Caspian J. Env. Sci. 2011, Vol. 12 No.2 pp. 215~224

CJES
Caspian Journal of Environmental Sciences

[Research]

Status and prediction of ozone as an air pollutant in Ahvaz City, Iran

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(Received: July. 17. 2013, Accepted: Dec. 07. 2013)

ABSTRACT

In the present study, air quality analyses for ozone (O_3) were conducted in Ahvaz, a city in the south of Iran. The measurements were taken from 2009 through 2010 in two different locations to prepare average data in the city. Relations between the air pollutant and some meteorological parameters were calculated statistically using the daily average data. The wind data (velocity, direction), relative humidity, temperature, sunshine hours, evaporation and rainfall were considered as independent variables. The relationships between concentration of pollutant and meteorological parameters were expressed by multiple linear and nonlinear regression equations for both annual and seasonal conditions using SPSS software. RMSE test showed that among different prediction model, stepwise model is the best option. The average concentrations were calculated for every 24 hours, each month and each season. Results showed that the highest concentration of ozone occurs generally in the afternoon, while the least concentration is found at the beginning of the morning. Monthly concentrations of ozone showed the highest value in August, while the least value was found in October. The seasonal concentrations showed the highest amounts in summer.

Keywords: *Ozone, Air pollution, Meteorological Parameters, Regression model*

INTRODUCTION

Air sustains life. But the air we breathe is not pure. It contains a lot of pollutants and most of these pollutants are toxic (Sharma, 2001). While developed countries have been making progress during the last century, air quality has been getting much worse especially in developing countries air pollution exceeds all health standards. For example, in Lahore and Xian (china) dust is ten times higher than health standards (Sharma, 2001).

At ground-level, ozone is a pollutant, but in the stratosphere it screens UV radiation. Ozone (O_3) is one of the seven conventional (criteria) pollutants (including SO_2, CO, particulates, hydrocarbons, nitrogen oxides, O_3 and lead). These pollutants produce the highest volume of pollutants in the air and the most serious threat for human health and welfare. Concentration on these pollutants, especially in cities, has been regulated by Clean Air Act since 1970 (Cunningham & Cunningham, 2002).

Some characteristics of Ozone include: colorless, unpleasant odor, Tri-atomic form of molecular oxygen and the major component of photochemical smog. About its production, it should be said that the background levels are found naturally. Ozone in the lower atmosphere is formed by reaction of NOx and VOC's (volatile organic compounds or hydrocarbons) in the presence of sunlight. Cars, industry, gas vapors, chemical solvents, fuel combustion increase ozone production. Half of emission of HC and NOx in cities is produced by Motor vehicles (Asrari *et al*., 2007).

The presence of pollutants in the atmosphere causes a lot of problems, thus the study of pollutant behavior is necessary (Asrari *et al*., 2007). Some of the main health effects of ozone are as follow: lung inflammation, reduced lung elasticity, transient cough, chest pain, throat irritation and nausea. Other effects include damages on plants and materials such as retard the growth, effect on pollen germination, reduce photosynthesis, crack rubber and react with fabric (Sharma, 2001).

Status of pollutants concentration and effects of meteorological and atmospheric parameters on these pollutants compose the base of following studies: Ho and Lin (1994) studied semi-statistical model for evaluating the NO_x concentration by considering source emissions and meteorological effects. Street level of NO_x and SPM in Hong Kong has been studied by Lam *et al*. (1997). In a study, the relationship between monitored air pollutants and meteorological factors, such as wind speed, relative humidity ratio and temperature, was statistically analyzed, using Software Package of Social Sciences, V. 20 (SPSS). According to the results obtained through multiple linear regression analysis, for some months there was a moderate and weak relationship between the air pollutants like O_3 level and the meteorological factors in Trabzon city (Cuhadaroglu and Demirci, 1997).

Mandal (2000) has shown the progressive decrease of air pollution from west to east in Kolkata. Statistical modeling of ambient air pollutants in Delhi has been studied by Chelani *et al.* (2001). Abdul-Wahab and Al-Alawi (2002) developed a neural network model to predict the tropospheric (surface or ground) ozone concentrations as a function of meteorological conditions and various air quality parameters. Results showed that nitrogen oxide, sulfur dioxide, relative humidity, non-methane hydrocarbon and nitrogen dioxide have the most effect on the predicted ozone concentrations. In addition, temperature had an important role while solar radiation played a lower effect than expected. The results of this study showed that the artificial neural network (ANN) is a promising method for air pollution modeling. Also for predicting CO, Sabah *et al.* (2003) used a statistical model.

In another research, data on the concentrations of seven air pollutants (CH_4, NMHC, CO, CO_2, NO, NO_2 and SO_2) and meteorological variables (wind speed and direction, air temperature, relative humidity and solar radiation) were used to predict the concentration of ozone in the atmosphere using both multiple linear and principal component regression methods (Abdul-Wahab *et al.*, 2005). Results showed that while high temperature and high solar energy tended to increase the day time ozone concentrations, the pollutants NO and SO_2 being emitted to the atmosphere were being depleted. However, the model did not predict the night time ozone concentrations as precisely as it did for the day time. Asrari *et al.* (2007) studied effect of meteorological factors for predicting CO. Also variations in concentration of CO in different times have been shown in this study.

Li *et al.* (2014) presented the spatial and temporal variation of Air Pollution Index (API) and examined the relationships between API and meteorological factors during 2001–2011 in Guangzhou, China. Relationships were found between API and a variety of meteorological factors. Temperature, relative humidity, precipitation and wind speed were negatively correlated with API, while diurnal temperature range and atmospheric pressure were positively correlated with API in the annual condition. Yoo *et al.* (2014) mentioned that all of the pollutants show significant negative correlations between their concentrations and rain intensity due to washout or convection. The relative effect of the precipitation on the air pollutant concentrations was estimated to be $PM_{10} > SO_2 > NO_2 > CO > O_3$, indicating that PM_{10} was most effectively cleaned by rainfall. The analysis showed that the O_3 concentrations may increase due to vertical mixing leading to its downward transport from the lower stratosphere/upper troposphere.

The present study exhibits diurnal, monthly and seasonal variations of concentration of ozone and also a statistical model that is able to predict amount of ozone. This is based on linear regression technique. Linear Regression estimates the coefficients of the linear equation, involving one or more independent variables that best predict the value of the dependent variable (ozone amount in this study). So, a large statistical and graphical software package (SPSS) as one of the best known statistical packages has been used (Kinnear, 2002).

MATERIALS AND METHODS

Study area

The research area, Ahvaz, capital of Khuzestan Province, is the biggest city in the south-western part of Iran (Fig. 1) located around 31° 19' N and 48° 40' E and the elevation is about 20 m above the mean sea level. Annual precipitation of Ahvaz is about 230 mm. It has arid climate and residential population was 1,425,000 in 2006. Ahvaz is consistently one of the hottest cities on the planet during the summer, with summer temperatures regularly at least 45°C, sometimes exceeding 50°C with many sandstorms and dust storms common during the summer period, while in winters the minimum temperature could fall around +5°C. Ahvaz is built on the banks of the Karun River and is situated in the middle of Khuzestan Province. Iraq attempted to annex Khuzestan and Ahvaz in 1980, resulting in the Iran–Iraq War (1980–1988). Ahvaz was close to the front lines and was suffered severe damages during the War. There are lots of cars driven in the city and also many factories and industrials around it. So, Ahvaz is one of the most polluted cities in Iran and needs to carry out an ambient air quality analysis in this city.

Fig 1. Location of Ahvaz city in Iran.

Recently, Ahvaz is considered as the worst polluted city of the world according to a survey by the World Health Organization in 2011 because of high concentration of dust during all the year (Guinness World Records, 2013). Increasing amount of dust (Fig. 2) can cause different problems such as increasing number of cancer and lung damages.

Data and methodology

Two available sampling stations in the city called Edareh-Kol and Naderi, belong to Environmental Organization of Iran were selected to represent different traffic loads and activities. The sampling has been performed every 30 minutes daily for each pollutant during all months of 2009 and 2010. Among the measured data in the two stations ozone was chosen. Then the averages were calculated for every hour, monthly and seasonally for the both stations by Excel. Finally averages of data at two stations were used to show air pollution situation as diurnal, monthly and seasonal graphs of concentration of ozone in the city. Studying correlation of ozone and metrological parameters of synoptic station of city was the next step. The metrological parameters studied include: temperature (min & max), humidity (min & max), precipitation, sunshine, wind direction, wind speed and evaporation. In the next step, daily average data at two stations in 2008 was considered as dependent variable in statistical analysis, while daily data of meteorological parameters during this year were selected as independent variables in SPSS programme and the linear regression equation showed that the concentration of ozone depends on the kind of meteorological parameters and also gives an idea about the levels of this relation. The relationship between the dependent variables and each independent variable should be linear. The significant values in output are based on fitting a single model. Also linear regression equation was made for different seasons maybe show those relationships which are not observed using annual data.

A B

Fig 2. Two photographs from the same place in Ahvaz showing impacts of dust pollution during recent years (A in clean condition and B in worse condition).

The model for predicting ozone was determined using two multiple regression modeling procedures of 'enter method' and 'stepwise method'. In 'enter method' all independent variables selected are added to a single regression model. In 'stepwise' which is better, all variables can be entered or removed from the model depending on the significance. Therefore only those variables which have more influence on dependent variable are observed in a regression model.

RESULTS AND DISCUSSION

In Figs. 3 - 5, the diurnal, monthly and seasonal variations in concentration of ozone have been presented. As shown in fig. 3 the high concentration of ozone occurs in the afternoon in agreement with other results reported by Masoudi *et al.* (2014). Actually ozone in the lower atmosphere is formed by reaction of NOx and VOC's in the presence of sunlight. Monthly concentration of ozone showed the highest values in August and the least in October (Fig. 4). Highest amounts were also found in summer (Fig. 5) which is in agreement with results obtained in Tehran (capital of Iran) (Masoudi *et al.*, 2014). Fortunately, all graphs showed that the concentrations of ozone are lower than Primary Standards of ozone (120 and 50 ppb) recommended by National Ambient Air Quality Standards (NAAQS) of USA and Iran, respectively. However, these graphs are almost about annual and monthly, but not about hourly conditions, while these amounts are the Primary Standards for the latter condition. Therefore the real annual and monthly amounts of standards should be less than these amounts (120 and 50 ppb) and then it is assumed that some of these amounts in the fig.s are more than the real standards which shows unhealthy condition.

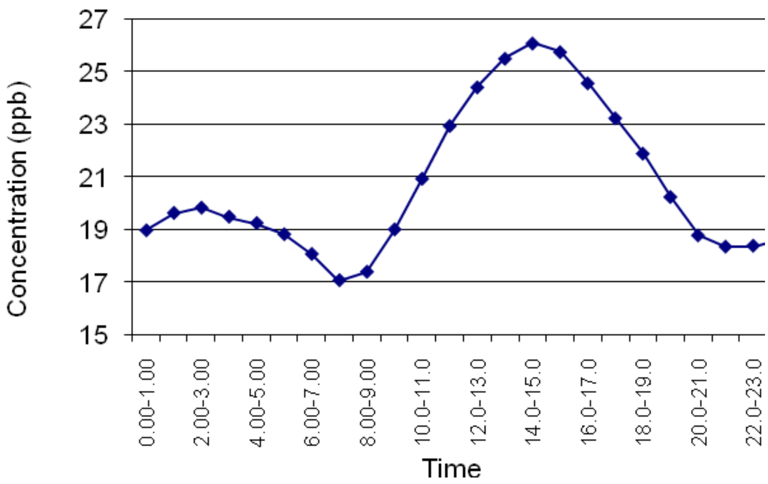

Fig 3. Diurnal variation of ozone concentration in Ahvaz (2009-2010).

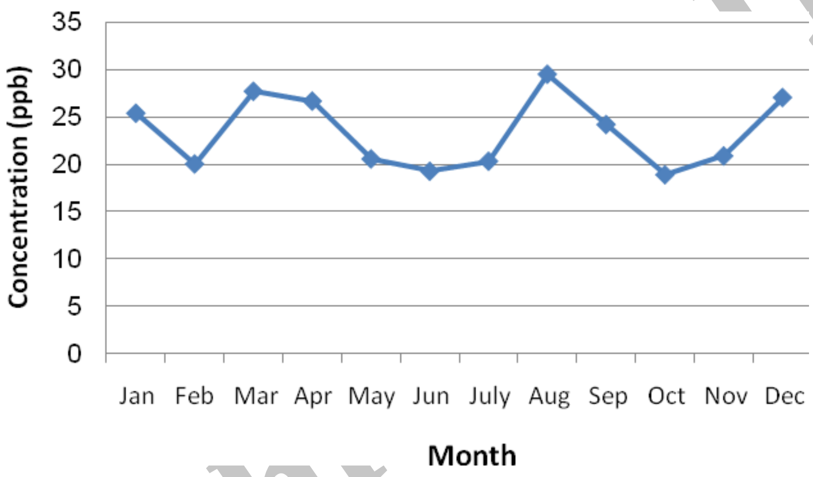

Fig 4. Monthly variation of ozone concentration in Ahvaz (2009-2010).

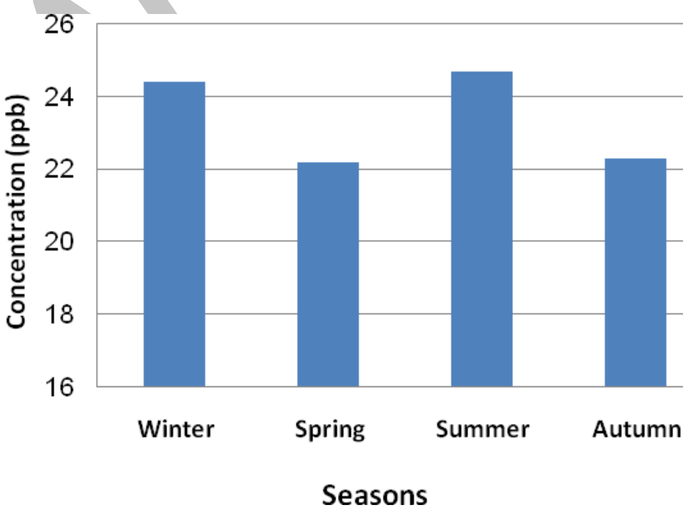

Fig 5. Seasonal variation of ozone concentration in Ahvaz (2009-2010).

Table 1 shows the relationships between ozone and other air pollutants. For example the concentration of ozone shows negative correlation with CO and PM_{10} while it shows positive correlation with NO, NO_2, NOx and SO_2. Ozone is increased with reaction between nitrogen oxides and sunlight. Therefore it was assumed that ozone shows positive relation with nitrogen oxides. Also Sulfur dioxide and nitrogen dioxide have the most effect on the ozone concentrations. These results are almost in good agreement with other results regarding relationships between ozone and other air pollutants in other regions (Abdul-Wahab & Al-Alawi, 2002; Masoudi *et al.*, 2014). Correlation coefficients significant at the 0.05 level are identified with a single asterisk (significant), and those significant at 0.01 level are identified with two asterisks (highly significant).

Table 1. Correlation between air pollutants and ozone.

	CO	NO	NO_2	NOx	PM_{10}	SO_2
Pearson Correlation	-0.399**	0.252**	0.419**	0.315**	-0.137**	0.569**
Sig. (2-tailed)	0.000	0.000	0.000	0.000	0.009	0.000
N	298	353	353	353	365	365

Table of analysis of variance (Table 2) shows that both regressions of 'enter' and 'stepwise' methods for annual condition are highly significant, indicating a significant relation between the different variables.

Table 2. Tables of analysis of variance for both regressions of 'enter' (a) and 'stepwise' (b) methods for annual condition.

Analysis of variance (a)

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	9608.446	10	960.845	10.140**	.000
Residual	33545.536	354	94.761		
Total	43153.982	364			

Predictors: (Constant), Rain, Wind direction (max), Wind speed (max), Temperature (max), Temperature (min), Sunshine Hours, Ratio of Humidity (min), Ratio of Humidity (max), Humidity (avg), Evaporation.
Dependent Variable: Ozone

Analysis of variance (b)

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	9133.044	2	4566.522	48.590**	.000
Residual	34020.937	362	93.980		
Total	43153.982	364			

Predictors: (Constant), Sunshine Hours, Ratio of Humidity (min)
Dependent Variable: Ozone

In Table 3 the coefficients of ozone pollution model and regression lines for both enter and stepwise methods in annual condition are presented. Regression coefficients, standard errors, standardized coefficient beta, t values, and two-tailed significance level of t have been shown in the Table 3.

Table 3. Coefficients of ozone pollution model and regression lines for both enter (a) and stepwise (b) methods for annual condition.

Coefficients (a)

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		
Constant	18.400	7.122		2.583	.010
Temperature (max)	-.084	.247	-.079	-.342	.733
Temperature (min)	-.063	.278	-.045	-.225	.822
Ratio of Humidity (max)	-.003	1.040	-.008	-.003	.997
Ratio of Humidity (min)	.276	1.040	.476	.266	.791
Ratio of Humidity (mean)	-.059	2.082	-.117	-.028	.977
Rain	-.031	.167	-.010	-.187	.852
Sunshine hours	.507	.204	.166	2.481*	.014
Evaporation	-.091	.221	-.048	-.411	.681
Wind Direction (max)	-.008	.007	-.059	-1.027	.305
Wind Speed (max)	-.127	.185	-.035	-.685	.494

Dependent Variable: Ozone

Coefficients (b)

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		
(Constant)	7.781	1.790		4.346	.000
Ratio of Humidity (min)	.300	.031	.517	9.686**	.000
Sunshine hours	.503	.163	.165	3.092**	.002

Dependent Variable: Ozone

The linear regression equations show that the ozone pollution depends on the meteorological parameters and also give an idea about the levels of relations. The linear model equations after using 'enter method' and 'stepwise method' for annual condition are:

Ozone amount (ppb) using 'enter method' for annual condition = 18.4 + (-0.063) $T_{(min)}$+ (-0.084) $T_{(max)}$ + (0.276) $RH_{(min)}$ + (-0.003) $RH_{(max)}$ + (-0.059) $RH_{(mean)}$ + (-0.031) R + (0.507) SH + (-0.008) $WD_{(max)}$ + (-0.127) $WS_{(max)}$ + (-0.091) ER= 0.472 (significant at 0.01)

Note: $T_{(mean)}$=Temperature (mean) , $T_{(max)}$ =Temperature (max), $T_{(min)}$ =Temperature (min), $WS_{(mean)}$ = Wind speed (mean), $WS_{(max)}$ =Wind speed (max), $WD_{(max)}$ =Wind direction (max), $RH_{(mean)}$ = Ratio of Humidity (mean), $RH_{(max)}$ =Ratio of Humidity (max), $RH_{(min)}$ = Ratio of Humidity (min), DP =Dew Point, SH= Sunshine Hours, R=Rainfall, E=Evaporation.

Ozone amount (ppb) using 'stepwise method' for annual condition = 7.78 + (0.300) $RH_{(min)}$ + (0.503) SH, R= 0.460 (significant at 0.01). Results of regression model show that temperature, ratio of humidity (maximum and average), rainfall, evaporation and wind parameters have reverse effect on concentration of ozone. So that, when these parameters increase, the concentration of ozone decreases, although these results are not significant (Table 3a). When sunshine hours and ratio of humidity (min) increase, the concentration of ozone significantly increases (Table 3b). These results are almost in good agreement with other results regarding ozone measurements in Tehran (Masoudi *et al.*, 2014) and other regions (Abdul-Wahab *et al.*, 2005; Li *et al.* ,2014). Actually some of these events happen in real condition. Rainfall and wind usually decrease most of air pollutant (Asrari *et al*., 2007). But with increasing sunshine hours, we expect ozone amounts to be increased. The following reactions occur in the lower atmosphere for producing O_3 (Sharma, 2001):

$N_2 + O_2 \Rightarrow 2NO$

$2NO + O_2 \Rightarrow 2NO_2$ $NO + VOC \Rightarrow NO_2$

NO_2 + sunlight => NO+ O

$O+O_2$+sunlight => O_3

$O_3 + NO \Rightarrow NO_2 + O_2$

The values and significance of R (multiple correlation coefficient) in both equations show capability of them in predicting ozone amount. The amount of Adjusted R^2 in both equations is almost 0.20 showing that different parameters can calculate almost 20% variability of ozone. This result indicates for predicting most of air pollutants like ozone, the meteorological parameters are not enough and we should take into consideration consumption of fossil fuel especially in motor vehicles. Half of emission of (VOC) hydrocarbons and NOx in cities is produced by motor vehicles. The automobile exhaust produces 75% of total air pollution. Release poisonous gases of CO (77%), NOx (8%) and Hydrocarbons (14%) (Sharma, 2001). On the other hand, R in enter method (0.47) is equal to stepwise method (0.46), showing no difference. Therefore, second equation based on stepwise method can be used to predict ozone in the city instead of using first equation which needs more data. On the other hand, no difference between the two R values indicates that the excluded variables in second equation have less effect on measuring of ozone in the city. Beta in Table 3 shows those independent variables (meteorological parameters) which have more effect on dependent variable (ozone). The beta in the Table 3 shows a highly significant effect of some variables like sunshine hours and ratio of humidity compared to other meteorological parameters for measuring the ozone which is close to the results of Masoudi *et al.* (2014). Parameter Sig (p-Value) from Table 3 shows amount of relation between ozone and meteorological parameters. For example, Table 3a shows that wind speed has higher effect on ozone than wind direction.

On the other hand, in Table 4 the linear regression equations of ozone amount are presented for both enter and stepwise methods in different seasonal condition. Almost all of the models except summer model of enter method are significant which is close to the results of Masoudi *et al.* (2014). Stepwise methods show those meteorological parameters which are most important during these seasons for estimating the pollution. Again those parameters showing increasing in sun radiations like temperature and sunshine hours are observed as the most important among the others. Among the models, autumn models have the highest R while the R of summer models shows the least. R in autumn models is higher than in annual models, also, indicating that relations between the pollutant and meteorological parameters are stronger than the other conditions during this season.Also the nonlinear multiple regression equation of Ozone amount using parameters of linear stepwise method for annual condition is calculated which is significant:

Table 4. Ozone amount (ppb) using two methods of enter and stepwise for different seasonal condition.

Season	Enter Method	R	Stepwise Method	R
Spring	= 11.748 + (-0.126) $T_{(min)}$ + (0.060) $T_{(mean)}$ + (-0.109) $RH_{(min)}$ + (-0.312) $RH_{(max)}$ + (0.460) $RH_{(mean)}$ + (-0.262) R + (0.233) SH + (-0.003) $WD_{(max)}$ + (-0.038) $WS_{(max)}$ + (0.046) E	0.462 (significant at 0.05)	= 8.679 + (0.197) SH	0.309 (significant at 0.01)
Summer	= 1۳.۸۶۷ + (0.۵۸۴) $T_{(min)}$ + (-0.۱۰0) $T_{(max)}$ + (1.380) $RH_{(min)}$ + (2.111) $RH_{(max)}$ + (-4.140) $RH_{(mean)}$ + (0.204) SH + (-0.008) $WD_{(max)}$ + (-0.531) $WS_{(max)}$ + (-0.023) E	0.294 (not significant)	= 22.518 + (-0.597) $RH_{(min)}$	0.251 significant at 0.05)
Autumn	= 50.671 + (-0.449) $T_{(min)}$ + (-0.578) $T_{(max)}$ + (2.037) $RH_{(min)}$ + (1.812) $RH_{(max)}$ + (-3.764) $RH_{(mean)}$ + (-0.240) R + (0.140) SH + (-0.026) $WD_{(max)}$ + (-0.074) $WS_{(max)}$ + (0.880) E	0.690 (significant at 0.01)	= 44.467 + (-0.925) $T_{(mean)}$	0.616 (significant at 0.01)
Winter	= -9.537 + (0.909) $T_{(min)}$ + (0.367) $T_{(max)}$ + (-0.914) $RH_{(min)}$ + (-1.304) $RH_{(max)}$ + (2.457) $RH_{(mean)}$ + (0.125) R + (1.062) SH + (0.018) $WD_{(max)}$ + (0.401) $WS_{(max)}$ + (-0.120) E	0.499 (significant at 0.01)	= 16.453 + (0.761) $T_{(min)}$	0.262 (significant at 0.05)

Ozone amount (ppb) using nonlinear regression for annual condition = -11843. 847 + (-0.561) $RH_{(min)}$ + (-0.023) $RH_{(min)}{}^{2}$+ (0.001) $RH_{(min)}{}^{3}$+11859.342+ (-0.702) SH + (0. 371) SH^{2}+ (-0.025) SH^{3} R_2= 0.242 (significant at 0.01)

To test which annual model is better to use, RMSE (Root Mean Square of Error) is calculated for different linear models of enter and stepwise and nonlinear model. Predicted amounts using the different annual models for 30 days during 2009 are calculated and compared with observed data during those days using RMSE equation:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(O_{obs} - O_{cal})^2}{n}}$$

O_{obs}: observed Ozone value, O_{cal}: predicted Ozone value using model. The values of RMSE in both linear models of enter (91.65) and stepwise (16.63) show capability of stepwise model in predicting Ozone amount compared to nonlinear model value (57.51). This result which is close to the results of Masoudi *et al.* (2014) indicates for predicting most of air pollutants like Ozone, we may take into consideration only linear models of stepwise which need less data compared to enter model and also its calculation is easier than nonlinear model.

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وضعیت و پیش بینی ازن به عنوان یک آلاینده هوا در شهر اهواز، ایران

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(تاریخ دریافت:۹۲/۴/۱۶ - تاریخ پذیرش: ۹۲/۹/۱۶)

چکیده

در تحقیق فوق تجزیه و تحلیل کیفیت هوا بر روی ازن در شهر اهواز در جنوب ایران با در نظرگیری داده های سالهای ۲۰۰۹ و ۲۰۱۰ انجام شد. اندازه گیری ها در دو مکان متفاوت شهر برای بیان میانگینی از شهر صورت گرفت. روابطی آماری بین آلاینده و پارامترهای جوی با استفاده از داده های میانگین روزانه به دست آمد. داده های باد (سرعت و جهت)، رطوبت نسبی، ساعات آفتابی، تبخیر و بارش به عنوان متغیرهای مستقل در نظر گرفته شد. میزان روابط بین آلاینده و پارامترهای جوی با استفاده از معادله های رگرسیون خطی و غیر خطی در محیط SPSS برای دو مقطع زمانی سالانه و فصلی تهیه شد. نتایج تست میانگین مربعات خطا بیان کننده مناسب بودن مدل گام گام نسبت به روشهای دیگر بود. همچنین در این تحقیق میانگین غلظت ساعتی، ماهانه و فصلی برای آلاینده فوق مشخص شد. نتایج نشان می دهد که بیشترین غلظت ازن در هنگام بعد از ظهر و کمترین آن در هنگام سپیده دم روی می دهد. بیشترین غلظت ماهانه نیز در ماه آگوست و کمترین در ماه اکتبر و بیشترین غلظت فصلی در تابستان مشاهده شد.

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