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Prediction of long-term NH_3 concentration using the superstack model

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Abstract

The long-term multiple-point source plume model, described by Ahmad and Bouhamra was applied to describe the dispersion and predict the concentration of NH_3. Different NH_3 emitting stacks from all chemical and petrochemical industries in the Shuaiba Industrial Area in Kuwait were represented by one superstack. The model prediction was compared with the measurements of seven monitoring stations inside and outside Shuaiba. The model gave the best concentration prediction at stations between 1 and 10 km away from the source. Measurements of the stations lying outside this range were underestimated by one order of magnitude. The model was also used to predict NH_3 concentration in Kuwait city, Kuwait International Airport and Ahmadi city where NH_3 is not monitored.

The normalized mean square error (NMSE) and the weighted average fractional bias (FB) for the monthly values of sixteen months at the seven stations ranged from 0.8 to 13.3 and from -1.6 to 1.4, respectively. The mixing height (L) was found to have a significant effect on the model prediction up to an L value of 350 m. Beyond this value the mixing height showed no significant effect on concentration prediction.

1. Introduction

The atmospheric dispersion of effluents or pollutants from vents and stacks depends on many interrelated factors. These factors include the physical and chemical nature of the effluent, the meteorological characteristics, source properties, location and the nature of the terrain downwind. The ability to predict the pollutant concentrations and relate them to their source is essential if the air quality standards are to be attained and maintained. The necessity for air pollution prediction has tremendously increased in the recent decade, especially with the increasing interest in the pollution early warning systems. Several attempts to develop different mathematical models describing the distribution of contaminants released into the atmosphere are available in

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the literature. Several workers have studied the dispersion of SO_2 since it is the major constituent of the flue gases emitted from almost all power plants and industrial processes, particularly the combustion of coal and oil. However, among these published studies and publicly available models, very few have considered multi-stack sources. This type of source is the most common in the industry. The interaction between the plumes coming out of the different stacks is a very important factor in modeling such sources. In a previous work [1] a new long-term multiple source plume model, based on a modified form of the Gaussian dispersion equation, was developed. This model was applied to the dispersion of SO_2 gas emitted from multiple sources in the major industrial area in Kuwait. All stack properties and emission variables were represented by a single stack using the mixing rule. The prediction of the multiple-source model was compared with measured SO_2 concentrations at different monitoring stations inside the industrial area and in one residential location. The model was found to be valid for and applicable to short and long distances.

The validity of the Gaussian model has been studied by many investigators. Calder [2] found that mathematically consistent values could be obtained by the use of a Gaussian plume model modified for limited urban mixing layer. Miller and Hively [3] reported that the annual average of gaseous pollutant concentrations in the air over flat terrain can be predicted within a factor of 2 to 4 using the Gaussian plume model. Thomas and Kumar [4] developed a statistical model for NO_x and SO_2 pollutant from multiple sources. Hanna et al. [5] evaluated fourteen publicly available models using ammonia and hydrogen fluoride field data. Their study showed that many of these models are capable of predicting the downwind plume centerline concentrations at distances of a few hundred meters within a factor of two. The studied models showed better predictions at distances more than 100 m and less than 1000 m from the source. However, four of the models overestimate the NH_3 concentration in the Desert Tortoise 100 m arc by one order of magnitude. Even the Gaussian based model (ALOHA) which was expected to underestimate gave an overestimation by the same order of magnitude.

Ammonia is the primary basic gas in the atmosphere. Natural sources such as animal waste or biological decay contribute significant amounts of NH_3. On the other hand, the man-made sources, e.g., waste treatment plants and petrochemical industries, such as the urea and the fertilizers production plants, form another major source of NH_3. The gas-phase chemistry of NH_3 in the atmosphere is not yet well understood. Ammonia is not stable and can be readily absorbed by surfaces such as water and soil; in addition, its residence time in the lower atmosphere is quite short. Wet and dry deposition of NH_3 is probably the main atmospheric removal mechanism for NH_3. There is no direct way to measure the amount of NH_3 in air; actually, the total nitrogen and NO_x compounds are measured and then the concentration of NH_3 is calculated. All of the above-mentioned factors make the prediction of NH_3 dispersion in the atmosphere not an easy task.

The negative effect of ammonia on the environment as a primary gaseous pollutant and its potential role in the formation of other secondary pollutants (for example ammonium nitrate aerosols) have been given little attention in air pollution prediction studies. The monitoring and modeling of the dispersion of NH_3 is very important if the chemistry of ammonia in the atmosphere and the mechanism of formation of ammonium nitrate are to be thoroughly studied. Gaseous ammonia and particulate nitrate are of great concern to many pollution protection bodies worldwide. Nevertheless, there are insufficient studies of NH_3 in the recent literature. In this study, the prediction of the dispersion of gaseous ammonia emitted from an industrial area where petrochemical, chemical and petroleum refining processes exist is presented.

The ability of the superstack model, described elsewhere [1], to predict NH_3 concentration was verified by comparing it to the monitored concentrations of ammonia in seven different stationary stations for sixteen months during the period January 1988–April 1989. The application of the model was then extended to predict the concentration of NH_3 in other selected areas in Kuwait where NH_3 is not monitored. All NH_3 emitting stacks from petrochemical and other industries in Shuaiba — a major industrial area in Kuwait — were considered. Comprehensive meteorological data for Kuwait were incorporated in this model. The study is thought to be an initiation phase for the investigation of the activity of NH_3 in the atmosphere and the mechanisms of formation of different nitrate aerosols in Kuwait.

2. Modeling

The presence of an elevated inversion layer strongly influences the ground level concentration downwind from the stack. Accounting for the stable layer and ground reflections can be made through the summation of the following terms shown in eq. (1). The end result is an expression of the form

$$C=\frac{Q}{2\pi\sigma_y\sigma_z u}\left[\exp\left(\frac{-y^2}{2\sigma_y^2}\right)\Sigma\left\{\exp\left[\frac{-(Z-H+2jL)^2}{2\sigma_z^2}\right]+\exp\left[\frac{-(Z+H+2jL)^2}{2\sigma_z^2}\right]\right\}\right] \tag{1}$$

where the summation is carried out from $j=-\infty$ to $+\infty$. This series converges rapidly for the j values ranging from -4 to $+4$. In Kuwait the height of the inversion layer (L) varies from day to night and it ranges from 60 to 400 m during the year. The horizontal standard deviation (σ_y) and the vertical standard deviation (σ_z) of the plume distribution were calculated using Martin's [6] expressions based on the dominant stability condition in Kuwait. The effective height, H, was calculated by considering four different models of the plume rise described in ref. [7].

The majority of the plume rise equations contain a momentum term and a thermal bouncy term. The former accounts for the vertical momentum of the

stack gas due to its own velocity (v_s), and the latter accounts for the difference between the stack and ambient temperatures (T_s and T_a). There is an implicit effect of the gas density on the dispersion model prediction since it affects the velocity of the stack gas. The gas velocity is inversely related to the molecular weight of the gas (M) as shown in the following equation:

$$v_s = \frac{mRT}{MPA_s} \tag{2}$$

The heavy gas effect of NH_3 on the dispersion equation and its impact on the model estimation will be accounted for in the evaluation of the gas velocity using eq. (2).

3. Program structure

3.1. Estimation of superstack properties and location

The full description of the point sources such as stack heights, diameters, temperatures of effluent gases, emission fluxes and operation hours were fed into the main program. The model estimates the location and the properties of the superstack using the concept of the mixing rule as described by Ahmad and Bouhamra [1]. Typical ranges of the stack properties are shown in Table 1.

3.2. Meteorological data

Numerous data of wind speed and wind direction were taken from one of the monitoring stations of the Meteorological Department of the General Administration of the Civil Aviation. These data, in addition to the height of the inversion layer, are measured every 15 min. A subroutine in the model was used to obtain the monthly average of the wind speed, wind direction, relative humidity and ambient temperature. The average ambient temperature was then fed into the plume rise subroutine.

TABLE 1

Stack information

Property	Units	Min.	Max.
Stack height	m	10.1	72.2
Exit diameter	m	0.1	0.5
Stack temperature	°C	20.0	100.0
Emission rate	g/s	1.0	82.3
Volume flow	m^3/s	0.2	0.8

3.3. Monitoring stations

The model prediction was compared to the measurements of seven monitoring stations. Six stations were located inside Shuaiba (stations 2, 3, 4, 5, 7 and 8) and one station outside Shuaiba (station 9) in Riqqa residential area. The measured concentrations at these stations were obtained from the monthly reports of the Environmental Protection Center of the Public Authority of the Shuaiba Industrial Area (SIA) and the Environmental Protection Department (EPD) of the Environmental Protection Council (EPC). The locations of the monitoring stations and the superstack determined by the model, in terms of (x, y) coordinates, are represented in Fig. 1.

3.4. Rotation of the coordination of the receptors according to the location of the superstack and wind direction

The data obtained from the Meteorological Department define the wind direction as angle (θ) where θ equals zero if the wind is blowing from north, and increases clockwise. In this model, the west direction ($\theta = 270°$) was selected as a reference direction since it corresponds to the positive Cartesian x axis. The angles of the actual wind direction were then corrected according to the reference direction by subtracting from 270° to rotate all angles to the x axis. A subroutine in the program performs such a rotation in order to unify the coordination of the source and receptors so that they all refer to one origin.

3.5. Concentration calculations

The model utilizes the Gaussian expression given in eq. (1) to calculate the ground level concentration. The wind speed, which was reported at the standard elevation, was corrected in this model to the corresponding height of the superstack. Most of the correlations describing the horizontal and vertical standard deviations (σ_y and σ_z in eq. (1)) for atmospheric dispersion predictions

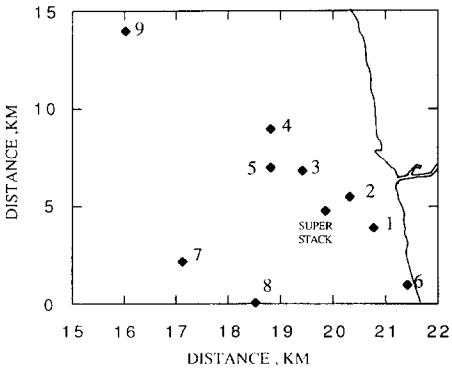

Fig. 1. Locations of the ammonia superstack and the monitoring stations.

are based on a standard sampling time of 10 min. In order to correct for the sampling time of the monitoring stations, the following formula, described by Wark and Warner [7] was used.

$$C_2 = C_1\left(\frac{t_1}{t_2}\right)^q \tag{3}$$

where C_2 is the corrected concentration, C_1 is the estimated concentration, t_2 is the sampling time in minutes, t_1 is 10 min, and q is a positive constant between 0.17 and 0.2. Eq. (3) corrects for the sampling time between a few minutes and two hours when estimating the concentration of a single source.

A sensitivity analysis for a sampling time ranging from 5 to 20 min and q values of 0.17, 0.18, 0.19 and 0.2 was conducted. The study showed that the model estimation is not sensitive to the sampling time correction. A 100% increase in the sampling time was corresponded by only 13% correction in the concentration estimation.

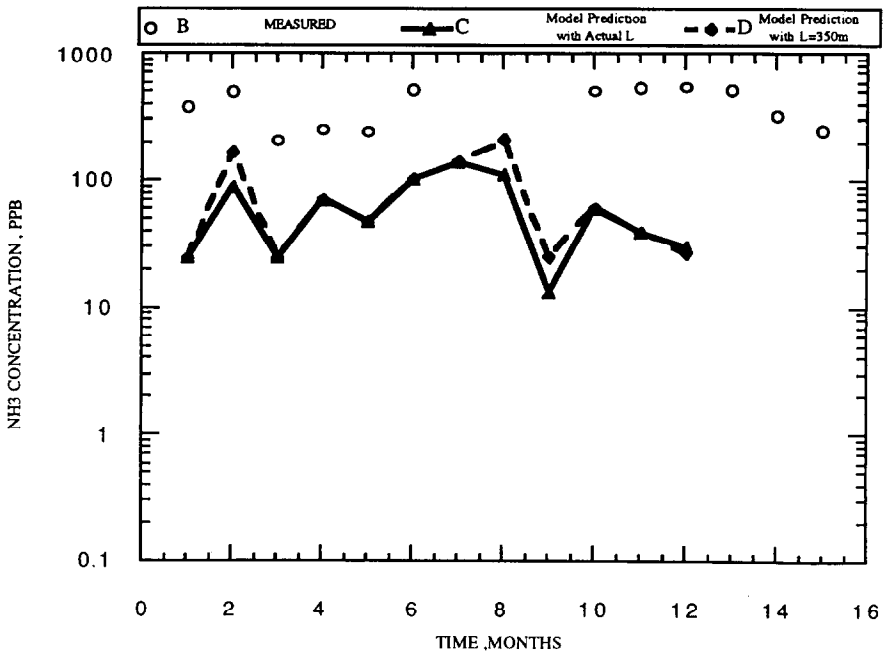

Fig. 2. Monitored ammonia concentration and model prediction in station 2 in Shuaiba Industrial Area in the period of January 1988–April 1989.

4. Results and discussion

4.1. Qualitative analysis of model results

The results of the superstack model were compared to the measured concentrations of seven monitoring stations over the period January 1988–April 1989 as shown in Figs. 2–8. These figures show two sets of predictions, one when the actual mixing height (L) was used (which varied monthly) and the second when a fixed mixing height ($L=350$ m) was selected. This fixed value of L was the value above which the mixing height showed no significant effect on the concentration as will be discussed below. Good predictions were obtained in some stations such as stations 4, 5, 7 and 8 shown in Figs. 4, 5, 6 and 7, respectively. On the other hand, the model underestimated the concentrations in stations 2, 3 and 9 as shown in Figs. 2, 3 and 8, respectively. For the monitoring stations which were very close to the source, such as stations 2 and 3, at distances less than 1 km, the model underestimated the concentration by one order of magnitude as shown in Figs. 2 and 3. Fig. 8 also shows that the model underestimated the measured concentration by one order of magnitude at station 9 which was more than 10 km away from the source. This behavior

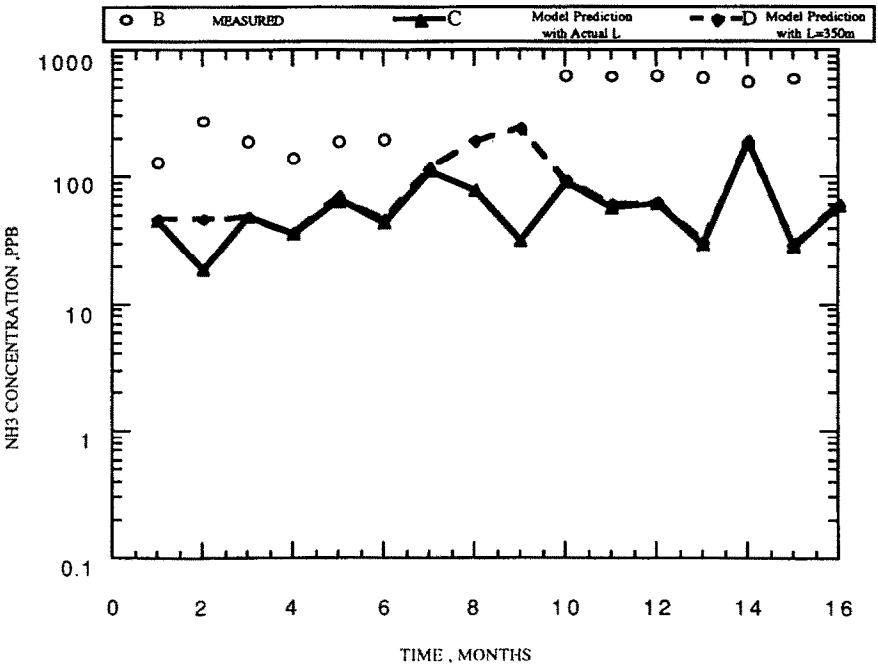

Fig. 3. Monitored ammonia concentration and model prediction in station 3 in Shuaiba Industrial Area in the period of January 1988–April 1989.

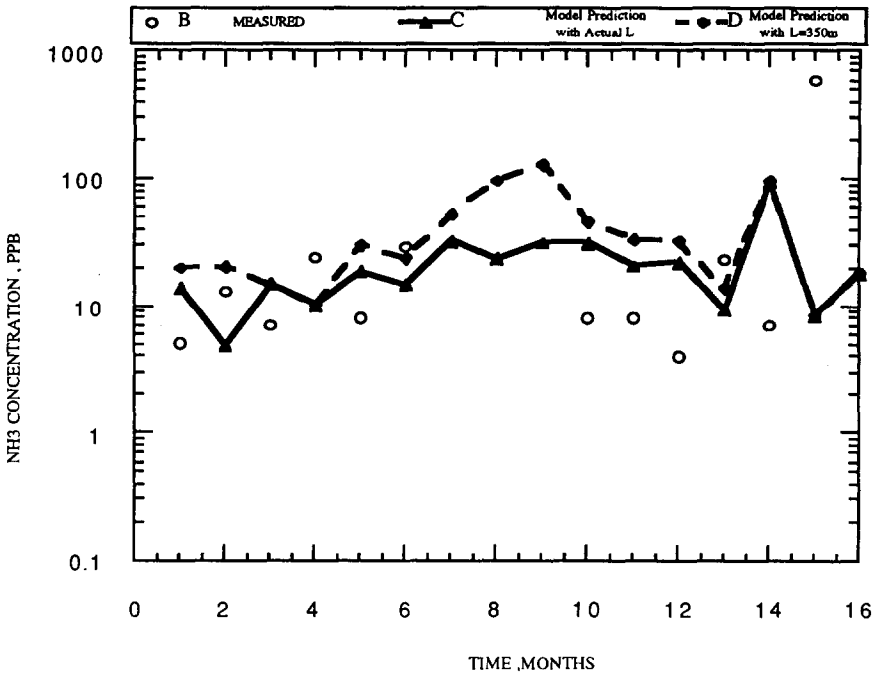

Fig. 4. Monitored ammonia concentration and model prediction in station 4 in Shuaiba Industrial Area in the period of January 1988–April 1989.

was also observed and discussed by Hanna et al. [5]. Since the Gaussian model assumes empirical formulas in which both σ_y and σ_z approach zero as x approaches zero, the predicted concentration becomes unrealistic near the source. Fig. 9 shows the monitored and predicted concentrations versus distance. The model prediction line showed a large deviation from the measured data as the distance between source and receptor approaches zero and as it becomes very large.

The underestimation of the model was explained by two major factors: the limitations of the Gaussian formula and possibly the presence of other NH_3 sources than the NH_3 emitting stacks in the area. These sources could be the storage facilities of urea, fertilizers and other N_2-containing compounds available in the area. Figs. 4 and 7 indicate an overestimation in the model estimation of $\frac{1}{2}-1$ order of magnitude for some months at stations 4 and 8. This was thought to be due to the failure of the model to account for the possibility of the particulates formation and the thermodynamic effects of nitrate aerosols and again to the limitations in the Gaussian model.

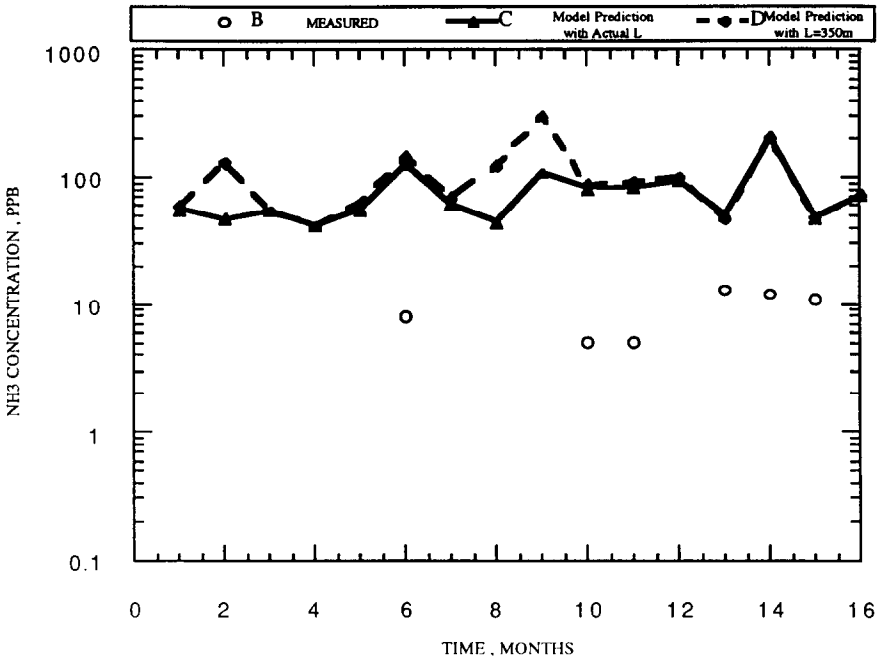

Fig. 5. Monitored ammonia concentration and model prediction in station 5 in Shuaiba Industrial Area in the period of January 1988–April 1989.

4.2. Quantitative analysis of model performance

In a similar way to the statistical analysis used by Gudivaka and Kumar [8] and Hanna et al. [5], the model was evaluated by calculating the normalized mean square error (NMSE) and the weighted average fractional bias (FB) using the monthly values. The NMSE ranges from 0.8 to 13.3 and the FB ranges from −1.6 to 1.4 for the seven stations. Fig. 10 shows these two statistical measures which indicates that the best predictions were for stations 4, 7 and 8 for distances between 1 and 10 km. These three stations fall in the block of −0.9 to −0.3 for FB and 0.1 to 3.5 for NMSE. The annual average of the NH_3 concentration was estimated at every station and compared with the measured data as shown in Table 2.

4.3. Extension of the model prediction

The model was used to predict the effect of only ammonia emitting stacks available in the Shuaiba Industrial Area (SIA) on some important locations in Kuwait where NH_3 is not monitored. The selected locations were

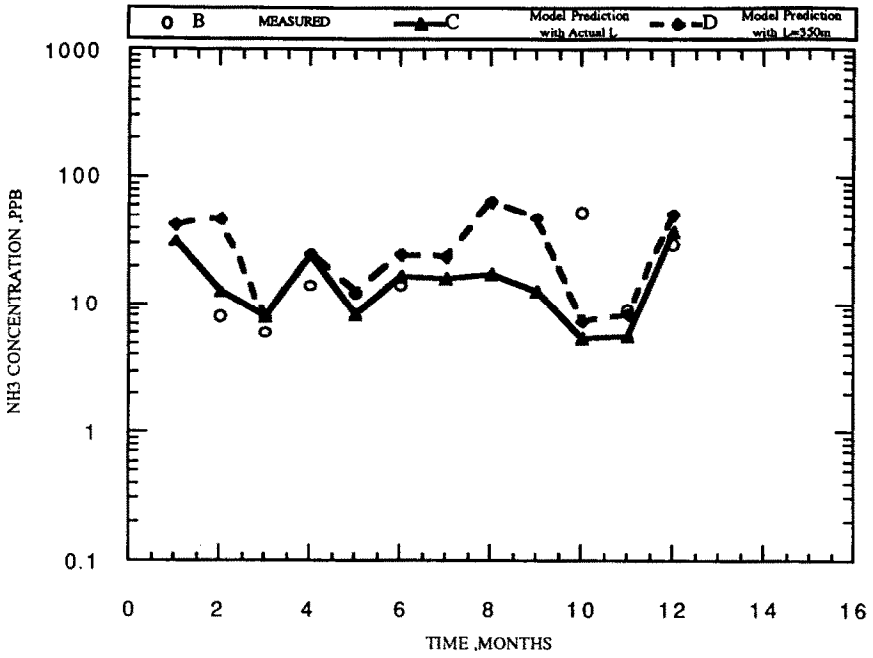

Fig. 6. Monitored ammonia concentration and model prediction in station 7 in Shuaiba Industrial Area in the period of January 1988–April 1989.

Kuwait city (the capital), Kuwait International Airport and Ahmadi city at distances of 45, 28.5 and 9 km to the north and west of SIA, respectively. The locations of these areas on the map are represented in Fig. 11. Table 3 shows the predicted concentrations at the selected locations compared to the estimated and measured NH_3 concentrations in the Riqqa residential area during the year 1988. In general, the data show that high concentrations in these areas could be found in September. The maximum predicted concentrations at Kuwait city, Ahmadi city, and Kuwait International Airport were 4.8, 22 and 8.5 ppb, respectively. The standard concentration of NH_3 in Kuwait, set by the Environmental Protection Council (EPC), is 800 ppb. Therefore, the predicted results indicate that NH_3 did not exceed the standard limit in any of these locations. Even if the underestimation of the model, which was at the most in the range of one order of magnitude, was considered, the estimated concentrations still give lower values than the standard concentration of NH_3. This indicates that industrial activities (not counting the storage facilities of N_2-containing compounds) responsible for NH_3 emission in the SIA has no potential impact on nearby areas.

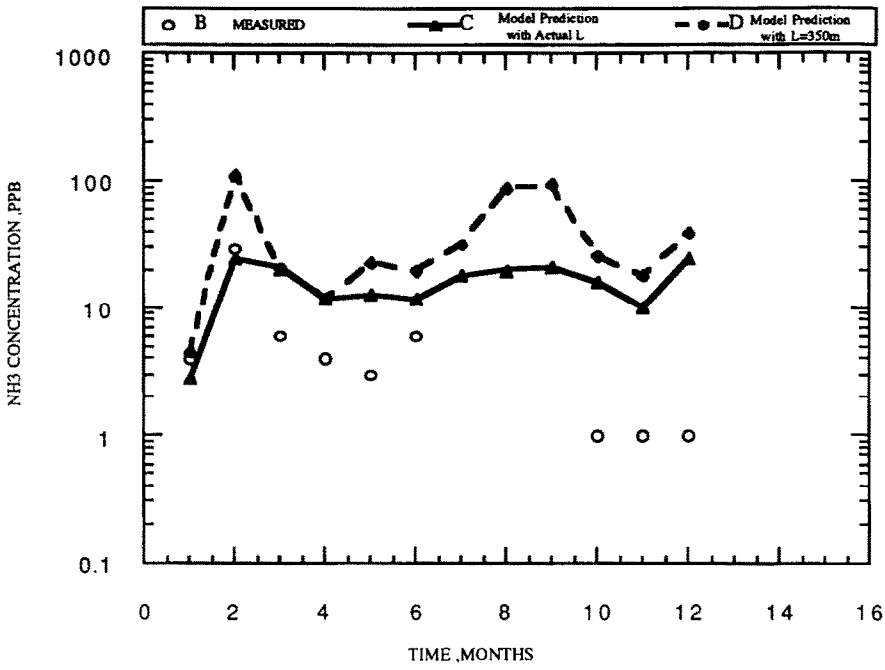

Fig. 7. Monitored ammonia concentration and model prediction in station 8 in Shuaiba Industrial Area in the period of January 1988–April 1989.

5. Effect of some parameters on the model performance

5.1. Extent of mixing height

In a previous work [1] it was concluded that two seasonal trends are greatly influencing the general dispersion of SO_2. These trends are due to the two major climatic seasons in Kuwait: summer and winter. It was also found that the inversion layer height or the mixing height (L) greatly affects the concentration prediction of the Gaussian model. Since this value varies from day to night, month to month and place to place, L must be read very carefully. In this model the mixing height information was taken from the Meteorological Department of the Public Administration of the Civil Aviation.

In order to study the sensitivity of the model to the mixing height, the model was executed for a number of arbitrarily selected L values. Table 4 shows the predicted concentrations at the seven stations corresponding to different L values as compared to the measured data. The selected mixing height values range from 70 to 500 m, which covers the range of variation of the mixing height in Kuwait. At low values of L, the dependency of the estimated concentration on the mixing height is fairly high, as about 30% decrease in the

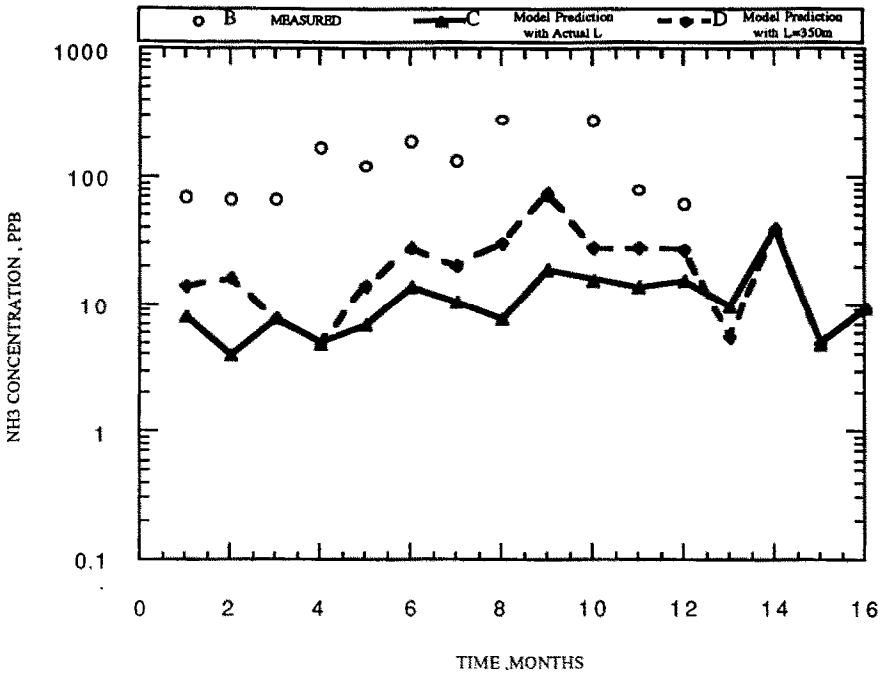

Fig. 8. Monitored ammonia concentration and model prediction in station 9 in Riqqa residential area in the period of January 1988–April 1989.

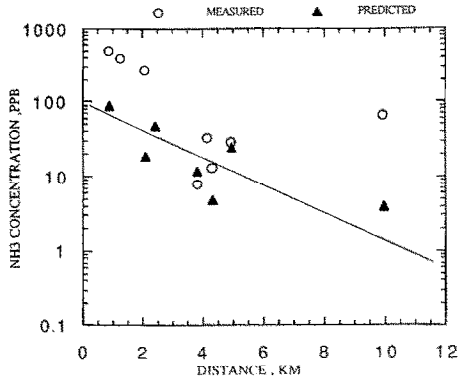

Fig. 9. Measured and predicted ammonia concentration versus distance from the source.

concentration corresponds to 40–50% increase in L value. This relation was weakened as L further increased. For station 2 a negligible effect was observed as L increased to above 150 m. Similarly a negligible effect of L was found at values of 250, 350, 300, 300, 350 and more than 500 m for stations 3, 4, 5, 7, 8 and

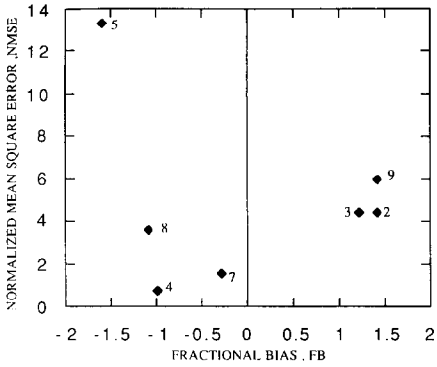

Fig. 10. Statistical analysis of the model prediction in the seven stations expressed as NMSE versus FB.

TABLE 2

Annual average concentration of NH_3 at the seven stations

Station	NH_3 measured concentration (ppb)	NH_3 predicted concentration (ppb)
2	397	50
3	395	64
4	13	24
5	9	106
7	15	17
8	8	23
9	130	25

9, respectively. Therefore a value of 350 m can be considered as the maximum mixing height above which the estimated concentration is not affected by this parameter. The same results were obtained in different months; however, just the results of one month are shown in Table 4. Beyond an L value of 350 m, the change in concentration was negligible.

5.2. Gaussian boundary extremes

The Gaussian plume model stated in eq. (1) for a source at elevation H from the ground could be reduced to the following equation for a ground level source and a receptor on the plume centerline:

$$C=\frac{Q}{\pi\sigma_y\sigma_z u} \tag{4}$$

Eq. (4) indicates that the model fails to predict the concentration when x approaches zero. Therefore, one solution to this problem would be the use of the

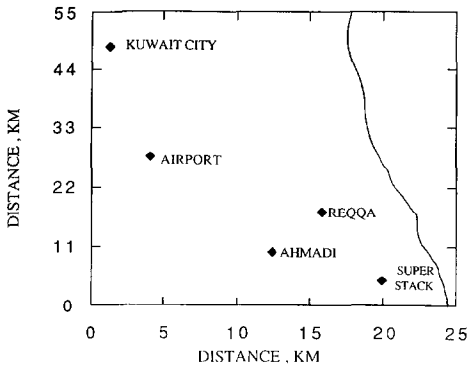

Fig. 11. Locations of the areas where ammonia is not monitored and the model used to predict the concentrations.

TABLE 3

Model prediction in locations that were not monitored in 1988

Month	Predicted NH_3 concentration				
	Kuwait city	International Airport	Ahmadi city	Riqqa	
				Predicted	Measured
January	2.0	2.9	8.8	9.7	70
February	1.0	5.3	22.0	5.1	66
March	1.4	1.9	4.0	4.5	67
April	0.9	1.8	6.0	2.6	167
May	1.9	3.8	5.5	10.5	121
June	3.3	8.5	5.5	11.9	188
July	2.7	2.3	8.1	17.1	134
August	2.3	2.6	11.5	22.9	285
September	4.8	5.9	17.8	40.0	71
October	4.4	3.0	8.2	25.4	278
November	3.6	3.7	5.0	18.6	79
December		4.5	7.5	18.6	62

following interpolation formula used by Hanna et al. [5]:

$$C=\frac{Q}{q_0+\pi\sigma_y\sigma_z u} \tag{5}$$

where q_0 is the initial volume flux (m^3/s). This forces the concentration to approach the initial concentration Q/q_0 at the release point.

5.3. Wind direction

The receptors which are directly downwind are more affected by the source than other receptors. The Gaussian plume model assumes the downwind

TABLE 4

Sensitivity test of the model prediction of the mixing height (L) at seven stations (January 1988)

Mixing height (L)	NH_3 concentration (ppb) at station						
	2	3	4	5	7	8	9
70	46.5	114.0	57.3	156.9	122.8	12.8	32.1
100	26.9	79.7	40.4	109.8	86.2	9.1	26.3
150	24.6	54.0	26.9	73.6	57.5	6.1	18.7
200	24.6	47.1	20.2	60.6	43.3	4.55	14.1
250	24.6	46.1	16.5	57.6	36.1	3.6	11.3
300	24.6	46.1	14.6	57.3	33.0	3.2	9.4
350	24.6	46.1	13.8	57.3	32.0	2.8	8.1
400	24.6	46.1	13.6	57.3	31.7	2.7	7.1
450	24.6	46.1	13.5	57.3	31.7	2.7	6.3
500	24.6	46.1	13.5	57.3	31.7	2.7	5.7
Measured NH_3 conc. (ppb)	379	128	5	N/A[a]	N/A[a]	4	7

[a] N/A No data available in this month.

direction as the positive x axis. Therefore, the exact information about the wind direction and its hourly variation is very essential. Our model incorporated data of the wind speed and wind direction that had been measured every 15 min. It was noticed that the predominant wind direction during the months considered is south-east. Fig. 12 shows the determined monthly wind roses for the year 1988.

6. Conclusion

The superstack model was used to predict the concentration of NH_3 at seven sites where NH_3 is measured and three sites where NH_3 is not measured. The model shows excellent prediction at four monitoring stations which were at intermediate distances from the source. The model, however, underestimated the NH_3 concentration at distances less than 1 km and more than 10 km by about one order of magnitude. The model was used to estimate NH_3 concentration due to NH_3 emission in the SIA at three major locations where NH_3 is not monitored; here no concentration above the standard value was observed. The model was found to be sensitive to the value of mixing height (L) up to a value of 350 m beyond which L has no significant effect on concentration.

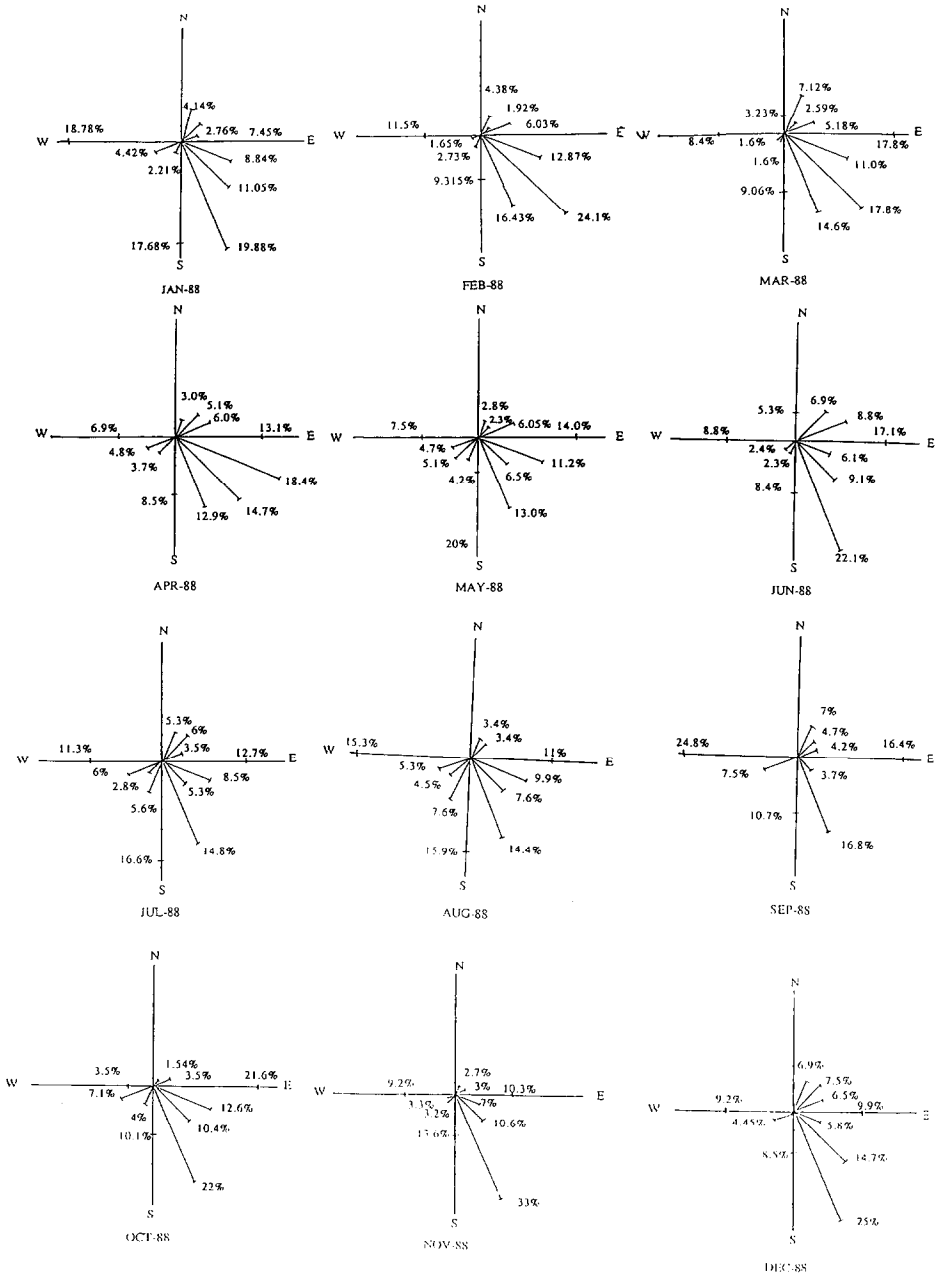

Fig. 12. The wind roses during the months of 1988.

Acknowledgement

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Notation

A	cross sectional area (m^2)
C	gaseous pollutant concentration ($\mu g/m^3$)
C_1	estimated concentration ($\mu g/m^3$)
C_2	corrected concentration for sampling time other than 10 min ($\mu g/m^3$)
D	stack diameter (m)
H	effective stack height (m)
m	gas mass flow rate (g/s)
M	gas molecular weight
P	total pressure (atm.)
Q	emission rate or volume flux (m^3/s)
R	gas constant
t_1	standard sampling time of 10 min
t_2	sampling time other than t_1 (min)
T	temperature (°C)
u	wind speed (m/s)
v	gas velocity
x, y, z	source and receptor coordinates (m)

Greek letters

σ_y	horizontal standard deviation (m)
σ_z	vertical standard deviation (m)
π	numerical constant (3.14)

Subscripts

0	initial conditions
a	ambient
s	stack

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