Deposition of Major and Trace Elements From Atmosphere Over Baghdad During the Year of 2010.

K.T.AL-Rasoul[1],F.H.Ali[1], S.I.Jubair[1], Q.M.Ali[2], A.A.Najim[2].M.A.Hussain[2], F.A.Ahmed[2]
[1]Department of Physics, College of Science, University of Baghdad, [2]Ministry of Science and Technology.

Abstract

Dust Samples depositions over Baghdad, from January to December 2010 were collected. The minerals and the concentration of both light elements (P, S, K, Ti, Mg, Ca, Si, Na, Al, and Fe) and heavy traces elements (Zn, Mn, Cu, Pb, Cr, Ni, As, Sr, Rb, and Co) were measured by using x-ray diffraction and fluorescence respectively. The minerals detected by x-ray diffraction were quartz, calcite, clay, gypsum, feldspar, chloride, and plagioclase. The average range for heavy elements are highly compared with the neighbor countries and similar or less than those reported for other urban worldwide, except for Ni,As,Cr,and Sr which record the highest comparing with other countries. The pH of dust was shifted to alkalinity for all samples with mean value of 8.5.

Keyword: Minerals ,Light and Heavy Element , Dust , Bagdad

تساقط العناصر الرئيسية والنزرة من الجو على مدينة بغداد عام ٢٠١٠

خالد طة الرسول[١]، فلاح حسن علي[١]، شوكت اسماعيل جبير[١]، قيس محمد علي[٢]، عبد الحسين نجم حسين[٢]، ميساء علي حسين[٢] و فردوس عباس احمد[٢]

[١]قسم الفيزياء، كلية العلوم، جامعة بغداد، وزارة العلوم والتكنولوجيا

الخلاصة:

تم جمع نماذج الغبار المتساقط على مدينة بغداد للفترة من كانون ثاني ولغاية كانون اول ٢٠١٠. تم تحديد المعادن في الغبار المتساقط اضافة الى العناصر الخفيفة وهي (P, S, K, Ti, Mg, Ca, Si, Na, Al, and Fe)، والعناصر الثقيلة النزرة وهي (Zn, Mn, Cu, Pb, Cr, Ni, As, Sr, Rb, and Co) اظهرت النتائج تواجد معادن الكوارتز والكالسايت و الجبسوم والفلدسبار والمعادن الطينية. تم مقارنة العناصر الثقيلة مع الدراسات العالمية وظهر بانها بنفس التراكيز او اقل الا النيكل والكروم والسترونتيوم والزرنيخ فقد كانت اعلى نسبيا كما كان مقدار الحامضية للغبار هو 8.5

Introduction

regions. The Arabian Peninsula is one of the five major regions where dust originates [1].Iraq is surrounded by desert areas and is therefore exposed to dust storms most of the year. The rates of the falling dust over Iraq region was increasing during the last two decade Figure1-. This might be due to the impact of Gulf war activities, which cause soil disturbance [2].In recent years attention has been given to dust deposition as a possible source for different heavy elements which cause the environmental pollution and that become a major environmental issue in many countries [3].Organic and inorganic pollutants enter the urban atmosphere as gases, particles, or aerosols, by evaporation of liquids, co-evaporation of dissolved solvents from.

Email: kmahdi39@yahoo.com

water and by wind erosion of soil [4]. Moreover certain elements in dust can serve as a tracer for air pollution; e.g., Mn, Co, Cu, Pb , As and Cd are initiators or promoters of carcinogenic activities in animals [5,6,7]. For that, many of these heavy metals are considered toxic to living organisms and even trace metals considered essential for life can be toxic when present at excessive levels that impair important biochemical processes and pose a threat to human health, plant growth, animal life and weather [8,9].One of the most important aspects of environmental pollution for humans is the intake of toxic elements through nutrition or by inhalation and then their cumulative nature in the different body organ leading to unwanted side effects. Therefore, studies the concentration of heavy metals in dust are important for the determination of the origin, distribution, environmental damage and health effects. The analysis of dust samples were performed by the x-ray diffraction (XRD) and x-ray fluorescence (XRF) techniques. The XRD was applied to detect the chemical composition of dust or in other world the minerals. Sami quantitative of calcite, quartz and gypsum were determined by the XRD method.XRF analysis method was selected to determine the elemental composition of dust because this method has many advantages [10]. It is fast, accurate, nondestructive and has a limit of detection in the range of few part per million (ppm) of most toxic heavy elements. For these reasons, the XRF analysis method is used in many fields such as metallurgy, industry, geology, mineralogy, food industry and environmental management [11,12,13]. The use of this technique in the analysis of elements has not been reported before for local dust analysis. Such studies would provide information that can be helpful in determining the pollution level at different locations in the country. The aim of this work is to evaluate the atmospheric inputs of nutrient (P, S, Mg, K, Ca, Na, Al, and Fe) elements and the traces of heavy elements (Zn, Mn, Cu, Pb, Cr, Ni, AS, Co,Rb, and Sr), on Baghdad for the year 2010. This data should provide new data for an estimation of the problems of inorganic pollution throughout Baghdad area.

Methodology

Falling dust samples were collected from four different locations almost covering Baghdad city area. Samples were collected monthly, or bimonthly when the rate of the falling dust was low, during the period extending from January to December 2010.The dust samples were collected from roofs of buildings about 3-8 m above ground level in the selected sites. Roofs were first thoroughly cleaned just before the onset of the specific period. The dust was then collected by gentle sweeping of the floor by means of a soft plastic brush. Dust samples were mixed well and made to pass through a 1 mm sieve and stored in a plastic jars before analysis. The pH and electrical conductivity (EC) for each sample was measured in 1:5 dust: distilled water (w/v) ratio by kept the mixture for 24h to allow the maximum salt to dissolved, after that the pH and EC were measured. For mineralogical analysis, the samples without any pretreatment were examined by x-ray diffraction using a Philips pw.1140/90 x-ray apparatus. For quantitative analysis x-ray fluorescence (XRF), Shimadzu 1800, was used, and the samples were prepared as glass disks in case of light elements analysis. The glass disks were prepared by using mixtures of lithium tetraborate and lithium metaborate, (Spectromelt A 12, Merck). For the dilution 4.2gm of this flux and 0.8gm of the sample are weighed in platinum-10% gold crucibles and fused for 15 min at 1100°C. The melt is poured into pre-heated, polished 32 mm-diameter moulds. While for heavy elements, the dust was pressed into 32mm diameter pellet to be ready for quantitative analysis.

Results and discussion

Mineralogical analysis

Mineralogical analysis of the dust samples indicated that the great bulk of the dust consisted of quartz, clay, plagioclase, calcite minerals with lower amounts of some other minerals, e.g. mica, gypsum, feldspar, dolomite, chlorite and other traces (Figures.1 and 2).The high values of quartz, calcite and clay are believed to have originated from soil rich in such minerals which are abundant in the area. The majority of mineral was variable depending on the direction of the wind.

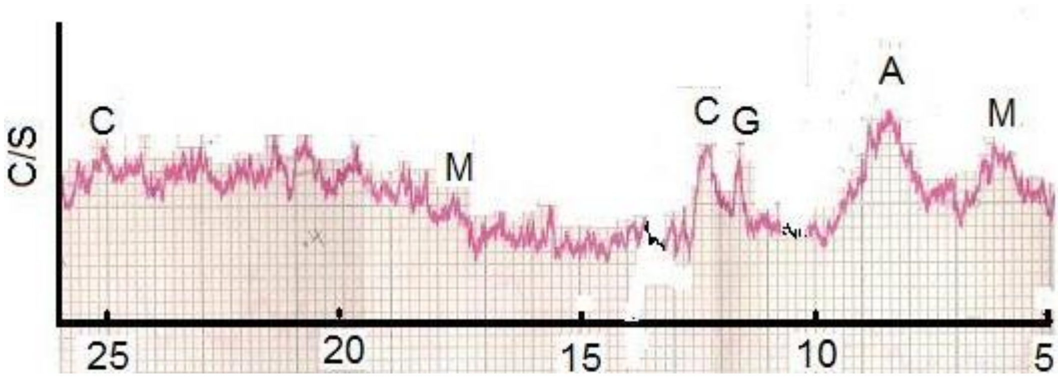

Figure 1- Portion of x-ray diffraction pattern of dust separated by water M-montmorenite, A-allite,G-gypsum,C-chlorite.

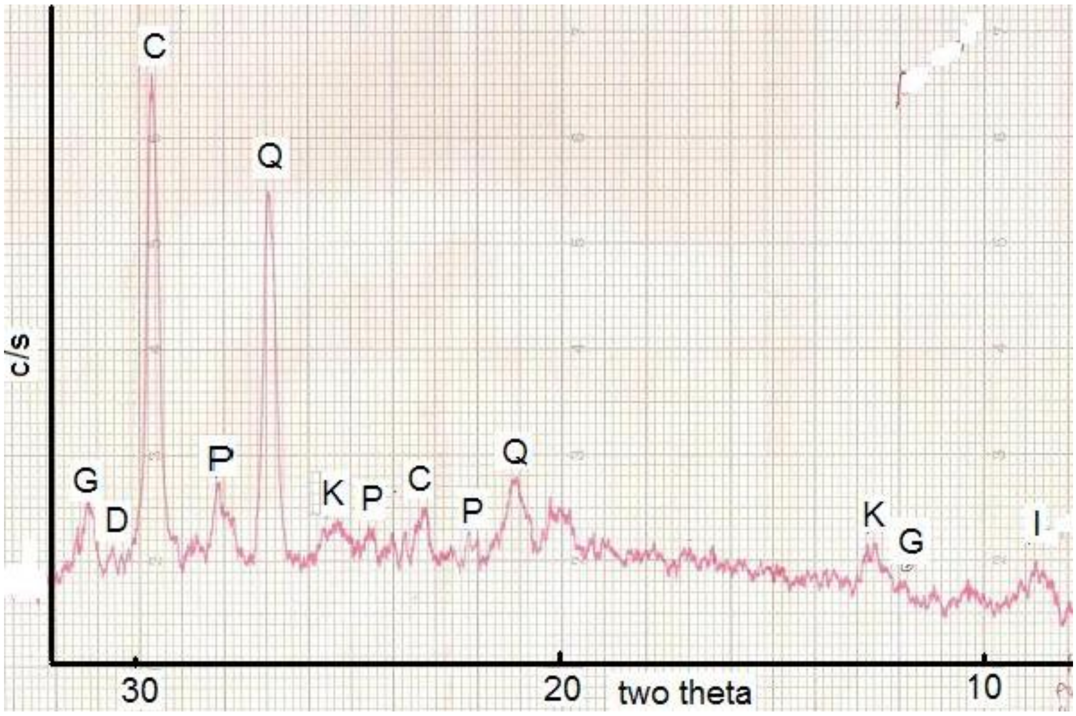

Figure 2- X-ray diffraction pattern of dust, I illite,G-gypsum,K-kaoline,Q- Quartz,P-plagioclase, c-calcite,and D-dolomite.Sample from University of Baghdad (15-5-2010).

pH values

Analysis of dust sediments revealed that most samples were alkaline in reaction, (Table 1), with pH values ranging from 7·5 to 9·5, average 8·5; these high values could be due to the high levels of gypsum, limestone and dolomite present in the dust samples. Soil pH determines the nutrient availability to plants. Some nutrients become “tied up”in the soil at certain pH levels. For example, highly acid soils can lead to deficient of phosphorus, calcium, magnesium and molybdenum. Alkaline soils may lead to deficiencies in iron, manganese, and boron, copper and zinc because PH can result in precipitation of certain nutrients. For plant roots to be able to absorb nutrients the nutrients must be dissolved in solution, for example iron is one essential plant nutrient whose solubility is affected by pH. The pH values above 7, less than 50% of iron is available to plants. At PH 8.0, no iron is left in solution due to iron hydroxide precipitation. Generally in the PH range 4.0 to 7.5 all nutrients are available to plants. Electrical conductivity (EC, also known as conductivity or soluble salt) is term used to measure the total concentration of salts in the water. The higher the EC, are the more salts that dissolved in water. The soluble salts in the dust were high (electrical conductivity of the saturated extract was 3.3–6·5 dSm^{-1}). The presence of these salts in high amounts is attributable to the saline soils from which the dust originated, e.g. the closed basins in southern of the country where the soils are severely saline and have a salt crust on the surface, and to the accumulation of salts on soil surface in arid regions due to high soil evaporation [12,13]. Table 2 also shows an estimation of minerals present in the dust by using semi quantitative x-ray diffraction analysis.

Table 1- Some properties of dust sample for year 2010.

	pH	EC	CaCO3*	Quartz*	Gypsum*	Clay*
Maximum	9.8	6.5	55	45	10	40
Minimum	7.3	3.3	23	15	02	12
Average	8.6	4.9	38	29	06	26

* Sami quantitative by x-ray diffraction.

Major elements contain

The total content of major elements was presented in Table 2. The data showed that the concentration of Silicate, Alumina and Calcite are highly probably due to the high content of quartz, clay and calcite, which detected by x-ray diffraction. The rest major elements are Mg,Fe,and Ti . Those might come from clay and dolomite mineral or from traces mineral which are undetectable in this work or as elements diffused into the detect minerals. All those elements could be harmful to the human depending on concentration and in some time on particles size. The total nutrients elements are also shown in Table 2. Their mean values were 0·2, 1·6, 0·12% for P, S, and K, respectively. The results show rather low concentrations of P,S and K whereas the Fe was relatively high with average of 3.7%. These findings were in agreement with some reported results obtained for nutrient elements [14]. Loss on ignition (LOI) measures change in mass when the sample is heated to $1050^{0}C$ due to decomposition of carbonates, clay, and gypsum mineral with loss of carbon dioxide, molecular water, and other volatiles.LOI values in the range of 13% to 45%.

Table 2- The maximum and minimum(%) of major elements in the fallout dust sample of Baghdad city.

Element	P_2O_5	K_2O	SO_3	Fe_2O_3	Na_2O	CaO	MgO	TiO_2	SiO_2	Al_2O_3	LOI*
Maximum	0.3	1.4	2.9	5.2	1.1	40	4.6	0.63	38	12	45
Minimum	0.1	1.0	0.3	2.3	0.3	08	1.4	0.22	20	06	13
Average	0.2	1.2	1.6	3.7	0.6	24	3.0	0.43	29	09	29

*loss on ignition

Heavy metals concentration

Dust is now considered a significant source of trace metals in the urban environment; therefore there have been a considerable number of studies assessing the concentration of heavy metals in dust fallout. However, the majority of these studies have been carried out in developed countries and very few have been made in developing countries such as Iraq. Thus, an attempt has been made to assess the trace elements in the dust samples. Table 3 shows the total concentrations of Zn, Mn, Cu, Pb, Ni, Co, Cr,As, Rb, and Sr .The heavy metals concentration in Baghdad dust compared with data reported for other cities in the world .Comparatively high levels of Pb, Zn, Mn,Cr and Ni. It is believed that the bulk of the trace elements in the dust is coming from weathered materials. However, the higher values of the trace elements reported here may suggest that other sources have had a contribution to the elevated concentrations of these metals. In this respect motor vehicles may form a major source of these metals in the dust samples. The elevated levels of Pb in the dust samples are not surprising since the traffic density is high and leaded gasoline is the only fuel available for automobiles firstly in Baghdad .Secondary lead smelting together with lead acid battery manufacturing facilities are known from these and other metropolitan. In addition, lead is also used in manufacture of pesticides, paints, and dyes. Also, another source which perhaps contributed to the elevated concentrations of these heavy metals was smoke coming from the burning of gasoline. The maximum acceptable limit of lead normal soil is 100ppm. Zinc concentration is slightly above the maximum acceptable limit which normally. Since no smelting industry existed within the study area which is a major industrial source of dust pollution.

But in local, the concentration of zinc could be came from tiers which used as a vulcanization agent in tiers, and that is the most likely source resulting from attrition of motor vehicle tire rubber exacerbated by poor road surfaces. Specially, in a semi arid environment the abrasion of car tires increases. Lubricating oils also contain zinc as additives such as zinc dithiophosphates. Copper concentration in local dust samples was found between 34-35pm which was similar to other levels reported and its value acceptable. The main source of copper may arise from the corrosion of metallic vehicles parts, wear and tear of the car engine, bearing metal. Nickel metal dust and soluble salts nickel are extremely carcinogens to the environmental after inhalations, but also that the carcinogenic risk is limited to conditions of exposure .In this work the concentration of nickel in dust fallen over Baghdad is to high ranging from 85-110ppm and this values exceeded the maximum acceptable limit of 50ppm.So these result of nickel might become a serious to our health and environment in the long run. The main source of nickel in dust we expected came from combustion of diesel fuel. Strontium also found in high level concentration. The non – radioactive strontium and its radioactive isotopes(Sr-90) have the same physical properties. Strontium is chemically similar to calcium, and tends to deposit in bone and blood-forming tissue (bone marrow). Thus, strontium-90 is referred to as a "bone seeker." Internal exposure to Sr-90 is linked to bone cancer, cancer of the soft tissue near the bone, and leukemia. However, Sr90 are very low in environmental since as we know that the source of such radioactive come from the fission of uranium and plutonium in nuclear (half live is 29 year).As and Cr are also record highly concentration, and those are highly dangerous. The source could be came from certain alloys as it know that Cr is alloying element. The source of As, could be came from a pesticide material. In general the metal compounds in dust can enter the body through breathing air and then deposited in the respiratory tract and absorbed into the blood depending on the size of the particles. If the particles are large (10um) they stay in the nose. If the particles are smaller (2um), they can enter deep into the lung and if the salt is soluble in water then it can go to the bloodstream .Most of the elements compounds gets into the blood can go to all organs, but it mainly goes to the kidneys and then leaves in the urine . Figure 3- show the data of particles size collected from different side in Baghdad. The average size distribution occur at about (12-24) um, but there are also a particles detected within 1um or less, as shown in Figure 3-.These result need more investigation to know weather the heavy elements present in all the particles size or missing at certain volume, and at what kind of chemical they present.

Table 3- Total content (ppm) of trace elements in the fallout dust samples of Baghdad year 2010.

Element	**Zn**	**Mn**	**Cu**	**Pb**	**Ni**	**Co**	**Cr**	**As**	**Rb**	**Sr**	**Ref.**
Maximum	332	403	89	600	108	22	202	77	25	115	This work
Minimum	77	38	34	57	85	7	30	10	2	22	This work
Madrid	467	362	188	192	44	3	15	---	---	---	(10)
Oslo	412	833	125	180	41	19		15			(10)
Calcuta	159	619	44	536	42	16	54	16			(8)
Ottawa	112	431	66	39	15	8	43	17			(10)
Amman	370	12	17	4	5		5	18			(8)
Riyadh	141	318	37	66	26	20					(4)
Kuwait	22		133	19							(4)
Cairo	146			64	11	16	3	1			(3)
Ankra	443	394	39	20	79	15	21	23			(9)
Iran	86	302	71	26	16						(14)

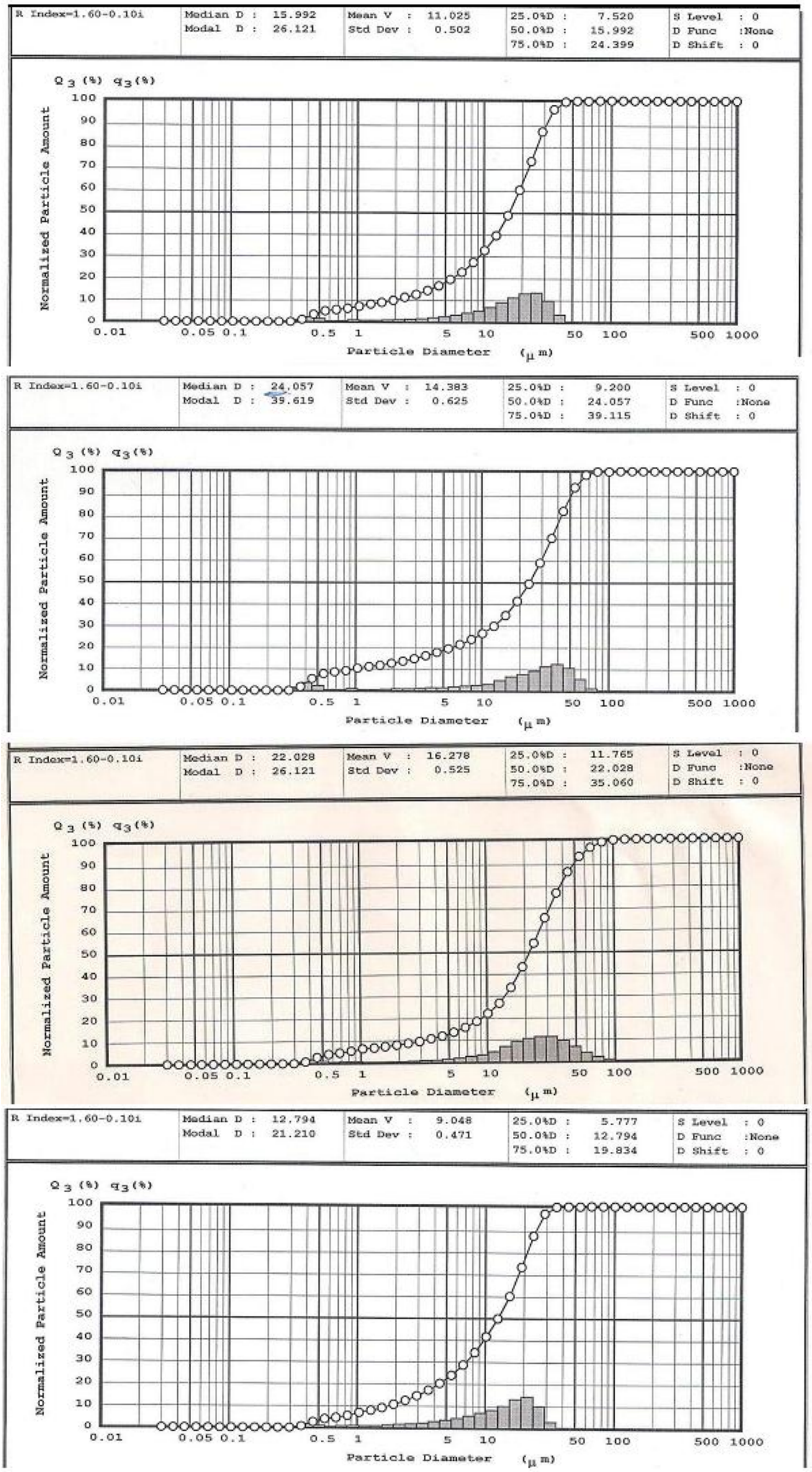

Figure 3- particles size distribution for the dust (from different locatiom).

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