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Measuring some polluting gases emitted from vehicle exhaust in Kirkuk Governorate and their environmental effects

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***Abstract*---**The current work in all semesters under study (fall, winter, spring) studies the estimation of gases emitted from vehicle exhausts (formed as a secondary pollutant SO_2, NO_2, O_3). The study aims at determining its environmental and negative effects and identifying the extent of the effect of the gases that cause acid rain on the pH values of rain water in a number of specific study sites within the city of Kirkuk: the entrance to Kirkuk check point, June 1, the beginning of the Shuhada Bridge, the Castle, and Doctors Street, the old discipline and the New Tisin. Because the movement of cars is dense and the different sources of emitted gases compared to the fifth site (Yayci). The results showed that there is a temporal and spatial variation in the concentrations of gases, and the values of the concentrations of gases emitted from vehicle exhausts did not exceed the values of the Iraqi national environmental determinants of ambient air quality and the determinants of the World Health Organization and did not reach the degree of the strong pH or the strong basal pH, as it recorded the lowest value in the site of The New Tisin and for the winter.

***Keywords*---**Gasses, emissions, SO_2, NO_2, O_3, pH.

Introduction

Breathing clean air is one of the most important components of a healthy environment, and clean air is free of pollutants and toxic elements(Youssef, Ismail, & Bashir, 2007). The accumulation of harmful substances in the atmosphere in different concentrations and ratios has negative effects on the environment and living organisms(Al-Hassan, 2014). An air pollutant in the form of liquid or solid droplets or gases is called air pollutants(Kumar et al., 2020).

Air pollutants such as sulfur dioxide, nitrogen oxides, and ozone are among the external air pollutants that are major factors in respiratory diseases and delay recovery of diseases, including Covid-19, and leads to more serious and fatal forms of this disease(Domingo & Rovira, 2020). Sulfur dioxide is colorless and smelly, its density is 2.63 kg / m 3 and its molecular weight is 64.07 g / mol(Chang, 2014). Its sources are natural volcanoes represented while human being resources are industrial processes and burning oil derivatives that contain sulfur compounds and household uses, as well as transportation based on gasoline fuel because of its high levels. The most important sources of sulfur in thermal power plants are the combustion of sulfur-containing fuels(Zangana, 2018). Gas SO_2 is a dangerous air pollutant that turns in the air and due to photochemical reactions to sulfur trioxide SO_3 after that it turns into sulfur acids that represent sulfuric acid H_2 SO_3 and sulfuric acid H_2 SO_4 and air humidity, which leads to the formation of acid rain Sulfur dioxide is a main and primary cause of acid rain, and they are secondary pollutants in the air that have environmental and health damages. Also, they cause erosion of buildings, properties, bridges and statues that damage them early(Lei, Zhang, Nielsen, & He, 2011; Obaid, 2014; Rosyid, Boedisantoso, & Iswara, 2020). Additionally, nitrogen dioxide is made of nitrogen oxides, which consists of combining oxygen with nitrogen with the help of lightning and thunderbolts and the internal combustion processes of gasoline and diesel in car engines. Also, the proportions vary according to the high efficiency of the engines, operating efficiency, vehicle speed and the type of fuel used(Hamid, 2015). The movement of vehicles is the main source of the nitrogen oxides in the city's atmosphere(Holnicki, Nahorski, & Kałuszko, 2021), and it is found in the form of gas in the air and heavier than it has a distinctive pungent smell that can be perceived at a concentration of 0.1 parts per million, an oxidizing substance that is soluble and corrosive in water Acids(Jarvis, Adamkiewicz, Heroux, Rapp, & Kelly, 2010).

The term ozone comes from Greek, meaning inhalation. It consists of atmospheric oxygen. The difference between it and molecular oxygen is that ozone is triple united. As for molecular oxygen, which is inhaled by living organisms, it consists of two oxygen atoms and has the same chemical formula whether it is far from the earth surface or at the surface level. It is harmful or beneficial depending on its location in the atmosphere(Abbas, Wafaj, & Sultan, 2014). The scientist Christian Friedrich Schönbein was first who discovered Ozone in 1839(Rubin, 2001), and it is called the active oxygen, toxic, transparent, tends to bluish, has a permeable smell, and it is one of the secondary pollutants in the air. Ozone gas is one of the gases polluting the air because it is a strong reactive oxidizing agent that causes tissue damage when inhaled when its total dose exceeds the threshold limit(McDonnell, Stewart, Smith, Kim, & Schelegle, 2012). With the increase in

industrialization and urbanization, acid rain has become a source of widespread concern due to its potential negative effects (Liu, Yang, Zhang, Xiang, & Wei, 2019) and due to the emissions of nitrogen oxides and sulfur oxides, which represent the main component of acid rain. When it interacts with water vapor molecules, acid rain forms and falls in the form of sulfuric and nitric acid. It changes the agricultural soil layer and dissolves a number of elements and Compounds that flow into the soil and from there to groundwater(Hussein, 2021), and lead to acidification of the soil and affect the fine structure of natural soil(Xiao, Guo, Chang, Yang, & Chen, 2022).

Materials and Methods

1- Estimation of the percentage of gases in the specified locations for the study

The gases under study, namely sulfur dioxide gas (SO_2), nitrogen dioxide gas (NO_2) and ozone gas (O_3) for the five sites specified for study, were estimated by taking samples from each site of the air using an AC Electric Air pump (HT-196) device which draws the air, and through it, the American-made TEDLAR BAG bags are filled by the RESTEK company, a capacity of (5) liters, for each site a bag. It was then closed tightly, and the percentage of health and safety was transferred after that. The HORIBA process & Enivronmental (AP-370series) which is a device manufactured by a Japanese company approved by European agencies. It is turned on an hour and a half before the start of the measurement, and when the device is stable, the gas inside the bags is passed and emptied inside the device, giving a direct reading of the concentration of the specified gases. Sulfur dioxide (SO_2) ppm, nitrogen dioxide (NO2) ppm, and ozone gas (O 3) ppm(EPA, 2006).

2- Estimation of the pH level in rainwater

Rainwater samples were collected during the winter and spring seasons for the purpose of measuring the acidity of rain. The pH was measured using locally made plastic basins with tight lids. According to Whitehead and Feth (1964), collecting rainwater samples in a large plastic container with a diameter of 50 cm and Height 70 cm covered with a circular piece of plastic inclined towards the center of the container. The contents of the basins were emptied into one-liter bottles made of plastic. This arrangement protects the model from evaporation and direct exposure to air and from entering contaminated organic materials into the bottle. The collected bottles are replaced after each rain gauge with empty bottles these plastic basins were placed in the study sites and the samples were transferred to the Environment Department for the purpose of measurement by the device (PH213 Microprocessor PH Meter). The collection was collected more than once and one rate was extracted during the study period.

Results and Discussion

1-The concentration of SO2 gas in the air

The results show that there is a discrepancy in the values of gas concentrations and agree with what Syafei (2014) indicated. The time difference strongly affects the concentration of pollutants, and the climatic conditions and their interaction with pollutants cause different concentrations of gaseous pollutants, including sulfur dioxide. Most of the sites recorded a decrease during the winter season, and this was indicated by E Al-Defiery, Al-Muttarri, T Mukhalif, and Abdul Razzak Hassan (2015), as they showed a decrease in the values of sulfur dioxide gas during the cold season and its relationship to relative humidity because it is one of the gases responsible for acid rain. It is clear from the results of Table (1) that the highest spatial rates were recorded at the site of the beginning of the Shuhada Bridge (the castle) with a concentration of (0.0094) ppm, and the reason for this is due to the presence of the popular market in this location, which caused a heavy movement of vehicles and buses, and agrees with Saltos (2018). The means of transportation, including vehicles, are mobile sources that emit various gaseous pollutants, including sulfur dioxide, which affect air quality in urban areas and their health effects on humans(ValverdeMorales, 2016). Li (2014) indicated in his study that Sulfur dioxide gas with polluting gases in the urban city determines the state of pollution in the city's atmosphere and linking it to traffic. Li also stated that gas is related to respiratory diseases, eyes and heart diseases in terms of the proximity of the work environment to the source of pollution. As for the lowest concentration recorded in the Yayci site, at a spatial rate (0.002) ppm due to the lack of sources of emissions of this gas, including the movement of vehicles. The results of the current study showed that the spatial rates of the studied sites shown in Table (1) and their comparison with the Iraqi and WHO did not exceed the Iraqi environment determinants exceed the annual, (24) hours and one hour concentrations, and the WHO determinants of the annual concentrations and one hour Table (5).

Table (1) values of sulfur dioxide concentrations (ppm)

Location	Autumn	Winter	Spring	Average	Environmental determinants				
					Iraqi			WHO	
					annual	**24**hrs	One hr	annual	One hr
The entrance to the Check of Kirkuk June 1	0.0033 ppm	0.0025 ppm	0.0065 ppm	0.0041 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
The beginning of Al-Shuhada'a Bridge (the Citadel)	0.0035 ppm	0.0043 ppm	0.0204 ppm	0.0094 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
Street doctors old Officers	0.0051 ppm	0.0038 ppm	0.0049 ppm	0.0046 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
Tissen	0.01 ppm	0.0031 ppm	0.0075 ppm	0.0068 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
Yayci	0.0026 ppm	0.0018 ppm	0.0016 ppm	0.002 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed

2- The concentration of nitrogen dioxide, NO2 in the air

The results showed that there is a discrepancy in the values of nitrogen dioxide concentrations while these results are consistent with what was explained by Al-Zaidi (2016) who showed that the climate characteristics cause the concentration and deposition of air pollutants and their temporal and spatial variation. The results confirm the study of K. H. M. Al-Yasiri (2020), where he explained that the time difference strongly affects the concentrations of air pollutants, as an interaction occurs between pollutants and atmospheric factors that contribute to changing concentrations. The high gas concentrations in the winter season contributed to raising the spatial rate of gas concentration, and these results are consistent with the study of H. A. M. Al-Shammari (2022). The weak dispersion during the winter season and the slow movement of the wind speed leads to a prolonged stay of the pollutant and an increase in its concentration in the air in some locations. This was explained by Syafei (2014). When temperatures drop in winter, the air layer is thicker and closer to the surface of the earth, thus it prevents pollutants from spreading in the area surrounding the source of the pollutant. So, the pollutants are forced to travel long distances in the upper atmosphere so that they can descend after their atoms cool down, increase their weight and match their temperature with the temperature of the air below them(Matar, al-Huwais, & Kalef, 2020). Yet, lower values in gas in the sites during the winter season are due to the presence of moisture and rain falling in the transport of air pollutants, as the pollutants in the air interact with water vapor to form acids, including the interaction of nitrogen dioxide with water vapor forming nitric acid. Also, the rain falls and precipitate on water and soil cause different degrees of pollution(I. M. K. Al-Shammari & Al-Akanani, 2012). Table (2) shows that the highest spatial rates were recorded in the New Tisin site with a concentration of (0.0039) ppm because it is a site that includes different sources such as the movement of vehicles and being a residential area characterized by various human activities such as ovens and bakeries in addition to the public and private generators. However, the lowest spatial average recorded at the entrance to Kirkuk check point, June 1 (0.0009) compared to the concentration of gas in the Yayci site, which recorded an increase compared to sites containing different sources of gas emissions, and this is consistent with Al-Azzawi (2018). Also, the factors causing pollution in Kirkuk governorate are different, such as industry and the population increase, urban sprawl and the expansion of the urban space near the industrial facilities. Additionally, burning of fuel in the industrial facilities and the sources of nitrogen dioxide emissions cause a temporal and spatial variation from one region to another. Furthermore, Yayci is ite is one of the sites near the North Gas Company and its gas emissions and wind movements cause pollutants to spread and this was shown by the study of Al-Alali (2013). Its danger is its transformation, after inhalation into the body, into dilute nitric acid, which affects the lung tissue and causes irritation and damage to its lining, and then acute pneumonia(F. H. K. Al-Yasiri, 2009). The results of the current study that the spatial average concentrations of the sites specified under considerations (Table 2) did not exceed the national determinants of Iraqi and international schedule (5) annual and (24) hours and one hour.

Table (2) values of nitrogen dioxide concentrations (ppm)

Location	Autumn	Winter	Spring	mean	Environmental determinant				
					Iraqi			WHO	
					Annual	**24**hrs	One hr	annual	One hr
The entrance to the Check of Kirkuk June 1	0.001 ppm	0.0006 ppm	0.0013 ppm	0.0009 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
The beginning of Al-Shuhada'a Bridge (the Citadel)	0.0034 ppm	0.003 ppm	0.0045 ppm	0.0036 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
Street doctors old Officers	0.002 ppm	0.0011 ppm	0.0006 ppm	0.0012 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
Tissen	0.0017 ppm	0.0053 ppm	0.0047 ppm	0.0039 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed
Yayci	0.0016 ppm	0.0013 ppm	0.0021 ppm	0.0016 ppm	did not exceed	did not exceed	did not exceed	did not exceed	did not exceed

3- The concentration of ozone gas O3 in the air

The results of the current study showed that there are temporal and spatial variations in the concentrations of ozone gas. These results are consistent with what was indicated by Saree (2014), as he showed that ozone gas is one of the gaseous air pollutants that vary spatially. Also, Mustafa, Afaj, and Mohammed (2011)showed that the best season for ozone formation is spring and autumn, and the results of Table (3) showed that the values of gas concentrations recorded the highest value for some sites during spring and autumn, which caused the highest spatial rate to be recorded at the entrance site of Kirkuk checkpoint in June 1 site, its amount was (0.0051) while the lowest concentration of ozone gas was at the site of Doctors Street, the old discipline, and the site of Yayci, with a spatial rate of (0.0017) ppm. In these sites have high ozone concentrations in autumn season compared to the location of Doctors Street, the Old Discipline because villages and rural areas can have high ozone values and due to the transfer of ozone from urban areas to villages and rural areas by winds that reach long distances estimated at hundreds of miles(Arya, 1999). The current study of the values of the spatial average concentrations of the specific locations of the study shown in Table (3) and their comparison with the Iraqi environmental determinants indicated by Table (5) showed that they did not exceed the Iraqi determinants concentrations (8) hours and hours one time.

Table (3) Ozone gas concentrations (ppm)

location	Autumn	Winter	Spring	mean	Environmental Determinants Iraqi	
					8 hrs	One hr
The entrance to the Check of Kirkuk June 1	0.0062 ppm	0.0037 ppm	0.0054 ppm	ppm 0.0051	did not exceed	did not exceed
The beginning of the Al-Shuhada'a Bridge (the Citadel)	0.0035 ppm	0.0021 ppm	0.0050 ppm	ppm 0.0035	did not exceed	did not exceed
Street doctors old Officers	0.0006 ppm	0.0014 ppm	0.0033 ppm	ppm 0.0017	did not exceed	did not exceed
Tissen	0.0025 ppm	0.0035 ppm	0.0046 ppm	ppm 0.0035	did not exceed	did not exceed
Yayci	0.0018 ppm	0.0013 ppm	0.0022 ppm	ppm 0.0017	did not exceed	did not exceed

4- Measuring the pH of acid rain:

Table (4) shows the highest spatial average recorded in Yayci site, which amounted to (6.85), and the lowest spatial average recorded in The New Tisin site, which amounted to (5.76). The decrease in some pH values of rain water during the winter season is due to the fact that precipitation removes air pollutants, which causes a decrease in pH values due to the dissolution of gases in the air. This agrees with Al-Hamdani (2012). Acid rain is formed due to the dissolution of nitrogen and sulfur oxides, resulting from human activities such as factories and the emission of vehicle exhaust, which interact in the air to form acids. The scale of the degree of acidity of rain water is a logarithmic scale with 14 degrees, when its value ranges from (5-6) natural rain and when its value is from 5-4 moderate acidic rain without 3 highly acidic rain. Yet, the value of 7 is a natural pH and represents the degree of natural water and that the gases that form acid rain, SO2 and NO2, mix with the air and carry it with it in every direction. Thus they seem unrelated to the source from which they were emitted and transmitted to long distances (Rahman, 2018). The acidity (Hussein, 2021)and the fluctuation is the first characteristic of rain in the city of Kirkuk, and the lack of falling rains and drought are predominant in recent years as Al-Jubouri (2014) explains. The spatial average in the New Tisin site was (5.76). Table (1) shows that this site that the concentration of sulfur dioxide gas increased during the autumn season, which declined during the winter season due to the melting of this gas with rainwater, the reason for the decrease in the pH value, but it was within the normal pH range.

Table (4) PH values of rain water

Location	Winter	Spring	Mean
The entrance to the Check of Kirkuk June 1	6.59	6.80	6.70
The beginning of the Al-Shuhada'a Bridge (the Citadel)	6.08	5.71	5.90
Street doctors old Officers	6.39	6.45	6.42

Tissen	5.41	6.10	5.76
Yayci	6.76	6.93	6.85

Table (5) Iraqi and global environmental determinants of air pollutant concentrations (Al-Ajrash, 2020; Al-Rubaie, 2021; " The Iraqi environmental determinants (determinants of exposure to gases), published in the newspaper," 2012)

No	Pollutant	Exposure time	Environmental Determinants	
			Iraqi **(2012)**	WHO **(2020)**
1	SO_2	Annual (ppm) 24hrs (ppm) 8hrs (ppm) hr (ppm)	0.02 0.06 - 0.15	0.03 - - 0.1
2	NO_2	Annual (ppm) 24 hrs (ppm) 8hrs (ppm) One hr (ppm)	0.02 0.05 - 0.1	0.02 - - 0.11
3	O_3	Annual (ppm) 24hrs (ppm) 8hrs (ppm) One hr (ppm)	- - 0.06 0.1	

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