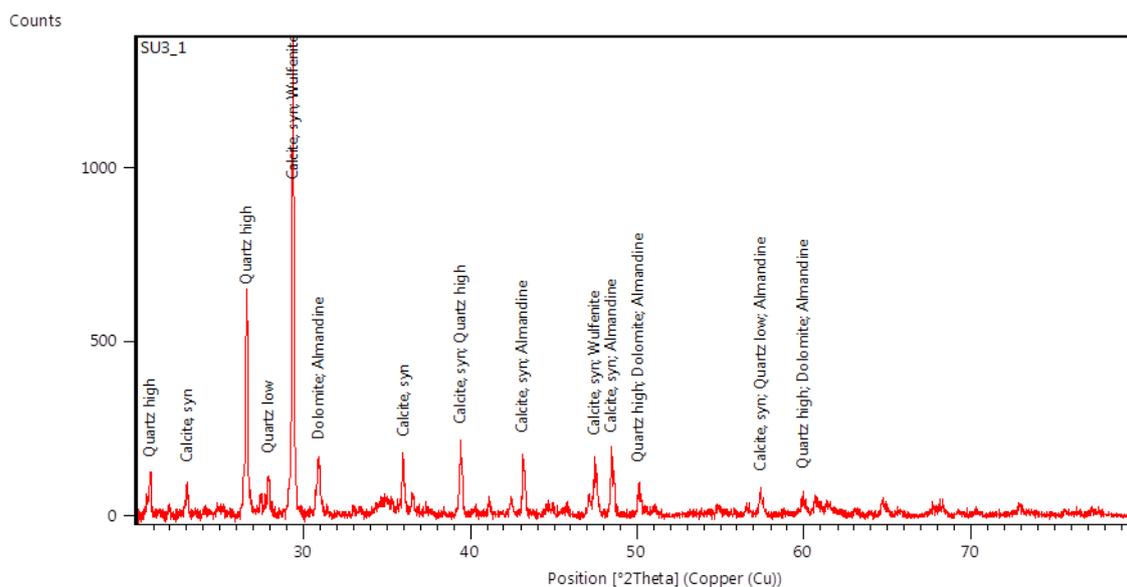


Figure 12. XRD patterns of the dust

SEM, EDX, XDR and AAS has been successfully used in the analysis of dust particles in the city of Duhok, Iraq. The effects of meteorological parameters (T, AP, RH and WS) on air pollutant concentrations of SO₂ and CO were evaluated during the summer seasons of 2012 and 2017. Linear regression was used to find the correlation coefficients and relationship between variables. The results indicated that there is a weak and moderate relationship between air PC and MP. Optical microscopy is a useful tool in dust characterization. Due to the various origins of dust such as transport and emissions, dust has shown to have a heterogeneous composition. Determining the size of the dust particles can be somewhat difficult using optical microscopy but it is relatively easy with the SEM, with the latter indicating that dust particles have different sizes and shapes, such as irregular, angular, sub-spherical to oval like aggregate shapes of various diameters. Compositional EDX analysis of the dust collected from DC indicated the presence of Si, Ca, C, Mg, Al, K, and a significant oxygen (O) peak. Silicon and calcium were found to be the most abundant elements of the collected dust particles. Also, compositional analysis of EDX indicated that the predominant elements were Ca (25.76 Wt%), Si (13.37 Wt%). The mineralogical composition of the dust sample was investigated via XRD, with the most intense peak found to be related to calcium carbonate (CaCO₃) and wulfenite (PbMoO₄).

ACKNOWLEDGMENTS

The authors would like to acknowledge the Directorate of Meteorology & Seismology and Directorate of Environment in Duhok City, Iraq for their support, supplying the data and providing some of the information used in this work.

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