Measurement of Fall Rate and Analysis of Atmospheric Falling Dust in Duhok Governorate of Iraq by Using Atomic Absorption Spectrometry and X-ray Diffraction

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Abstract. This study was conducted in Duhok Governorate (DG) to study the mineralogical and chemical properties of atmospheric falling dust (AFD) and to measure the fall rate of AFD. AFD samples were collected at different locations and times by a funnel on the nozzle of a plastic bucket (pail) of dimensions (1 m²) on the veranda of the building, ~3-4 m high the ground level. To compare between chemical properties of AFD and street dust that people are exposed to, the dust accumulated on car engine air-filters (CAFs) have been examined. Atomic absorption spectrometry (AAS) was used to study the chemical composition of the particles. X-ray diffraction (XRD) was used to investigate mineralogical characterization. The result shows that the traffic emissions and increasing population density as anthropogenic sources, in addition to natural dust particles in Duhok governorate have been the main role in the dust fall rate. The results show that the monthly dust fall rate was recorded in Duhok (3.35 gm/m².month). The higher average concentration value for heavy metal was (Cu=11.5 ppm). The study includes qualitative identification of clay minerals by X-ray diffraction data. Peak height was used as a rough indicator of the relative abundance of minerals. The major minerals observed in the AFD sample are Calcite (CaCO₃), Quartz low, Silicon Oxide (SiO₂), and Dolomite (CaMg(CO₃)₂).

Keywords: Fall rate, Duhok Governorate, Atomic absorption spectrometry, X-ray diffraction, Mineralogical Characterization

1. Introduction
Recently, attention has been increased for the study of the quality of air in the atmosphere [1,2]. Atmospheric falling dust (AFD) is considered a general and important component of atmospheric particles, and due to their gravitation, these particles fall to the ground. These particles have a diameter of less than 100 μm and more than 10 μm. One of the important significant indicators of environment quality is dust deposition [3,4]. From an Aerodynamic point of view, because the dust particles are easily deposited, therefore, the AFD that carried pollutants may cause pollution near the source [3,4].

AFD has a convoluted chemical and mineral, structure because it is obtaining from various sources and operations [5,6]. Falling dust particles render as transports carrying anthropogenic materials far away from their sources, and may supply reaction sites for many heterogeneous reactions including SO₂, NOₓ, O₃, etc.
Any changes in the characteristic of anthropogenic aerosols and dust might be caused by such reactions. Therefore, for the hazard estimation of dust for ecology, air quality, and human health, studies on origin, composition, and the content of AFD are important. In the study of climate change internationally, the characterization of falling dust is also important because the amount of dust-climate impact is governed by the physical and chemical characteristic of mineral particles, involving their form, size, type, chemical structure, morphology, and particle numbers or concentration [8]. These effects have created interest in AFD, and it has become a multidisciplinary object for research like geochemistry, atmospheric physics and chemistry, environmental science, and environmental engineering [3,9].

Due to wind erosion in semi-arid surfaces and arid regions, mineral dust aerosols produce that considered important components of the atmosphere that impact the atmospheric chemistry, Earth radiative budget, biogeochemical cycles, radiative forcing, cloud characteristics, and precipitation. According to dust aerosols’ origin, a lifetime in the atmosphere, and size distribution effects these processes [10-12]. Also, mineral dust has significant effects on the environment and ecosystem, through the deposition of organic materials and minerals on the earthly ecosystem [13, 14]. Dust deposition can influence the nutrient levels in the aquatic system and it adversely impacts human health [14, 15]. The composed of dust aerosol particles are a complex mixture of different minerals, calcite, mainly clays, quartz, iron oxides, and feldspars.

Heavy metals can contain dust particles such as dust from the industrial sector and can be distributed or redistributed into the atmosphere directly from sources such as road traffic, road dust resuspension, and industrial processes. [16-22]. Dust particulates from these sources may contain risky metals and can have both non-carcinogenic and carcinogenic impact. Heavy metals have long been well-known toxicity, as well as their threat to the environment and public health [23,24]. Street dust contaminated with heavy metals elements is the most appropriate route for human toxic element exposure. Through various pathways such as ingestion, inhalation, and dermal absorption, these contaminants enter the human body. Once they enter the human body, most toxic elements are adsorbed, accumulated, and biomagnified in the human body, resulting in a wide variety of diseases. [25,26]. Heavy metal contamination has been a serious human health problem, such as damaging the neurological system, kidney function, ossification process, and various other health issues [27]. 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 [28] (including DG) in the northern region of Iraq. The air pollution in DG may be related to the increase in the number of both people and vehicles, as can be observed from the congested roads and streets located within the DG road network.

The purpose of the present study is to measure the fall rate of dust in Duhok Governorate and study the chemical composition of the AFD and CAFs (i.e. concentrations of heavy metals). The study includes qualitative identification of clay minerals of AFD in Duhok.

2. Materials and Methods

2.1. Samples collection

Measurements were performed in the city of Duhok, northwest of Iraq [29]. Dust samples were collected by a funnel on the nozzle of a plastic bucket (pail) of dimensions (1 m²) at different times and locations were placed on the veranda of the building, ~3-4 m high the ground level. To compare between atmospheric falling dust (AFD) residential areas and street dust or street-level air that people are exposed to, the dust accumulated on car engine air-filters (CAFs) was examined. The sample consisted of the removal of CAFs directly from the plastic box connected to the throttle body with an intake duct. Dust or particle matter on the filter separated gently with a fine brush.

Dust samples were collected carefully in very clean containers and were placed in clean plastic bags and then they were transported to the laboratory. Afterward, the samples were dried at a temperature of 105°C.
overnight using a digital furnace to control the heating temperature and passed through 2mm sieve, then their weights were measured and recorded and stored in plastic bags before use.

2.2. Samples Analysis
Mineralogical analyses of AFD were performed using X-ray diffraction (XRD). XRD tests were conducted using automated diffractometer equipment (PAN analytical XPert) with a Bragg–Brentano θ:2θ configuration, using a Cu target. Cu Kα (Cu Kα = 1.5406 Å) radiation source. the scanning rate was 2°/min from 20-80° 2θ, with accelerating voltage of 45 kV and the electric current of 40 mA.

Chemical analysis of AFD and CAFs were performed using an Atomic Absorption Spectrometer (AAS) (type AA240FS, Varian). AAS was used to determine the concentrations of Fe, Mn, Cu, Pb, Zn, Cd, Co, and Ni. This was achieved after digesting the sample [30, 31].

3. Results and Discussion
3.1. Rate of dust
Dust fall rate (FR) or flux of dust is the:

\[ FR = \frac{M}{A \cdot T} \]  

Where M is the dust's deposited mass, A is the area, and T time [32]. The fluxes of dust fall varied from point to point and from time to time depending on the nature of the collect sample's point [33]. The dust fall rate was recorded in Duhok for one month in summer season is about (3.35 gm/m².month), and fall rate of three month or for one season: summer (Su) is about (19.02 gm/m².season), autumn (Au) is about (20.22 gm/m².season), winter (Wi) is about (12.32 gm/m².season) and (Sp) spring is about (9.72 gm/m².season). The dust fall rate was recorded in Duhok for one year is about (61.28 gm/m².year), this study site has a lower range of FR as compared to the other regions in Kurdistan of Iraq except Koya as shown in Table 1 and Figure 1. The high concentration of dust fall rate in other regions, which might be due to deposited particulates are emitted from moving vehicles, vehicular fuel combustion, and rapidly developing area with a high population [34].

| Sample site | Fall rate         | Reference       |
|-------------|-------------------|-----------------|
| Duhok       | (61.28 gm/m².year) | This paper      |
| Koya        | (59.24 gm/m².year) | [34]           |
| Pirmam      | (61.34 gm/m².year) |                 |
| Makhmur     | (65.02 gm/m².year) |                 |
| Erbil       | (97.6  gm/m².year) |                 |
3.2. Mineralogical Analysis of AFD

X-ray diffraction analysis was used to obtain dust mineralogical characteristics. Typical XRD pattern of dust samples for four seasons as shown in Figure 2 (a, b, c and d). The major minerals with its chemical formula observed in the AFD samples were shown in Table 2. The major minerals observed are Calcite (CaCO₃), Silicon Oxide- Quartz (SiO₂), and dolomite (CaMg(CO₃)₂). It could be noted from Figure 2 (a, b, c and d) that the highest intense peak belongs to calcite and quartz for Su₄ (a), Quartz, calcite, and zeolite for Au₄ (b), Magnesium calcite and dolomite for Wi₄ (c) and Graphite 2H, quartz low, calcite and Tisinalite for Sp₄ (d). Magnesium calcite was recorded in winter sample dust which was equal to (52.6 %). While Silicon Dioxide-Quartz and Dolomite were recorded in the Wi₄ dust sample which was equal to (4.9 %) and (42.5 %), respectively.
Figure 2. X-ray diffractogram of AFD samples at different times.

Table 2. Existing of the mineralogical composition of AFD samples of four times (existing (+), missing (-)).

| Minerals               | Chemical formula | Su4 | Au4 | Wi4 | Sp4 |
|------------------------|------------------|-----|-----|-----|-----|
| Calcite                | CaCO₃            | +   | +   | -   | +   |
| Silicon Oxide-Quartz   | SiO₂             | +   | +   | -   | -   |
| Dolomite               | CaMg(CO₃)₂       | +   | +   | +   | -   |
| Tellurium              | Te               | +   | -   | +   | -   |
| Protoenstatite         | MgSiO₃           | +   | -   | +   | -   |
| Zeolite                | SiO₂             | -   | +   | +   | -   |
| Goethite               | HFeO₂            | -   | +   | +   | -   |
| Boehmite               | Al(OH)₂          | -   | +   | +   | -   |
| Magnesium calcite      | (Ca₀.₉₇,Mg₀.₀₃)CO₃| -   | -   | +   | -   |
| Silicon Dioxide-Quartz | SiO₂             | -   | -   | +   | -   |
| Indium                 | In₃.₁₉           | -   | -   | +   | -   |
| Selenide               | Se₂.₁₉           | -   | -   | +   | -   |
| Telluride              | Te₂.₃₁           | -   | -   | +   | -   |
| (3.19/2.19/2.31)       |                  |     |     |     |     |
| Graphite 2H            | C                | -   | -   | -   | +   |
| quartz low             | SiO₂             | -   | -   | -   | +   |
| Blossite               | Cu₂V₂O₇          | -   | -   | -   | +   |
| Tisinalite             | Na₃H₃(Mn,Ca,Fe)TiSi₆(O₂,OH)₁₈·2H₂O/| - | - | - | + |
|                        | H₃.₄ Ca₀.₁₂₆₇ F₀.₁₃ Mn₀.₄₂ Na₂.₀₈ Nd₀.₁₃₃₃ O₁₈ | -   | -   | -   | +   |
|                        | Si₆ Ti₀.₄₆₆₇ Zr₀.₁₄ | -   | -   | -   | +   |
Typical XRD pattern of dust samples for four sites in one season time shown in Figure 2 (d) Figure 3 (a, b and c). The major minerals observed with its chemical formula in the AFD samples were shown in Table 3. The major minerals observed are dolomite (CaMg(CO3)2), quartz (SiO2), and Calcite (CaCO3). It could be observed from Figures that the highest intense peak belong to Trinepheline for Sp1 (a), quartz low and Calcite for Sp2 (b), quartz low, Arsenolite and Calcite for Sp3 (c) and Graphite 2H, quartz low, Calcite and Tisinalite for Sp4 (d).

The land cover pattern and land use, road length, vehicular flow, and geographical characteristics of soil as well as from building construction processes may cause the mineralogical composition of the dust. Dust is originating mainly from local sources and it is mainly full of quartz, feldspar, and carbonates [35, 36]. Some studies elucidate that the mineralogical composition of dust particles is influenced by the geology of the particulate’s origin [37, 38]. If we consider soil and dust having a similar origin, it ought to have a similar mineralogical structure however may that the chemical characteristics hanging soil fundamentally change in the atmosphere as the dust particles cooperated with air contamination [39]. The significant conversion in atmospheric dust is due to the effects of particulate pollutants as well as transported gaseous and local. The significant data about the district, conceivable human health effects, and radiative forcing implications obtain from the mineralogical structure of soil dust [40].
Figure 3. X-ray diffractogram of AFD samples in different sites.
Table 3. Existing of mineralogical composition of AFD samples of four sites (existing (+), missing (-)).

| Minerals             | Chemical formula | Sp1 | Sp2 | Sp3 | Sp4 |
|----------------------|------------------|-----|-----|-----|-----|
| quartz low           | SiO₂             | +   | +   | +   | +   |
| Aragonite            | CaCO₃            | +   | -   | -   | -   |
| AlPO-16              | C₆H₂₅Al₂NO₂₄P₅  | +   | -   | -   | -   |
| Sodium Chloride      | NaCl             | +   | -   | -   | -   |
| Zeolite              | SiO₂             | +   | -   | -   | -   |
| Garnet               | A₄₄.4Ca₀.78Cr₀.2O₁₂Si₀.₄Y₂.₂₂ | + | - | - | - |
| Trinepheline         | Na₁₇₇₅Al₁₇₅S₁₈₅O₃₂ NaAlSiO₄ | + | - | - | - |
| Calcite              | CaCO₃            | -   | +   | +   | +   |
| Dolomite             | CaMg(CO₃)₂       | -   | +   | +   | -   |
| Pyrope, ferrian      | Al₁.₇Fe₃.₃O₁₂Si₃/ | - | + | - | - |
|                      | Al₂Mg₃O₁₂Si₃/    | -   | +   | -   | -   |
|                      | Mg₃Al₃Si₂O₁₂      | -   | +   | -   | -   |
| Warwickite (Fe-,Cr-rich) | B₃₉₆Cr₀.₁₆Fe₂.₆Mg₄.₆₄O₁₆Si₇.₀₄Ti₀.₆ - - + - |
| Arsenolite           | As₂O₃            | -   | -   | +   | -   |
| Graphite 2H          | C                | -   | -   | -   | +   |
| Blossite             | Cu₂V₂O₇         | -   | -   | -   | +   |
| Tisinalite           | Na₃H₅(MnCaFe)TiSi₆(O₅OH)₁₈·2H₂O | - | - | - | + |
|                      | H₄₂Ca₀.₁₃₂₇Fe₀.₁₂Mn₀.₄₂Na₂.₀₈ | - | - | - | + |
|                      | Nb₀.₁₃₃₃O₁₈Si₆Ti₀.₄₆₀₇Zr₀.₁₄ | - | - | - | + |

3.3. Chemical Analysis of AFD and CAFs

The concentrations of eight heavy metals in atmospheric falling dust samples and CAFs dust samples (Fe, Mn, Cu, Pb, Zn, Cd, Co and Ni) obtained by using AAS are given in Figure 4. The order of concentrations of heavy metals in AFD was Fe>Pb, Mn>Zn>Cu and CAFs dust was Cu>Fe>C>Co>Pb>Mn>Zn>Cd, Ni. Comparison of the average heavy metals concentrations in AFD and CAFs dust is shown in Figure 4. The average concentration of Fe, Mn, Cu, Pb, Zn, Cd, Co and Ni in AFD are 5.2 ppm, 1.8 ppm, 0.6 ppm, 1.8 ppm, 1.5 ppm, 0 ppm, 0.2 ppm, and 0 ppm respectively and in CAFs are 9.4 ppm, 2.7 ppm, 11.5 ppm, 8.2 ppm, 2.6 ppm, 0.2 ppm, 8.9 ppm, and 0.2 ppm respectively. The results show that the concentration of heavy metal in CAFs dust is higher than in AFD residential areas because CAFs dust is contacted with vehicles.

The major source of the Pb pollution in the dust of the study area may be concerning to the motor vehicles burning leaded gasoline (that contains tetraethyl lead as an anti-knock agent) [41]. through the vulcanizing process, Zn added to tires [42]. Corrosion of galvanized automobile parts and wear and tear of vulcanized
vehicle tires may be the origin of Zn in dust [43]. Cd is released as a combustion product in the accumulators of motor vehicles or carburetors [44]. The wear of metallic parts of automobiles can release Cu to the urban environment [43,45]. Cd and Pb heavy metals are highly toxic and can stay in the environment for longer periods [46].

Heavy metals such as Fe, Cd, Pb, Cu, and Zn in the atmosphere usually occur as a result of oil lubricants, vehicle exhaust emissions, automobile parts, corrosion of building materials along industrial discharge [47]. Consequently, it can be deduced that these metals most likely originate from the same sources, namely vehicular emissions and industrial activity. The urban area is consisting of varying concentrations of trace elements from anthropogenic and natural sources [48]. The deposited dust on roads doesn’t remain for a long time, quickly and easily suspended back into the atmosphere, where they may contain an important amount of trace elements [49]. Alahmr et al. reported that high automobile exhaust emissions in urban areas are the main source to generate particulate pollution and the result of road dust and emissions from moving vehicles [50]. Kleeman and Cass argued that traffic is one of the important sources of atmospheric particulate pollution in urban areas [51]. Moreover, Amato et al. indicated that particulate matter of road dust on the pavement could be resuspended by traffic in the urban area and become important sources of atmospheric particulate [52].

![Figure 4. Concentrations of heavy metals (ppm) in AFD and CAFs dust.](image)

4. Conclusion
The study measured the fall rate of atmospheric dust and used X-ray diffraction (XRD) and atomic absorption spectrometry (AAS) to analyze atmospheric dust in Duhok Governorate of Iraq. From the results obtained we conclude that the traffic emissions and increasing the population density as anthropogenic sources, in addition to natural dust particles from dust fall and dust storm in Duhok governorate have been the main role for dust fall rate and dust elements. The results show that the yearly dust fall rate was recorded
in Duhok (61.28 gm/m².year). the result shows that the highest intense peak belongs to Calcite and quartz, Zeolite, Magnesium calcite, dolomite, Graphite 2H, quartz low, Tisinalite, Trinepheline, and Arsenolite. The order of concentrations of heavy metals in AFD was Fe>Pb, Mn>Zn>Cu>Co and CAFs dust was Cu>Fe>Co>Pb>Mn>Zn>Cd, Ni. The results show that the concentration of heavy metal in CAFs dust is higher than in AFD residential areas because CAFs dust is contacted with vehicles.

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