

# Environmental Management and Health

## **An analysis of pesticide impact on air quality, especially surface ozone**

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# An analysis of pesticide impact on air quality, especially surface ozone

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**Abstract** *The present study aims at shedding some light on the serious effect of insecure pesticides to the surface ozone as a secondary pollutant resulting from some photochemical reactions during the sunny days. The temporal variation in O<sub>3</sub> concentrations due to pesticide spray, the corresponding temperature and relative humidity have been monitored and discussed. The air quality index (AQI) for the maximum concentrations of O<sub>3</sub> within each day of study has also been deduced. The obtained results illustrated that O<sub>3</sub> concentrations had been increased after pesticide spray with different values from hour to hour and then began to decay after one day or more according to its concentrations. The second day had the highest concentrations of the O<sub>3</sub> including the maximum concentration, which was recorded at hour 14 local time. Furthermore, most of AQI values were restricted between harmful and very harmful index during the second days and only the third day of the first experiment. Moreover, temperature and relative humidity have significantly influenced ozone concentrations with positive and negative correlation coefficients, respectively.*

## Introduction

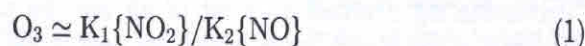
Pesticides, as is well known, play a serious role among the environment contaminating xenobiotics. First of all are the pesticide-exposed workers, humans, animals and plants, which are nearby the treated land. But the total number of those who may be endangered include those affected by the contamination of food, water, and air and indirectly through that sort of soil. Moreover, the toxicity of the pesticides, the organic carcinogenic components will be produced during the pesticide decomposition, photodecomposition and degradation by UV solar radiation. Many kinds of pesticides undergo photodecomposition and degradation in the environment hence they give rise to high concentrations of surface ozone and other hazardous pollutants.

One of the well known insecticides applied for cotton and other crops in Egypt is Lannate (Aly, 1989). Lannate represents a carbamate pesticide which has a methyl group (WHO, 1986). Thus, Lannate is a hydrocarbon organic pesticide, which acts as ozone precursor as n-methyl carbamates absorb radiation available in the solar region (wavelength,  $\lambda = 300\text{nm}$ ) and hence would be expected to undergo photooxidation as well as metabolic degradation



(Addison *et al.*, 1974). In spite of its distribution by air as a minor factor, its slow volatilization from water or soil at normal temperature may increase with high temperature (WHO, 1986; Aly, 1989). Another organic hydrocarbon, which has a considerable contact activity on cotton plants, is an organophosphorous systemic insecticide called Dimethoate. Apart from its toxicity, during photolysis under the climatic conditions in Egypt, particularly during summer (Khalil *et al.*, 1984a), this insecticide is enhanced by UV solar radiation (Mitchel, 1961). Furthermore, its decomposition and degradation in the environment may be an effective hydrocarbon precursor for surface ozone. Its photodecomposition and degradation, as many other insecticides like methyl parathion, in the environment during suitable climatic conditions may be an effective hydrocarbon precursor for surface ozone which increases its toxic effects and carcinogenic hazards, as well as enhancing the "greenhouse effects" (Khalil *et al.*, 1984b; Farag *et al.*, 1993). Photochemical reactions are of importance in air pollution because of their products, (mainly free radicals). These products initiate or participate in a number of other reactions leading to the conversion of primary pollutants to secondary ones. Ozone is a prevalent secondary pollutant and a photochemical oxidant, and the major component of smog.

Ozone is formed in air, in the presence of sunlight, as a result of the chemical combination of reactive hydrocarbons with nitrogen oxides ( $\text{NO}_x$ ). It is also deduced from the complex chemical interactions of  $\text{NO}_x$  and organic species (Haagen-Smit, 1952). Ozone is likewise considered as a product of the photochemical oxidation of carbon monoxide in presence of  $\text{NO}_x$  (Sanford *et al.*, 1990). Bottenheim *et al.* (1977) clarified the radical and vital role of the solar radiation and nitrogen oxides on the surface ozone formation from the following equation:



where  $K_1$ ,  $K_2$  are the specific reaction rate constants for the solar radiation (at  $\lambda < 430\text{nm}$ ) and nitrogen dioxide reaction which leads to ozone production. In winter  $k_1/k_2$  are about 30 per cent less than in summer because of lower solar intensity and temperature. Equation (1) also illustrates the increase in NO concentration will be decrease the level of the atmospheric ozone as reported by Kuklin (1987).

The prospective object of the present study is to highlight the serious effects of insecure pesticide spray, particularly through the sunny days which through the pesticides photolysis cause a high increase in surface ozone concentration in the ambient air and accordingly increases the dangerous smog level concentration.

### Materials and methods

The experimental work of the current study had been undertaken in a cotton farm of the Agricultural Research Institute in Giza through two months represented the spring and summer seasons. The farm locates at the south of

Cairo University and is downwind of an industrial area (Shoubra El-Kheima) and it is surrounded by a heavy vehicular traffic motion from the east and west side. The hourly O<sub>3</sub> concentrations, the temperature and relative humidity were recorded at a fixed site 500m from the treated farm and the site was at a height of 20m. The temporal variations in the O<sub>3</sub> concentration during the background (control) day (the day before the pesticide spray) and after spray process have been hourly measured by using Dasibi Ozone Monitor, which was directly calibrated before the experimental work. The monitor is based on UV absorption spectroscopy by ozone in the range of 200-300nm wavelengths (Hodgeson, 1972). While the temperature and relative humidity had been monitored by using a Sigma-II Thermohygrograph (NO 7210, SK Sato Keiryoki MFG-Co, Ltd, Japan).

It is necessary to denote to a close attention that the spray took place at morning (around 9 and 7hr local time through the cold and hot weather, respectively) and the second day means that day directly followed the spray day. Furthermore, the period between the first and the second experiments was about 50 days. Otherwise, there were only three days between the two following spray days during the second and third experiments. The day (14/7/1999) represented the third day through the second experiment and simultaneously represented the day before the third-pesticide spray process during the third experiment. Finally, there were no measurements of O<sub>3</sub> concentrations at the hour 15 during the third day of the first experiment and also at 8hr during the two background days of the second and third experiments.

Two different pesticide kinds were used during the present study the first of them was called Courakron and its formula is as following: O-(4-bromo-2-chlorophenyl)-O-ethyl 8-propylphosphorothionate.

While the second one was called Cutabroon and its formula is as following: N-(4-(3-chloro-5-trifluoromethyl 2-pyridyloxy 2-pyridyloxy) 3, 5-dichlorophenyl Ni (2-6 difluorobenzol urea). The pH of the solution of the used pesticide in distilled water was between 6 and 7.

The increase percentages in O<sub>3</sub> concentrations have been calculated by the following equation:

$$\text{Increase\%} = \left\{ \frac{(C_2 - C_1)}{C_1} \right\} * 100 \quad (2)$$

where:

C<sub>1</sub>: represents the hourly O<sub>3</sub> concentration in parts per billion (ppb) during the background day; and

C<sub>2</sub>: represents the corresponding O<sub>3</sub> concentration in ppb during the following day at the same hour.

On other hand, air quality index (AQI) was calculated according to Prusty and Rout (1993) equation which was firstly deduced by Ott and Thom (1976) as:

$$I = (X/X_s) * 100 \quad (3)$$

where  $X$  is the observed value of the pollutant and  $X_s$  is the prescribed standard for the pollutant. According to Egyptian environmental protection law (EEAA, 1995)  $X_s$  for  $O_3$  concentration equals 100ppb for one hour. If  $I \leq 100$  the given parameter is within the prescribed limit. But if  $I > 100$  it implies that the parameter exceeded the prescribed standard and the ambient air is harmful for inhalation by human lungs (Tiwari and Ali, 1987).

### Results and discussions

The results illustrated in Figures 1, 2 and 3 show the hourly  $O_3$  concentrations in ppb before and after pesticide spray from 8hr local time until 15hr during the investigated days through the first, second and third experiments beside the corresponding temperature and relative humidity. Figure 1 signifies that there is a direct relationship between ozone concentrations and the temperature degrees while it was reversal proportion with relative humidity. The figure also demonstrates that  $O_3$  concentrations were gradually increased towards the hour 15, whereas it increased during the background day from 40ppb (at 8hr) to 91ppb (at 15hr) with an average of  $O_3$  concentrations of order of 70ppb. The corresponding  $O_3$  concentrations during the spray day were suddenly increased after noon. Its measurements increased from 53 (at 8hr) to 73ppb (at 12hr) and jumped to 159ppb (at 15hr) with an average was found to be 91ppb. Figure 1 likewise manifests that the peak and the highest  $O_3$  concentrations were recorded during the second day which through  $O_3$  concentrations were increased from 150 to 175ppb (which represented the maximum of  $O_3$  concentration and was monitored at 14hr) with an average equalled 163ppb. While during the third day  $O_3$  concentrations were lower than that of the

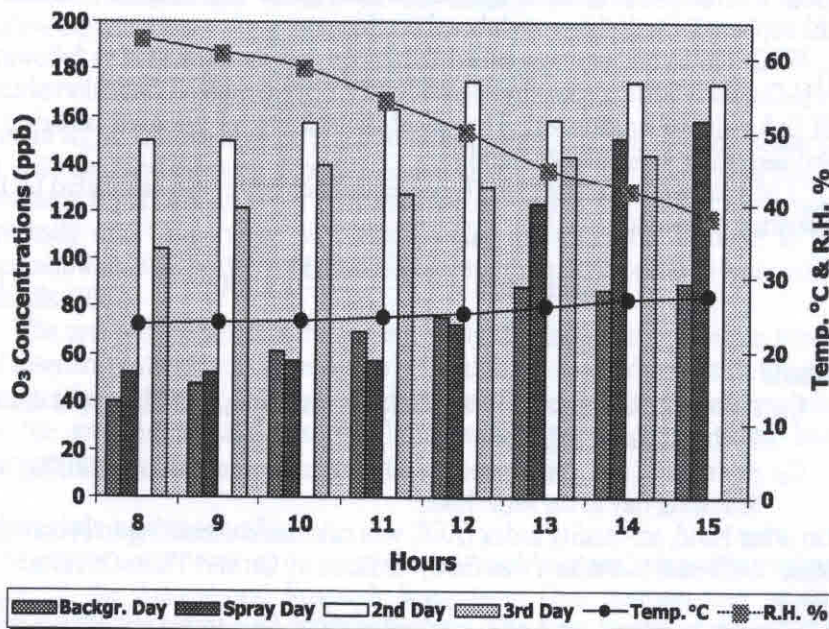


Figure 1. Pesticide effect on the hourly  $O_3$  concentration in ppb during and after spray day and the corresponding temperature, °C and RH per cent through the first experiment

second day and these concentrations were between 104 and 145ppb (at 14hr) with an average of O<sub>3</sub> concentrations of order of 130ppb. This means that there was a clear decay in O<sub>3</sub> concentrations through the third day after spray during the first experiment.

By examining Figure 2 it is evidently clear that, the trend of the relative humidity variations is somewhat different from that recorded during the first experiment particularly after 13hr. The figure also illustrates that during the background day O<sub>3</sub> concentrations were increased from 60 (at 9hr) to 86ppb (at 14hr) and decreased to 81ppb (at 15hr) with an average of order of 75ppb. Whilst during the spray day the corresponding O<sub>3</sub> concentrations increased from 50 (at 8hr) to 109ppb (at 14hr) and decreased to 106ppb (at 15hr) with an average was found to be 85ppb. Similar to first experiment the highest O<sub>3</sub> concentrations were found during the second day but here O<sub>3</sub> concentrations ranged from 83 to 145ppb (the maximum concentration of O<sub>3</sub> during the second experiment and was recorded at 14hr) with an average equaled 123.3ppb. In addition, during the third day O<sub>3</sub> concentrations increased from 70 (at 8hr) to 125 ppb (at 13hr) and decreased after that to be 122 and 117ppb at hours 14 and 15, respectively and the corresponding average equalled 106ppb.

From Figure 3 it can be clearly seen that, the trend of the hourly variations of the relative humidity during the third experiment is somewhat different from that recorded during the first experiment but similar to that obtained during

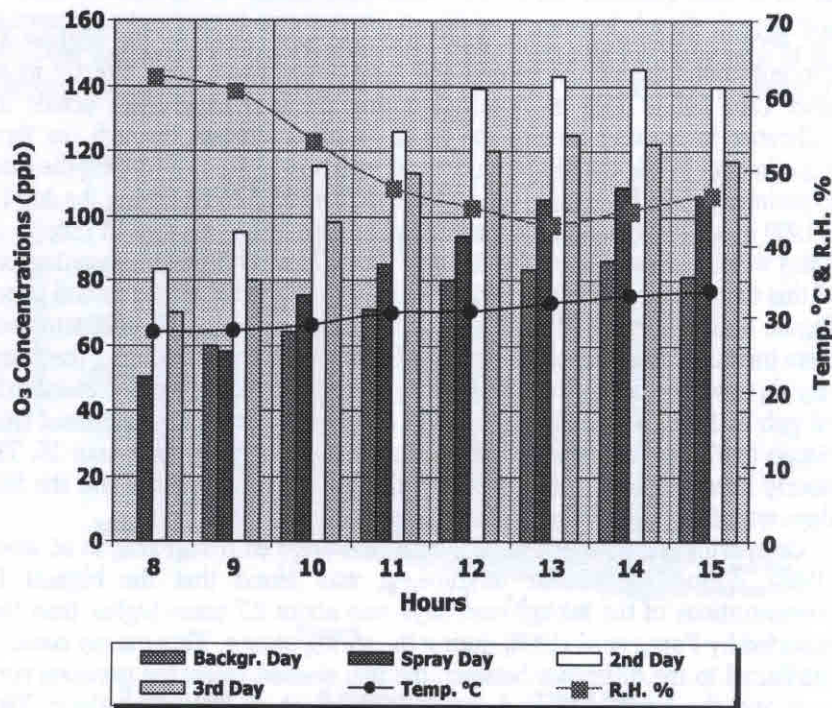
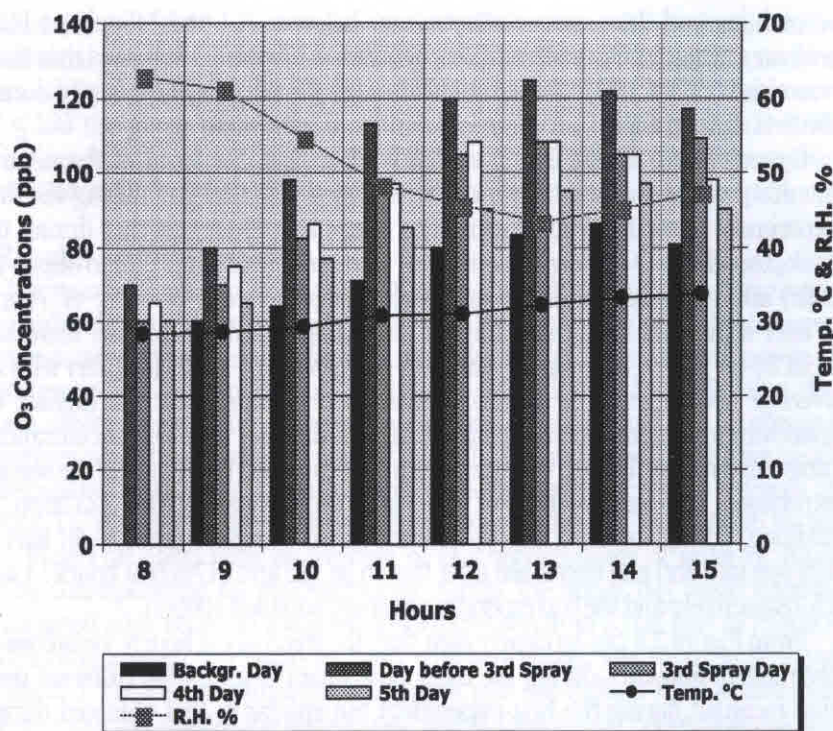


Figure 2. Pesticide effect on the hourly O<sub>3</sub> concentration in ppb during and after spray day and the corresponding temperature, °C and RH per cent through the second experiment



**Figure 3.** Pesticide effect on the hourly O<sub>3</sub> concentration in ppb during and after spray day and the corresponding temperature, °C and RH per cent through the third experiment

the second experiment. This may interpret why most of the highest O<sub>3</sub> concentrations during the second and third experiments were directly found after 13hr not at 15hr as occurred during the first experiment beside the difference in starting time of the pesticide spray process through the three experiments. While the temperature trend was nearly the same during the three experiments. The highest O<sub>3</sub> concentrations were monitored during the day 14/7/1999 in which O<sub>3</sub> concentrations increased from 70ppb (at 8hr) to 125ppb (at 13hr) with an average equalled 106ppb. The relatively high O<sub>3</sub> concentrations of this day could be motivated with; this day was affected by the second spray. Figure 3 also shows that during the spray day the hourly O<sub>3</sub> concentrations were increased from 60ppb (at 8hr) to 109ppb (at 15hr). While during the fourth day O<sub>3</sub> concentrations increased from 65 to 108ppb at 13hr then decreased to be 98 ppb at 15hr. Whilst during the fifth day O<sub>3</sub> concentrations increased from 60ppb to 97ppb at 14hr and decreased after that to be 90ppb at hour 15. The hourly averages of O<sub>3</sub> concentrations during the spray, fourth and the fifth days were found to be 92, 93 and 82ppb respectively.

Comparing the obtained results with that deduced from Farag *et al.* study (1993), during the similar daytime, it was found that the highest O<sub>3</sub> concentrations of the background days was about 2.7 times higher than that reported by Farag *et al.* (1993) during the spring season. This mainly could be attributed to the difference between the two studied areas; the previous rural area and the recently treated cotton farm which is located at about 30km



downwind of one of the three biggest industrial areas in Greater Cairo. Moreover, the farm is surrounded by a heavy vehicular traffic motion, which added more pollutants to the background of this area. Consequently, this contamination of air by incomplete combustion fuels or other carcinogenic organic gases or particulates which are photochemically oxidized by sunlight causes an increase in ozone concentrations (Meyer, 1983). Furthermore, the meteorological conditions, play a vital role in the ozone formation in the ambient air (Pearson and Mansfield, 1993). This may be also explain why the obtained  $O_3$  concentrations during the background days were higher than the prescribed limit of  $O_3$  concentrations during the clean background (the clean background concentration of ozone according to WHO, 1978 is 40ppb).

The results presented in Figures 4, 5 and 6 reveal the increase percentages in hourly  $O_3$  concentrations during the investigated days, compared to those during the background days. In general view, it could be noticed that there was a reduction in  $O_3$  concentrations at hours 10, 11 and 12 during the first spray day (Figure 4) and at 9hr during the second spray day (Figure 5). While this phenomenon disappeared during the third spray day because of this day was affected by the second spray for only three days before. The reduction percentages in  $O_3$  concentrations at these hours were 5.7, 17.9 and 3.9 per cent during the first experiment and 3 per cent during the second experiment, respectively. This could be attributed to the fact that during the pesticide photolysis some of the surface ozone molecules, which naturally exist in the air surrounding the treated cotton farm, would be consumed during the reaction. Whereas the pesticide spray process was often started at the early time of the morning (around 9 and 7hrs through the cold and hot weather, respectively

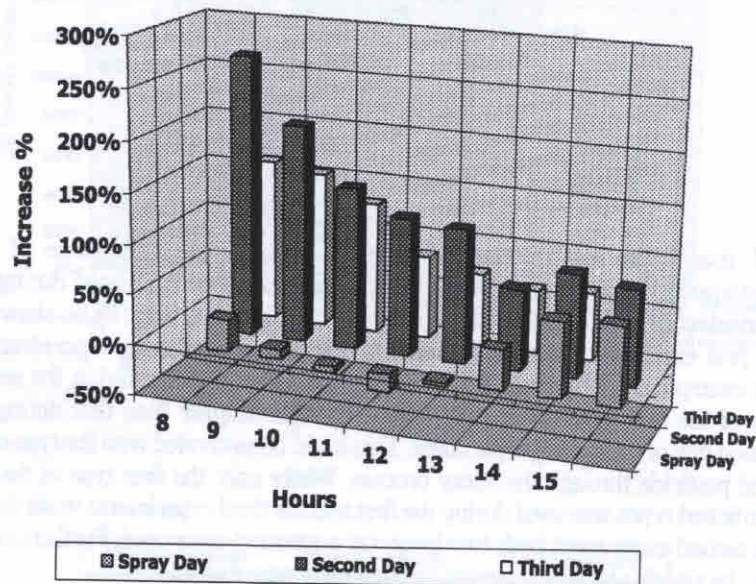


Figure 4. The increase in percentages in hourly surface  $O_3$  concentrations during the spray, second and third days of first experiment, compared to those of background day

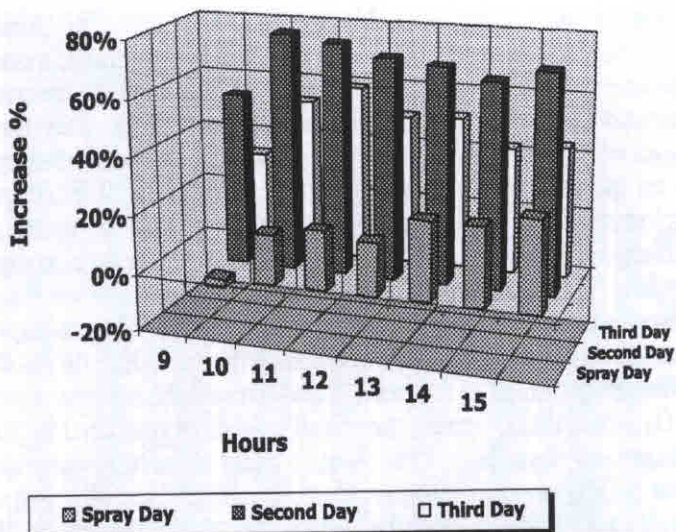


Figure 5. The increase percentages in hourly surface O<sub>3</sub> concentrations during the spray, second and third days of second experiment, compared to those of background day

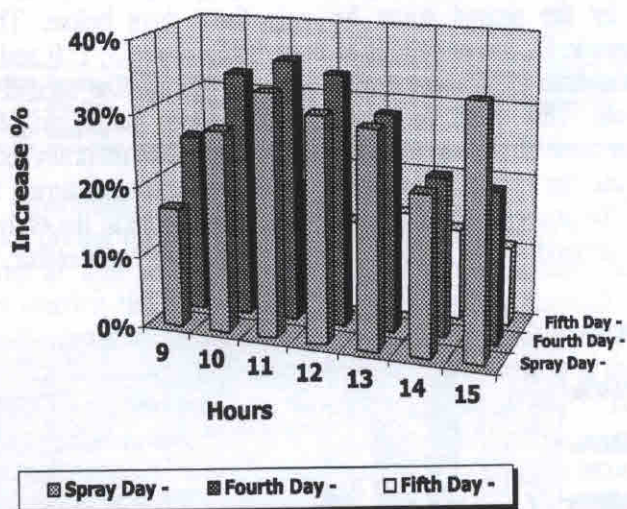


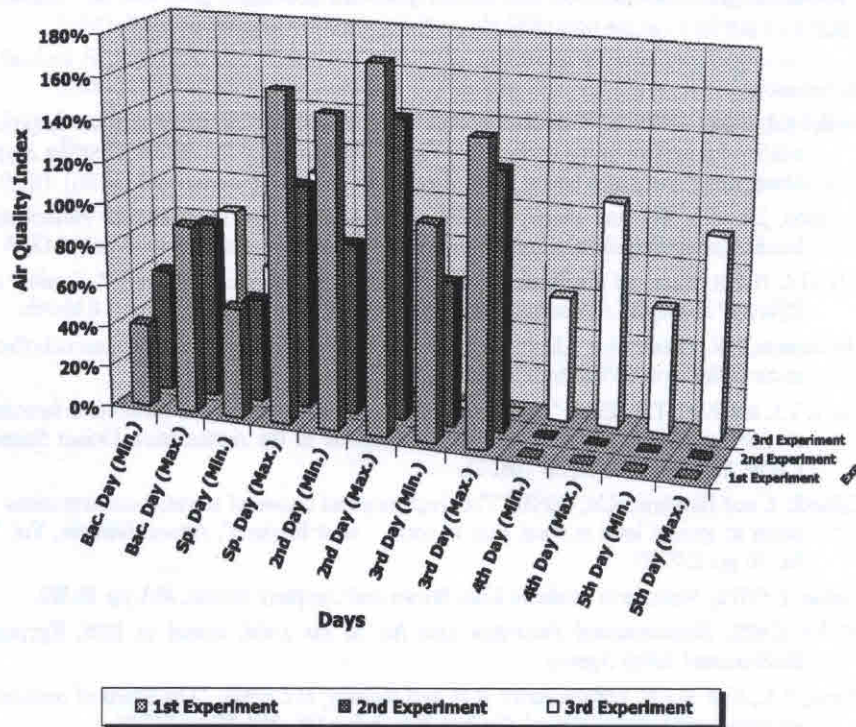
Figure 6. The increase percentages in hourly surface O<sub>3</sub> concentrations during the spray, fourth and fifth days of third experiment, compared to those of background day

and this would explain the difference in time of the appearance of this phenomenon). Consequently, O<sub>3</sub> concentrations might be decreased during the pesticide photolysis time. The results obtained in Figures 4, 5 and 6 also show that the first experiment had the highest increase percentages in O<sub>3</sub> concentrations. For example the increasing percentages in O<sub>3</sub> concentrations during the second day of the first experiment were (about 1.3 times) higher than that during the second day of the second experiment. This could be motivated with the type of the used pesticide through the spray process. Where only the first type of the two mentioned types was used during the first and the third experiments while during the second experiment both two kinds (as a mixture) were used. Furthermore, it may be also due to solar intensity through each experiment.

**Air quality index (AQI) study**

The AQIs were calculated for all O<sub>3</sub> concentration measurements according to equation (3). The output results clarified that during the first and the second experiments the AQI of the background days was unarmful before noon and increased to be an alarming index after noon. While during the first and second spray days it increased after noon to be a harmful and very harmful index, respectively. Furthermore, during the two second days most of the AQIs registered as very harmful during the first experiment (a peak had a magnitude about 175 per cent) and harmful during the second experiments. While during the two third days the index registered as harmful (for all the investigated hours during first experiment and after the hour 10 during the second experiment). On other hand, during the third experiment AQI values of the fourth day were alarming before noon and harmful indices after that. The index registered as alarming for all fifth day hours. The results presented in Figure 7 show the minima and the maxima of AQIs during the investigated days through the current study period.

Finally, the output results manifested that O<sub>3</sub> concentrations were correlated significantly positive with temperature and this is in accordance with Colton (1974), Clark and Karl (1982), Colbeck and Harrison (1985), Meleigy (1993) and Khoder (1997). The averages of the correlation coefficient of the hourly O<sub>3</sub> concentrations with temperature were found to be 0.85 and 0.91 during the



**Figure 7.**  
The minimum and maximum air quality indices during the investigated days through the three experiments

spring and summer seasons, respectively. Otherwise, the hourly O<sub>3</sub> concentrations were correlated negatively with the relative humidity during the two seasons which consider in agreement with Abdel-Aal *et al.* (1994). The averages of the correlation coefficient of the hourly O<sub>3</sub> concentrations with the relative humidity were of order of 0.90 and 0.97 during the spring and summer, respectively.

### Conclusion

The study illustrated that most of the hourly O<sub>3</sub> concentrations had been increased after pesticide spray with different values from hour to hour and then began to decay after one day or more according to the concentrations. The averages mean of the increase percentages in hourly O<sub>3</sub> concentrations, compared to those of background days, during the three spray days was found to be 32.4 per cent. While the corresponding mean of the second days of the first and second experiments equalled 110 per cent. Whilst during the third days of the first and second experiments the average mean of these percentages equalled 75.4 per cent. The averages of the increase percentages of the fourth and fifth days during the third experiment were 29.2 and 14.2 per cent respectively. Furthermore, the AQIs during the second days and only the third day of the first experiment were found between harmful and very harmful index with a peak had a magnitude about 175 per cent. Finally, it could be concluded that the use of poisonous pesticides might provide an insecure source of surface ozone particularly in the agricultural area in Egypt.

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### Environmental Management and Health

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To examine in a deep and objective manner the various environmental factors and their impact on human health, to suggest possible remedies and to adopt an interdisciplinary approach to the problem of managing the environment so as to reduce the deleterious effects of man's activities in this century. All papers are reviewed and subject to stringent consideration by subject specialists on the Editorial Review Board.

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Three copies of the manuscript should be submitted in double line spacing with wide margins. All authors should be shown and author's details must be printed on a separate sheet and the author should not be identified anywhere else in the article.

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