RESEARCH ARTICLE

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Relationship of Formaldehyde Concentration in Ambient Air with CO, NO_2, O_3, Temperature and Humidity: Modeling by Response Surface Model

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Background & Aims of the Study: Exposure to formaldehyde in ambient air has attracted a great attention, due to harmful health effects. This study was aimed to determine formaldehyde concentration in winter and spring seasons, in Azadi square region, Tehran, and the relation of variations of CO, NO_2, O_3, temperature and humidity with formaldehyde concentration was modeled based on Response Surface Methodology.

Materials & Methods: This cross-sectional study was conducted in 2014–2015 in Tehran, Iran. For measuring the formaldehyde concentration, NIOSH3500 method was employed. The concentration of formaldehyde was detected at 580 nm wavelengths by PerkinElmer LAMBDA spectrophotometer model of 25UV/Vis. Data of CO, NO_2 and O_3 concentration were attained from Tehran Air Quality Control Company. SPSS 16 and Design Expert (version 7) were used for analyzing data.

Results: Results showed the concentration of formaldehyde in the spring was on average 4.7 ppb more compared to winter season. The Model fitted for the prediction of formaldehyde showed a significant p-value (<0.001). Moreover, the R^2 and Adj-R^2 values were obtained about 0.8237 and 0.7607. In this model, it is observed the parameters of CO, NO_2, O_3 and temperature has a direct relation with the variations of formaldehyde, and humidity has an indirect relation.

Conclusions: Results indicated formaldehyde concentration in spring season is on overage higher than winter spring. The fitted model showed the CO, NO_2, O_3 and temperature is in a direct correlation with formaldehyde changes in ambient air, and humidity is in an indirect correlation.

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Background

In the last decades, air pollution in ambient air has become as one of the important and concerned environmental issues, because people information and sciences have grown increasingly in relation to the undesirable effects and risks of exposure to air pollution for human health (1). Formaldehyde (FA), a gaseous pollutant in ambient air, is well known in terms of aspects of its detrimental health effects (2). This is one of the main chemical of aldehydes family maybe exposed to human in indoor and outdoor environment, while is so toxic, stimulant and flammable (3). This compound mainly is used in order to the determination and awareness of atmosphere oxidation potential (4). Vehicles are the main resource of carbonyl compounds emission such as FA in urban regions, and the emission amount of FA is depended to fuel formulation, air to fuel ratio, and the contribution of ethanol and methanol in fuel (5,6). Among the groups of volatile organic pollutants playing the fundamental roles in photochemical phenomena, aldehydes have been recognized as an important group (7). FA, as intermediate product, also is formed due to the oxidation of hydrocarbons and volatile organic compounds under sunlight, being considered as a major resource of free radicals. As a result, photochemical processes are known as the other important source in producing and removing FA (8). Acute exposure to FA can result in numerous complications such as eye, respiratory system, and skin irritation, and in the case of permanent exposure, it is probable to appear chronic diseases, for examples a variety of cancers (4,9). U.S. National Toxicology Program and the International Agency for Research on Cancer (IARC) based on epidemiological studies have both introduced FA as a major agent in increasing leukemia risk (10). FA concentration in ambient air without the main emission resources is below 1 ppb, while in urban regions, the concentration is varied in the range of 1-25 ppb (11,12). In heavy traffic or temperature inversion, it is probable that FA concentration even increases by 100 $\mu g/m^3$ (13). The FA level of 0.03 mg/m^3 has been reported as the maximum permissible exposure for human in ambient air (14). In the study of Cerón-Bretón et al (2015), in which the seasonal and diurnal variations of carbonyl and criteria pollutants were evaluated in Monterrey, Mexico, it was found that the FA concentration in ambient air is about 35.74 and 33.67 in spring and winter, respectively (15). In the study of Granby et al (1997) in Copenhagen, Mexico, the FA concentration in winter season was reported nearly 2.6 ppb (8).

Aims of the study:

Since, Tehran city in terms of outdoor air pollution is in unhealthy condition, especially in winter season, it is expected that the FA concentration in the ambient air of this city, is high amounts, due to highly heavy traffic. Considering the undesirable influences of this compound on human health, it is very important to measure and determine exposure concentrations of human to the pollutant in ambient air in Tehran city. In the current study, the comparison of FA concentration between winter and spring seasons was firstly evaluated, and then relation between the factors of NO_2, CO and O_3, humidity and temperature with FA concentration was surveyed by using response surface methodology (RSM) (Design expert 7 software).

Materials & Methods

Site description:

This is a cross-sectional study carried out to determine FA concentration in ambient air of Azadi square (N"58'41°35، E"23'31°51), Tehran city, in 2014-2015. Fig.1 showed the sampling site, along with the effective agents in producing FA in ambient air. Overall, a total of 20 samples in the seasons of winter and spring were taken, and the period of sampling time took 180 minutes (9 to 12 AM). The sampling was conducted by personal sampling pump SKC (DELUXE, USA) calibrated at the flow of 1L/min for 180 L sampling volume. Two impingers, including back and frond impingers, were used for sampling operation, containing 20 ml bisulfate sodium ($NaHSO_3$ 1%) solution, being connected to pump by soft and flexible tube. Between impingers and pump, a filter with a 0.45-micron pore size was applied in order to trapping the mist or droplet, which may be thrown into pump. Moreover, the PTFE filter was fitted to the intake in order to prevent entering dust particles to the absorbent solution inside the each impinger. After end of sampling, samples were transferred to low-density polyethylene bottles, being shipped to laboratory.

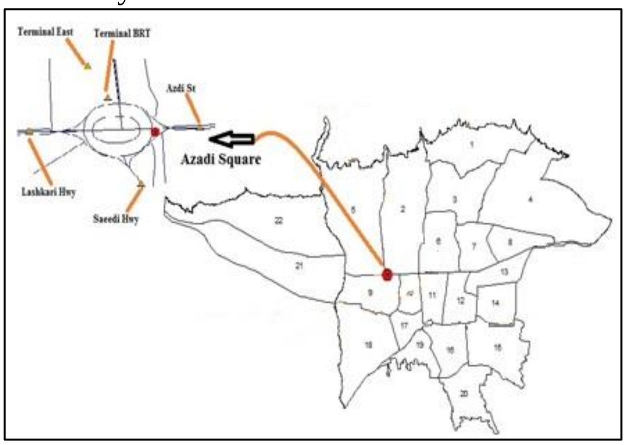

Figure 1) the location of sampling site to determine formaldehyde concentration, along with the heavy-traffic streets near to the sampling site

Analytical method:

NIOSH 3500 method was employed to measure the FA concentration in the collected samples. The solution of each sample was poured into 25-ml graduated cylinders to measure the accurate volume of the solution of both front and back impingers. After that, a 4-mL volume of solution was added to a flask, and then a 0.1-mL volume of Chromotropic acid 1% was poured into the flask and completely stirred. Finally, 6 mL of sulfuric acid 98% was slowly added into the flask and again stirred. After completely mixing, the solution was heated into a water bath for 15 min at 95°C temperature and then was cooled at room temperature for 2 hours. Spectrophotometer (Perkin Elmer UV-Vis LAMBDA 25) at the 580 nm wavelength was used to detect the FA concentration. The Eq.1 was used to calculate the FA concentration as follows:

$$C\left(\frac{\mu g}{L}\right) = (M_f + M_b - 2M_b)/V \quad (1)$$

Where, Mf, Mb and Mb are the μg of FA in front, back and blank impingers and V denotes air sampling volume (L), respectively.

In order to the determination of humidity (%), temperature (°C), Humidity/Barometer/Temp Meter (model PHB-318) was employed, and the hourly overage concentrations of CO, NO_2 and O_3 were attained from Air Quality Control Company. The software of SPSS (paired t-test analyses, with a significant level<0.05) and Design Expert7 (RSM method) were used to analyze the data.

Results

Seasonal variation of FA concentration:

The results of the average comparison of FA concentration between the seasons of winter and spring have been given at table 1. As showed in the table, the FA concentration in spring season is on overage 4.7 ppb (CI: -1.68, -7.72) higher than that in winter season. It should be noted the average of FA concentration in winter and spring seasons was observed as 18.1 and 22.8 ppb, respectively.

Statistical Analysis and Model Fitting:

By making a regression between the variations of CO, NO_2, O_3, temperature and humidity parameters with FA, a significant model (F-value=13.08 and p-value<0.001) was fitted, which the results of this model are given in the table 2 and 3.

Table 1) The average comparison of formaldehyde concentration in winter and spring seasons

Sampling season	Mean concentration (standard deviation) (ppb)	Mean difference (ppb)	95% confidence interval of the		p-value
			upper	upper	
winter	18.1	-4.7	-7.72	-1.68	0.006

spring	22.8

Table 2) The levels of input variables and actual and predicted FA concentrations in ambient air of Azadi square region, Tehran city

NO_2	CO	O_3	Temperature	Humidity	Actual FA concentration	Predicted FA concentration
36.95	4.136	0.0142	7.9	0.28	15	13.72
58.55	4.148	0.0129	12.3	0.39	19	19.03
73.75	4.224	0.043	12.7	0.39	20	23.33
25.95	2.964	0.0103	11.8	0.236	11	9.40
39.37	4.576	0.0177	9.9	0.306	17	17.02
46.58	4.224	0.0201	8.2	0.226	16	16.77
73.21	5.904	0.0224	3.5	0.368	28	24.49
39.37	3.92	0.0248	10.6	0.254	17	15.45
49.55	4.84	0.0295	12.9	0.308	19	22.10
48.15	4.486	0.0301	12.8	0.232	19	21.12
33.75	2.992	0.0366	18.9	0.141	16	16.97
52.5	3.168	0.0431	27.5	0.178	25	25.96
32.2	3.608	0.0413	23.4	0.203	19	21.42
23.71	2.376	0.0319	25	0.19	11	15.45
29.37	3.696	0.0413	26.2	0.214	23	22.81
36.75	2.992	0.0448	27.3	0.182	24	22.26
49.85	3.344	0.0449	31.6	0.133	29	29.16
40.75	2.992	0.0378	24.8	0.228	24	20.80
39.2	2.816	0.0537	26.7	0.224	26	21.46
40.85	3.784	0.0531	32.2	0.108	31	30.28

Table 3) ANOVA results for the model predicting FA concentration in ambient air of Azadi square region, Tehran, Iran

Factor	Sum of Squares	F Value	p-value
Model	498.29	13.08	< 0.0001
NO_2 (ppb)	38.40	5.04	0.0414
CO (ppb)	75.01	9.85	0.0073
O_3 (ppm)	0.79	0.10	0.7527
Temperature (°C)	68.55	9.00	0.0096
Humidity (%)	4.09	0.54	0.4756
Residual	106.66		
	R-Squared	Adj R-Squared	
	0.8237	0.7607	

The coefficient of determination (R^2) of this model was obtained as 0.8237, which means the model can predict 82.37% of FA variation. The Adj-R^2 was also obtained as high as 0.7607, which is desirably close to R^2 value, demonstrating the model was well fitted. Fig 2(a) showed the normal plot of residuals, where most of the residuals place on or near the straight line and a great part of this distribution was placed in the median of the line. This type of distribution illustrates a normal distribution of residual values. Fig 2(b) depicts the residual values VS. predicted values, where approximately half of the residual values place above, and other half below. This distribution illustrates the average of these values is close to zero and the residual values variations do not follow a particular trend, so that confirms the model adequacy.

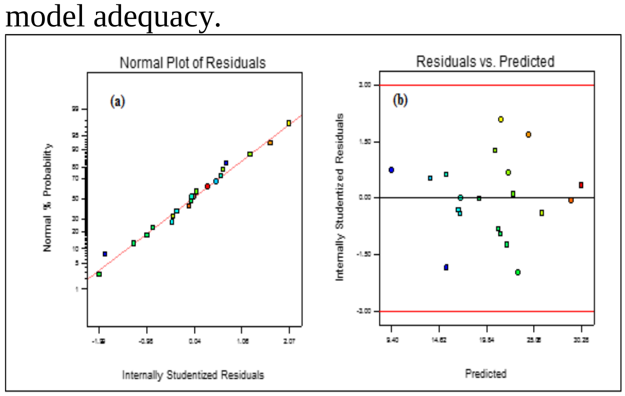

Figure 4) The adequacy plots of the fitted model for the model predicting the FA concentration in ambient air

Finally, an equation (2) was used to give the regression polynomial model revealing the relation between independent factors and FA concentration as follows:

$$R(\%) = -12.543 - 0.181NO_2 + 4.222CO + 33.057O_3 + 0.585\ \mathrm{Temp} - 10.624\ \mathrm{Hu} \quad (2)$$

Response surface and plot contour:

The Fig.3 shows the FA variations in ambient air and its relation to the other studied parameters. Fig.3 (a) exhibits the contour and response surface plots of variations of FA concentration as a function of CO and NO_2 variations. As it can be observed in this Fig, with increasing CO, NO_2 concentrations, the FA concentration enhances; therefore, there is a direct relation between variations of CO and NO_2 and FA concentration. The Fig.3 (b) exhibits the correlation between the variations of CO and O_3 with FA concentration. The relation of FA concentration variations with O_3 is direct but weak. The relation between temperature and humidity with FA concentration has been showed in Fig.3 (c). It is worth to noting the temperature got a direct relation with FA variations, whereas the humidity indicated an indirect relation.

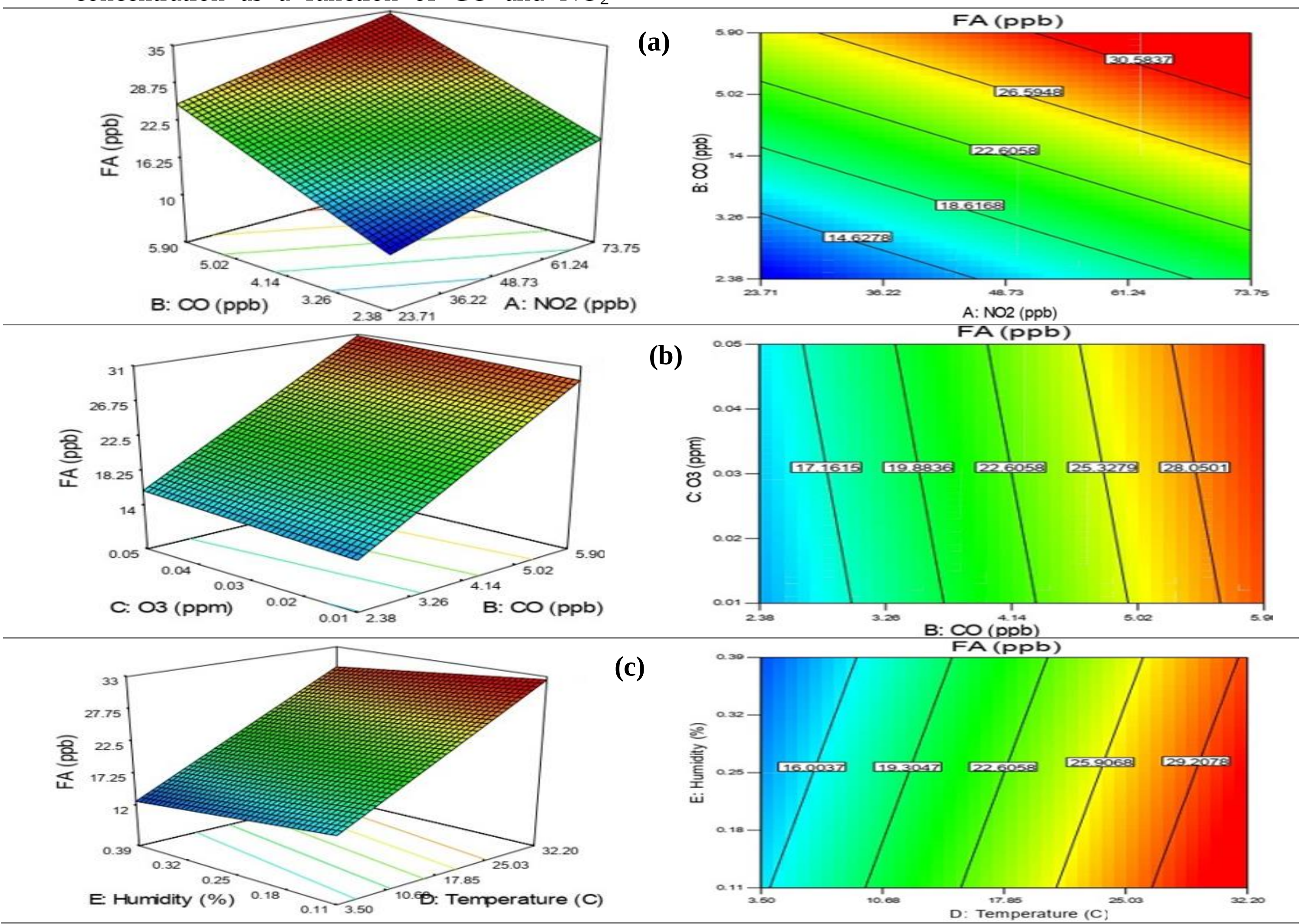

Figure 3) 3D and contour plots of FA concentration in ambient air of Azadi square region, Tehran, Iran, (a) CO concentration VS. NO_2, (b) CO VS. O_3, and (c) humidity VS. temperature

Discussion

In the survey of FA concentration in two studied seasons, it is observed that FA concentration in the spring season is higher than that in the winter season. With the change of season to spring and more and better distribution in this season, it is expected FA concentration decreases, whereas in turn, the FA concentration was higher in spring season. This increase can be attributed to the intensity increment of photochemical reactions known as the second important route in producing FA (the first route is incomplete combustion) (16). The photochemical reactions enhances with the change of season from winter to spring concluding the atmospheric condition variation, especially increasing temperature. Therefore, with the presence of hydrocarbons and VOCs released from exhausts of vehicles to ambient air and photochemical reaction intensified in spring, it is expected the FA concentration in spring take the higher amount (17). Therefore, the increase of photochemical reactions in spring than winter can be the main agent of the FA concentration difference in the two seasons. Possanzini et al (2002) found the main difference of FA concentration in ambient air of Rome city, Italy between two seasons of summer and winter is resulted from the increment of photochemical reactions in summer season (18). They also reported these reactions involve about 85% and 35% of producing FA in summer and winter seasons, respectively. Sin et al (2001) observed the highest concentration of FA happens in summer season (19). At the survey of the studied factors, it was observed all the factors; apart from humidity have a direct relation with FA concentration. The robust relation between the NO_2 and CO with FA concentration variations indicates that in addition to the photochemical reactions, direct emission from the exhausts of vehicles is another one of the most important route producing FA, because both CO and NO_2 were released from vehicles' exhaust. So that theirs relation with FA indicates the existence of a common source (8). In the study of Baez et al (2001), it was observed that there is a power relation between CO and FA variations, where the obtained R^2 in this study for the hour 8 to 10 AM was about 0.591 and for the hour 10 to 12 AM about 0.885 (20). On the other hand, the direct relation between O_3 and FA variations showed the photochemical processes have a substantial role in producing FA in ambient air, why the source of O_3 is the photochemical reactions between HCs and NO_2 under sunlight (8). Possanzini et al (2002) obtained the amount of R^2 between FA and O_3 concentration about 0.58 in summer season (18). This result (the effect of photochemical and sunlight in producing FA) can be confirmed by the direct power relation between temperature and FA concentration, and also temperature and the intensity of photochemical reactions. Mohamed et al (2002) in their study found a direct relation between carbonyl compound and temperature (21). In the study of Seo and Baek (2011) do not reported a significant relation between FA and humidity, while in the current study, an indirect relation was observed; however, this relation was not significant (22). Finally, the ability of the fitted model should be noted, because it can appropriately indicate the effect percentage of studied factors on FA concentration variations. This model showed to have a suitable power in predicting a great part of FA concentration variation in ambient air. As result, it can be concluded that in order to variation prediction of a number of dependent parameter in ambient air, from a series of independent variables could be used under modeling

Conclusion

The results showed the FA concentration in spring season is on overage higher compared to that in winter season. The fitted model showed a good prediction of FA concentration variations in ambient air. The developed model indicated that the variables of CO, NO_2, O_3 and temperature had a direct relation with FA variations, while in turn, humidity demonstrated an indirect relation. Overall, by modeling, the independent studied parameters can predict FA variations as well.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

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