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STATUS AND PREDICTION OF OZONE CONCENTRATION IN THE AIR OF ISFAHAN, IRAN

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ABSTRACT:

Introduction: Ozone (O_3) is one of the seven criteria pollutants. These pollutants can be a serious threat for human health and welfare.

Materials and methods: In the present study air quality analyses for ozone (O_3) were conducted in Isfahan, Iran. The measurements were taken in three different locations to prepare average data in the city. The average concentrations were calculated for every 24 h, monthly and every season. Relations between the air pollutant and some meteorological parameters were calculated statistically using the daily average data. The wind data (velocity, direction), temperature, evaporation and rainfall are considered as independent variables.

Results: Results showed that the highest concentration of ozone occurs generally in afternoon while the least concentration was found in the morning and midnight. Monthly concentrations of ozone showed the highest and least value in March and October, respectively. The seasonal concentrations showed the least amounts in autumn while the highest amounts in winter. The relationships between concentration of pollutant and meteorological parameters are expressed by multiple linear regression equations for both annual and seasonal conditions showing significant relationship. RMSE test showed that among different prediction models, stepwise model is the best option.

Conclusions: In the current research, air quality analyses for Isfahan, were conducted for ozone (O_3). Among different prediction models using some meteorological parameters, stepwise model was the best option. Also, different variations in concentration during day, months, and seasons were observed.

INTRODUCTION

Air pollutants may become injurious to human, animal, planet or microbial life or may interfere in life [1, 2, 3, 4]. Ozone (O_3) is an important pollutant in troposphere but plays an important role in stratosphere known as the ozone layer [1, 5]. Ozone (O_3) is one of the seven conventional (criteria) pollutants (including SO_2, CO, particulates, hydrocarbons, nitrogen oxides, O_3 and lead). The highest volume of these pollutants in the air are the most serious threat for human health and welfare [6]. Tropospheric ozone as the secondary pollutant and greenhouse gas is produced by photochemical oxidation of carbon monoxide (CO), methane (CH_4), and non-methane volatile organic compounds (NMVOCs), and

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nitrogen oxides (NO_x) in presence of hydroxyl radical (OH) [7, 8]. In recent years, there has been increasing concern on air temperature and ozone concentration due to climate change. Some studies ascertain that temperature constitutes a meteorological factor influencing surface ozone formation amongst other conditions [9, 10, 11]. According to the International Panel for Climate Change, surface ozone is expected to rise with an increase in temperature [12].

Pollutants concentration and the influences of meteorological factors on these pollutants form the base of some studies such as investigation of semi-statistical method for assessment the NO_x concentration based on source emissions and meteorological effects or a street level study of NO_x and SPM in Hong Kong [13, 14]. Analysis between air pollutants and meteorological parameters through multiple linear regression analysis showed that there was a moderate and weak relationship in some months between the air pollutants like O_3 level and the meteorological parameters in Trabzon city [15]. A neural network method was studied to foresee the tropospheric ozone concentrations as a function of meteorological status and various air quality factors. Results showed that temperature had an important role while solar radiation played a lower effect than expected [16]. In another study influence of meteorological parameters was investigated to prediction of CO [17]. Also variations in concentration of CO in different times have been shown in this study.

In a research, the air pollution behaviors were studied using principal component analysis and cluster analysis in an urban area [18]. Results showed despite having longer computation time, the non-linear models predicted better than the linear ones. Seasonal variation characteristics of ozone were presented during 2001-2004 in the two major urban areas of Greece, Athens, and Thessaloniki [19]. Also, some characteristics like the mid- day peak at the peripheral stations as well as the existence of relatively high rural background levels around the both urban areas were investigated in this research. The spatial and temporal variation of air pollution index (API) were studied during 2001–2011 in region of Guangzhou, China [20]. Then the relationships between API and meteorological parameters were examined. Results showed that the precipitation, relative humidity, temperature, and wind speed were negatively correlated with API, while atmospheric pressure and diurnal temperature range were positively correlated with API in the annual status.

Air quality in Chongqing, the largest mountainous city in China, was studied in another study [21]. The statistical analysis of SO_2, PM_{10}, and NO_2 concentrations was studied from 2002 to 2012. The analysis of Pearson correlation indicated that concentrations of SO_2, PM_{10}, and NO_2 were positively correlated with the atmospheric pressure but negatively with the temperature and wind speed. Tropospheric ozone in Irene city, in South Africa, was studied using SHADOZ network data to evaluate the relationship between the observed seasonal ozone enhancement and meteorological parameters (such as temperature and relative humidity) using multiple linear regression model [22]. Results showed that there were strong correlation between ozone and temperature in all seasons. Similar trends were also observed for relative humidity and ozone concentrations in Autumn, Spring, and Summer.

Statistical modeling of ozone was studied in Tehran [23], Ahvaz [24] and Shiraz [3]. According to the results obtained through multiple linear regression analysis, for seasonal and annual conditions, there were significant relationships between ozone and meteorological factors in these cities. The results between other pollutants and meteorological factors were observed in other cities of Iran; NO_2 in Ahvaz [25], NO_2 in Tehran [26], PM_{10} in Tehran [27] and CO in Shiraz [28].

The present study exhibits diurnal, monthly and seasonal variations of ozone concentration and also a statistical method that is able to predict amount of ozone. This is based on linear regression technique.

MATERIALS AND METHODS

Study Area

Isfahan city, center of Isfahan province, is the biggest city in the central part Iran (Fig. 1) located around 32° 38' N and 51º 40' E and the elevation is about 1590 m above the mean sea level. It has semi-arid climate with four distinct seasons. Residential population was 1834000 in 2011. Isfahan is built on the both banks of the Zayandeh-rud River. There is a lot of cars in city and many factories and industrials sites around the city. So Isfahan is one of the most polluted cities in Iran. So it is necessary to carry out an ambient air quality analysis in this city.

Data and methodology

Three available sampling stations in the city, Azadi, Bozorg-mehr and Laleh belong to Iranian Department of Environment were selected to represent different traffic loads and activities, (Fig. 2).

The sampling has been performed every 30 min daily for every pollutant during all months in 2010 and 2011. Among the measured data for every pollutant in three stations ozone data was selected for this study. Then the averages were calculated hourly, monthly and seasonally for three stations by Excel. Finally averages of data at three stations were used to show air pollution situation diurnal, monthly and seasonal graphs of ozone concentration in the city.

Studying correlation of ozone and metrological parameters of synoptic station of city was the next step. The metrological parameters included: temperature (min, max), rain, wind direction, wind speed and evaporation.

In the further action, daily average data at three stations in 2011 was considered as dependent variable in statistical analysis, while daily data of

Fig. 1. Two photographs from the same place in Isfahan showing impacts of dust pollution during recent years (in clean and polluted condition)

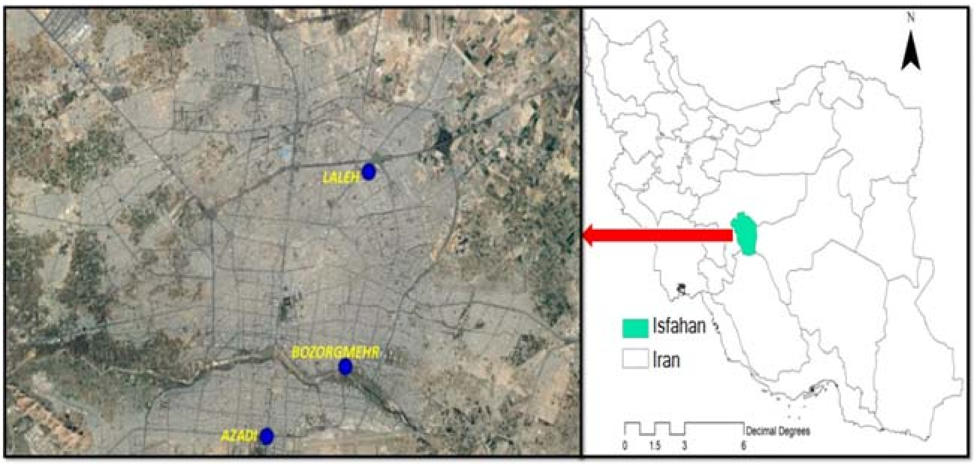

Fig. 2. Position of Isfahan in Iran and its air pollution measurement stations

meteorological parameters during this year were selected as independent variables in SPSS (V. 20). The linear regression equation showed that the concentration of ozone depends on the kind of meteorological parameters, so it gave an idea about the levels of this relation. Linear regression equation is based on different seasons and shows those relationships which are not observed using annual data.

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

RESULTS AND DISCUSSION

In Figs. 3, 4 and 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 noon and afternoon in agreement with the other results reported from the other cities in Iran [3, 23, 24]. 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 March and the least in October (Fig. 4). Seasonal concentration of ozone shows the highest values in winter and the least amounts in autumn (Fig. 5). 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. 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 some times especially in afternoon in the Figs are more than the real standards which show unhealthy condition.

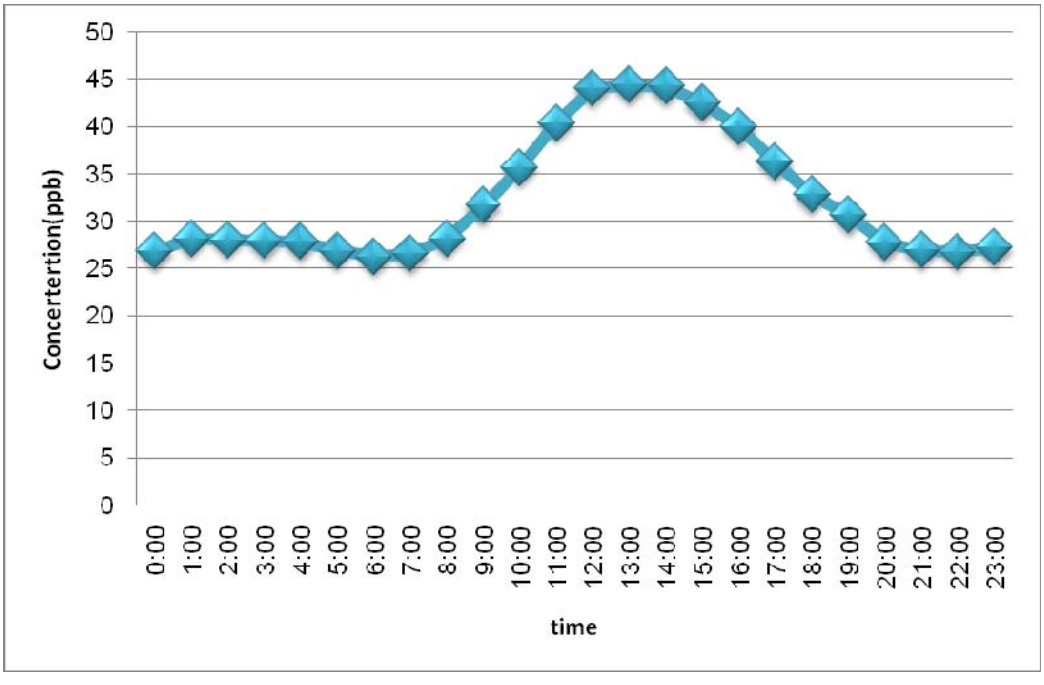

Fig. 3. Diurnal variation of ozone concentration in Isfahan.

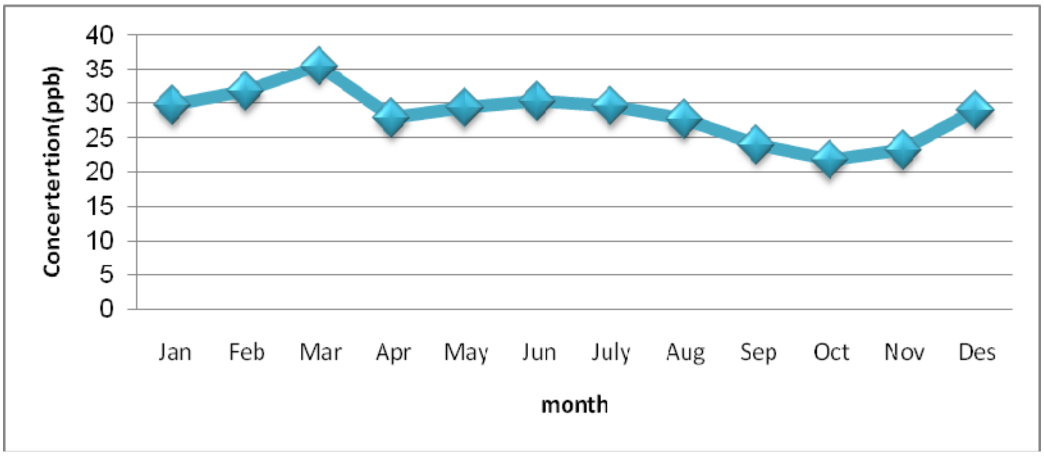

Fig. 4. Monthly variation of ozone concentration in Isfahan.

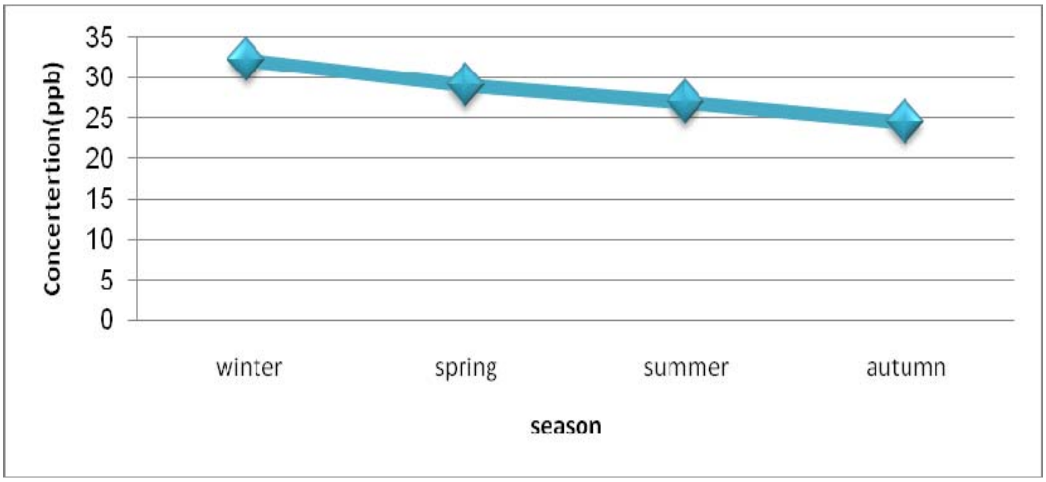

Fig. 5. Seasonal variation of ozone concentration in Isfahan.

Table 1 shows the relationships between ozone and the other air pollutants. For example the concentration of ozone shows significant negative correlation with PM_{10} and SO_2 while it shows significant positive correlation between NO_2 and NOx which is close to the results of Ahvaz city [24]. Ozone is increased when sunlight is increased while the other pollutants are related to traffic volume that is observed more in morning and evening.

Table 1. Correlation between air pollutants and ozone (*significant at 0.05 level; ** significant at 0.01 level).

	NO_2	NOx	PM_{10}	SO_2	CO
Pearson Correlation	.562**	.290**	-.334**	-.345**	.072
Sig. (2- tailed)	.000	.000	.000	.000	.182
N	344	344	344	344	344

Table 2. Analysis of variance for both regressions ; enter (a) and stepwise (b) methods for annual condition.

Analysis of variance (a)

Model	Sum of squares	df	Mean square	F	Sig.
Regression	2992.191	5	598.438	4.207 **	.001
Residual	48084.855	338	142.263		
Total	51077.046	343			

Predictors: (constant), rain, wind direction, wind speed (mean), temperature (max), temperature (min), dependent variable: ozone

Analysis of variance (b)

Model	Sum of squares	df	Mean Square	F	Sig.
Regression	2140.556	1	2140.556	14.960**	.000
Residual	48936.490	342	143.089		
Total	51077.046	343			

Predictors: (constant), wind speed (mean) dependent variable: ozone

Table 2 shows analysis of variance in both regressions of 'enter' and 'stepwise' methods for annual situation indicating a significant relation between the different variables.
In Tables 3 (a, b), 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 Tables.

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)	39.070	3.591		10.880	.000
Temperature (max)	-.415	.223	-.320	-1.860	.064
Temperature (min)	.501	.269	.315	1.864	.063
Rain	-.374	.367	-.059	-1.021	.308
Wind direction	.008	.006	.073	1.261	.208
Wind speed(mean)	.640	.231	.164	2.765**	.006

Dependent variable: ozone

Coefficients (b)

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		
(Constant)	34.338	1.387		24.754	.000
Wind speed(mean)	.801	.207	.205	3.868**	.000

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 = 39.070 + (0.501) Temperature $_{(min)}$ + (- .415) Temperature $_{(max)}$ + (- 0.374) Rain + (0.008) Wind direction + (0.64) Wind speed R= 0.242 (significant at 0.01)

Ozone amount (ppb) using 'stepwise method' for annual condition = 34.338 + (0.801) Wind speed R= 0.205 (significant at 0.01)

Results of regression model show that when wind speed increases, the concentration of ozone significantly increases (Table 3). Other meteorological parameters show different effects on ozone amounts, although these results are not significant. For example rainfall and temperature (max) have reverse effects on concentration of ozone while temperature (min) has additive effects (Table 3a). These results are almost in good agreement with the other results regarding ozone measurements in Tehran [23] and the other regions [20, 29]. Actually some of these events happen in real condition. Increasing in rainfall and wind speed usually decreases the air pollution [17]. 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 0.05 showing that the different parameters can calculate almost 5 % variability of ozone. This result indicates for predicting most of air pollutants like ozone, we should take into consideration consumption of fossil fuel especially motor vehicles. Half of emissions of (VOC) Hydrocarbons and NO_x in cities are produced by motor vehicles. The automobile exhaust produces 75 % of total air pollution; CO (77%), NOx (8%) and Hydrocarbons (14%) [6]. On the other hand, R in enter method (0.242) is equal to stepwise method (0.205), 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 both Table 3 shows a highly significant effect of some variables like wind speed compared to the other meteorological parameters for measuring the ozone. Parameter Sig (P_{value}) from Table 3 shows amount of relation between ozone and meteorological parameters. For example, Table 3a shows that wind direction has higher effect on ozone than rainfall which is the same as the results of Tehran city [23].

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 autumn models are significant. Stepwise methods show those meteorological parameters which are most important during these seasons for estimating the pollution. Among the models, spring models have the higher R compared to the other seasonal models. R in all seasonal models

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

Season	Enter method	R	Stepwise method	R
Spring	$=85.340 + (-1.351)\ T_{(max)} + (-0.884)\ T_{(min)} + (-0.436)\ WS_{(mean)} + (-0.009)\ WD_{(max)} + (-.154) + (-0.748)\ R + (0.692)\ E$	0.792 (significant at 0.01)	$=91.286 + (-1.745)\ T_{(max)} + (-1.065)\ R$	0.763 (significant at 0.01)
Summer	$= 21.381 + (0.260)\ T_{(max)} + (0.167)\ T_{(min)} + (-0.580)\ WS_{(mean)} + (-0.003)\ WD_{(max)} + (-2.276)\ R + (0.715)\ E$	0.545 (significant at 0.01)	$= 30.87 + (-0.708)\ WS_{(mean)} + (1.154)\ E$	0.511 (significant at 0.01)
Autumn	$= 36.608 + (.083)\ T_{(max)} + (-.058)\ T_{(min)} + (-.694)\ WS_{(mean)} + (0.011)\ WD_{(max)} + (-0.029)\ R + (0.071)\ E$	0.268 (Not significant	No variables were entered into the equation	
Winter	$= 34.896 + (-0.476)\ T_{(max)} + (2.001)\ T_{(min)} + (0.594)\ WS_{(mean)} + (0.003)\ WD_{(max)} + (-1.888)\ R$	.463 (significant at 0.01)	$= 30.558 + (1.884)\ T_{(min)}$	0.419 (significant at 0.01)

Note: $T_{(max)}$ = Temperature (max), $T_{(min)}$ = Temperature (min), $WS_{(mean)}$ = Wind speed (mean), $WD_{(max)}$ = Wind direction (max), R = Rainfall, E = Evaporation

except autumn models is higher compared to the annual models, also indicating that relations between the pollutant and meteorological parameters are stronger than whole year during the seasons.

To test which annual model is better to use, RMSE (Root Mean Square of Error) is calculated for the different linear models of enter and stepwise and nonlinear model. Predicted amounts using the different annual models for 24 days during 2012 are calculated and compared with the observed data during those days using RMSE Eq. 1:

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

O_{obs}: observed ozone value
O_{Pre}: predicted ozone value using model

The values of RMSE in both linear models; enter (11.02) and stepwise (10.52) show capability of stepwise model in predicting ozone amount compared to enter model. This result which is same as the results of other studies [3, 23, 24] indicates for predicting the most of air pollutants such as ozone. Maybe we consider only stepwise linear models which need less data and also the calculation is easier compared to the enter model.

CONCLUSIONS

In the current research, air quality analyses for Isfahan, were conducted for ozone (O_3). Isfahan is one of the polluted cities in Iran. So it needs to carry out ambient air quality analysis in the city. Results showed that there were significant relationships between O_3 and some meteorological parameters. Based on these relations, different multiple linear regression equations for O_3 for annual and seasonal conditions were prepared. Results showed that among different prediction models, stepwise model was the best option. Also, different variations in concentration during day, months, and seasons were observed. It was concluded some amounts for concentration of O_3 in afternoon (especially in cold months) showed that the concentrations of O_3 are upper than primary standards showing unhealthy condition.

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COMPETING INTERESTS

The authors declare that they have no competing interests.

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ETHICAL CONSIDERATIONS

The manuscript is original work of authors. All authors agree to submit their manuscript to JAPH. The authors confirm that the manuscript have not been submitted or published elsewhere in any language.

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