IMPACT OF PESTICIDES ON ATMOSPHERIC FORMALDEHYDE CONCENTRATION AND AMBIENT AIR QUALITY

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ABSTRACT: Hourly formaldehyde concentrations along with temperature and relative humidity were monitored before and after three spraying processes of chemical pesticides performed on sunny days of spring and summer in 1999. The results revealed that the pesticide spraying process (PSP) raised the atmospheric level of formaldehyde (HCHO) in the ambient air of the treated farm for five consecutive days reaching its maximum on the 2nd day. The peak (101 ppb) and highest percent enrichment (304%) in HCHO concentrations were found on the 2nd day of the 2nd summer PSP. The HCHO concentrations were higher after 1st and 2nd summer PSPs (about 1.3 and 1.6 times, respectively) than those of the spring PSP. The most hazardous levels were found around solar noon and 80% of them were found at 12 o'clock (local time). The formaldehyde concentrations positively (although insignificantly) correlated with the temperature and negatively with the relative humidity in both seasons investigated. In conclusion, chemical pesticides can be considered as a risky source of secondary formaldehyde formation.

KEY WORDS: Pesticide, formaldehyde, temperature, relative humidity, air quality

INTRODUCTION

Unquestionably, pesticides are essential elements of modern agriculture in that they contribute to improve the production rate. But unfortunately, chemical pesticides are being widely used in most of the developing countries that are being short of provisions and are compelled to overcome the obstinate gap between their principles and crop strategy. Beyond the common direct hazards of the use of pesticides, secondary affects may also take place. Certain climatic conditions and ultra violet radiation can lead to decomposition or photodecomposition of pesticides. The latter gives rise to some pollutants (such as surface ozone) raising the smog level resulting in an inferior air quality (Rizk et al., 2002). However, the degradation of pesticides yields some other organic compounds, too, aldehydes are one of them. They have been recognized to have a great impact on the human health because of their potentially carcinogenic and mutagenic properties (NRC, 1981; WHO, 1987; CEPA, 1993). Furthermore, aldehydes have the capability of forming toxic and phototoxic radical intermediates and stable species (Roberts, 1990).

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Many aldehydes are volatile and most of them are present in gaseous form in urban air. Volatile organic compounds are not only precursors of photochemical oxidants but also some species, such as formaldehyde, benzene and butadiene, are known to be carcinogens (Clarke and Ko, 1996). The sources of formaldehydes include natural and anthropogenic emission, mainly automobile exhaust as well as the products of photochemical oxidation of volatile organic compounds (VOCs). Photochemical production of formaldehyde is enhanced by oxidatative degradation of the most reactive VOCs (i.e., alkenes and dienes) promoted by OH radical or ozone attack (Carter, 1990, 1994; Altshuller, 1991; Atkinson, 1997).

In ambient air formaldehyde and acetaldehyde are the two most abundant aldehydes that may be considered as both primary and secondary pollutants (Grosjean et al., 1993; Possanzini et al., 1996; Williams et al., 1996; Müller, 1997; Corrêa et al., 2003). In an urban area it is difficult to establish whether formaldehyde arises from atmospheric photochemistry or directly as a primary pollutant from exhaust emissions (Ball et al., 1991). Recently, it has been calculated that the secondary formation of aldehydes may be larger than their primary emission (Altshuller, 1993).

The present paper aims to give emphasis to the impact of chemical pesticides on the quality of ambient air and to disclose relationships between the formaldehyde concentration and the current temperature and relative humidity in two different seasons.

MATERIALS AND METHODS

The present study was carried out at a cotton farm of the Agricultural Research Institute in Giza lying south of the Cairo University.

Pesticides used

Two different types of pesticides were used: O-(4-bromo-2-chlorophenyl)-O-ethyl 8-propylphosphorothioate named Courakron and N-(4-(3-chloro-5-trifluoromethyl-2-pyridyloxy) 3,5-dichlorophenyl-Ni-(2-6-difluorobenzol urea) named Cutabroon. The first one was sprayed in the spring and the 2nd summer periods (Experiment 1 and 3, respectively) while a blend of the two kinds of the pesticides was used in the 1st summer period (Experiment 2). The pH value of the pesticides dissolved in distilled water was between 6 and 7.

Sampling

After spraying two different kinds of pesticides, hourly air sampling for formaldehyde content was performed in the daytime (from 8 a.m. to 3 p.m. local time in sunny days of clear sky) at a height of 20 m from the earth surface and a distance of about 500 m from the farm. Ten replicate field samples were collected in the treated cotton farm for one hour. The selected days were the background (control) day (the day prior to spraying the pesticides), the spray day, the second, third, fourth, and fifth days after spraying.

The samples were collected in glass bubblers with a coarse fritted inlet containing 35 ml of 0.05% 3-methyl-2-benzothiazolone hydrazone hydrochloric (MBTH) solution, using a pump calibrated to draw 1 $L \cdot min^{-1}$. After each sampling time, the volume of absorbing solution was made up with distilled water to exactly 35 mL (to compensate for evaporation losses) and allowed to stand for 1 h. Three sampling series over two month-long periods represented the spring (Experiment 1) and summer (Experiments 2 and 3) seasons of 1999.

Temperature and relative humidity were simultaneously monitored using a Sigma-II Thermohygrograph (NO. 7210 SK Sato Keiryoki MFG-Co., Ltd., Japan).

Chemical Analysis

Ten mL of the sample solution were transferred into a clean gas stoppered tube washed with distilled water and an equal volume of unexposed reagent was placed in a second clean tube to serve as a blank. To oxidize the azines of the sample, 2 mL of an oxidizing solution consisting of 1.6 g sulfamic acid (Fluka) and 1.0 g ferric chloride (Sigma) dissolved in 100 ml distilled water was added to the sample solution and blank and mixed well. After allowing to stand for at least 12 min, the absorbance was determined at 628 nm against the blank with a Coleman, Junior II Spectrophotometer Model 6/20. The aldehyde contents (expressed as $\mu g \cdot mL^{-1}$ HCHO) were determined from a standard calibration curve. The air concentrations of total aliphatic aldehyde (as HCHO) were calculated according to Harrison and Perry (1986). The method applied is relatively free from interference and its collection efficiency is 84% (Harrison and Perry, 1986).

To prepare the calibration solution, a freshly made standard HCHO solution containing 10 $\mu g \cdot ml^{-1}$ HCHO was used. Replicate samples and blanks were handled and analyzed in the same manner as above. The calibration curve was constructed as absorbance against $\mu g \cdot mL^{-1}$ HCHO of the solutions. From 0.03 to 0.7 $\mu g \cdot mL^{-1}$ HCHO can be measured in a colour-developed solution (12 mL), with a detection limit of 0.03 $\mu g \cdot mL^{-1}$. This corresponds to a minimum detectable concentration of about 14 ppb aldehyde (as HCHO) in a 60 L air sample, absorbed in 35 mL MBTH. The relative standard deviation (RSD) for replicate analyses of the field samples was 5% (n=10), that of the calibration standard was 2% (n=12).

Using an estimated guideline value of formaldehyde concentrations (53 ppb see Discussion) and applying the equation of Prusty and Rout (1993), that had been derived from that of Ott and Thom (1976), the air quality index (I) was defined as:

$$I = \frac{X_m}{X_s} \times 100\,(\%)$$

where X_m is the measured concentration of formaldehyde and X_s is the suggested guideline value of formaldehyde concentration.

If $I \leq 100\%$ the given parameter is within the prescribed limit. However, if $I > 100\%$ it implies that the parameter have exceeded the suggested guideline value and the inhalation of ambient air is risky and hazardous for humans (Tiwari and Ali, 1987).

The hourly percent enrichment En%, i.e., the hourly percent increase in the concentration of formaldehyde due to PSP, relative to the corresponding formaldehyde concentration in background day was determined according to the following equation:

$$\text{En}\ (\%) = \frac{C_m - C_b}{C_b} \times 100\ (\%)$$

where C_b is the concentration of formaldehyde in background day (before spray day) at a fixed hour and C_m is the corresponding concentration of formaldehyde measured after PSP.

RESULTS

Formaldehyde concentrations

Hourly formaldehyde concentrations (in ppb) and the percent enrichment (En%) measured for 8 hours of daytime during the pesticide spraying process (PSP) in the 2nd and 3rd after-spray days in spring representing Experiment 1 are presented in *Fig. 1*. The peak of formaldehyde concentrations was found in the noonday hours while the minima at 8 o'clock. The average percent enrichment of formaldehyde concentrations displayed in similar course. After midday, both the concentration and

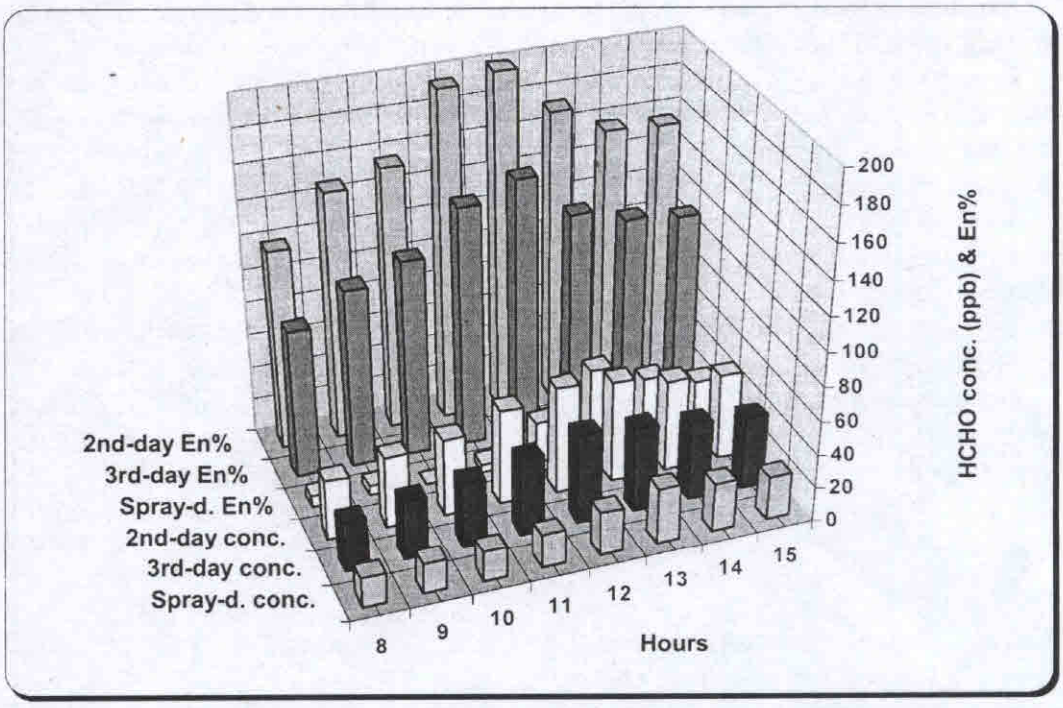

Fig. 1. Hourly HCHO concentrations (in ppb) and percent enrichment (En%) on the spray day, 2nd, and 3rd after-spray days of spring experiment

enrichment gradually decreased. The results of Experiment 2 (1st summer PSP) are given in *Fig. 2.* Using a blend of the two pesticides applied, the peaks appeared somewhat earlier and the decay was more delayed. *Fig. 3* presents the results of spraying the pesticide Courakron in the summer (Experiment 3). Obviously, in the hot season higher values were achieved than in the spring.

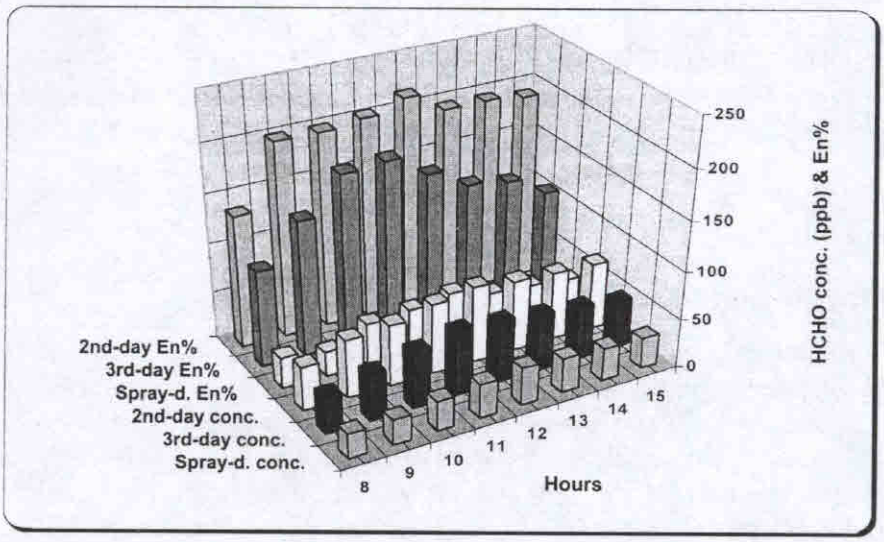

Fig. 2. Hourly HCHO concentrations (con. in ppb) and percent enrichment (En%) on the spray day, 2nd, and 3rd after-spray days of the 1st summer experiment

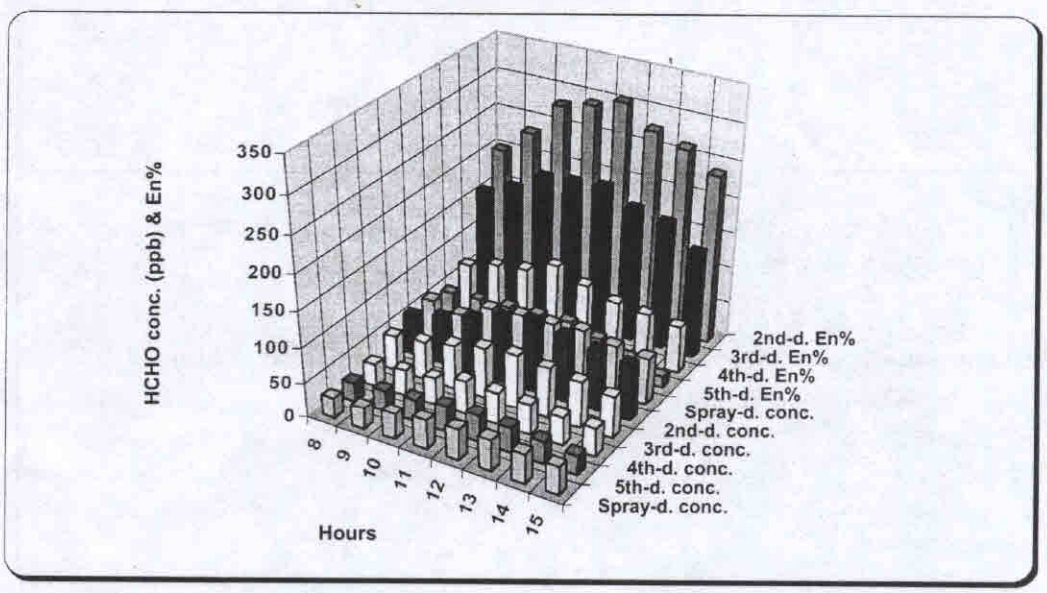

Fig. 3. Hourly HCHO concentrations (in ppb) and percent enrichment (En%) on the spray day, 2nd, 3rd, 4th and 5th after-spray days summer experiment

In each experiment, the formaldehyde concentration had reached its maximum on the 2nd after-spray day; in the following days the HCHO production, as a rule, gradually diminished.

Air quality indices

Fig. 4 presents the air quality indices obtained in all of the three experiments during the days (2nd and 3rd days) with the highest formaldehyde concentrations. The majority of the values proved to be higher than the estimated limit of 100%. The most hazardous values were found around the solar noon (80% of them at 12 h).

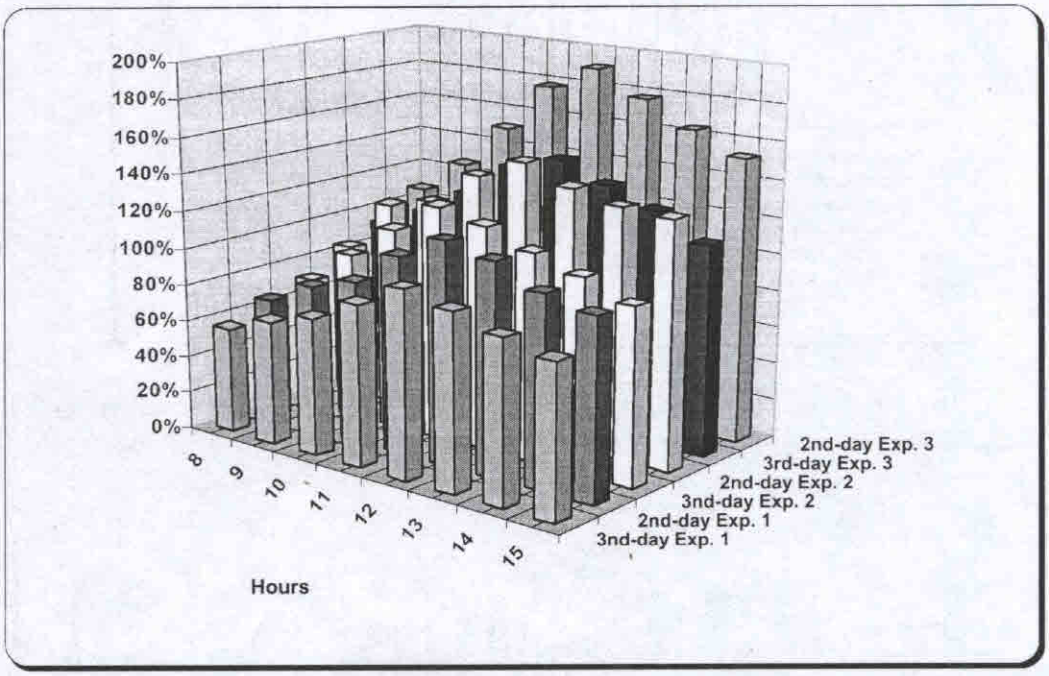

Fig. 4. Hourly air quality indices for formaldehyde on the 2nd and 3rd after-spray days of all three experiments

Formaldehyde concentrations vs. temperature and relative humidity

Eleven regression equations at a 95% confidence level were conducted to investigate the relationship between the formaldehyde concentrations with the corresponding temperature and the relative humidity values. Since in all the three experiments the second-day values had been the highest ones, they were chosen to depict these relationships.

The analysis of data revealed that the formaldehyde concentrations positively correlated with the temperature before and after PSP. However, these correlations did not reach the level of significance. In Experiments 1 and 2 the relationships be-

tween formaldehyde concentrations and temperature values were represented by quadratic equations in the background, spray, 2nd and 3rd after spray days. The correlation coefficients (r) were 0.80, 0.77, 0.82, and 0.80, respectively, during the spring PSP and averaged 0.80, 0.79, 0.81, and 0.81, respectively, during the 1st summer PSP. *Fig. 5* (A and B) show the relationship of the measured and predicted HCHO concentrations and the corresponding temperature values in the 2nd day of spring and 1st summer PSPs, respectively.

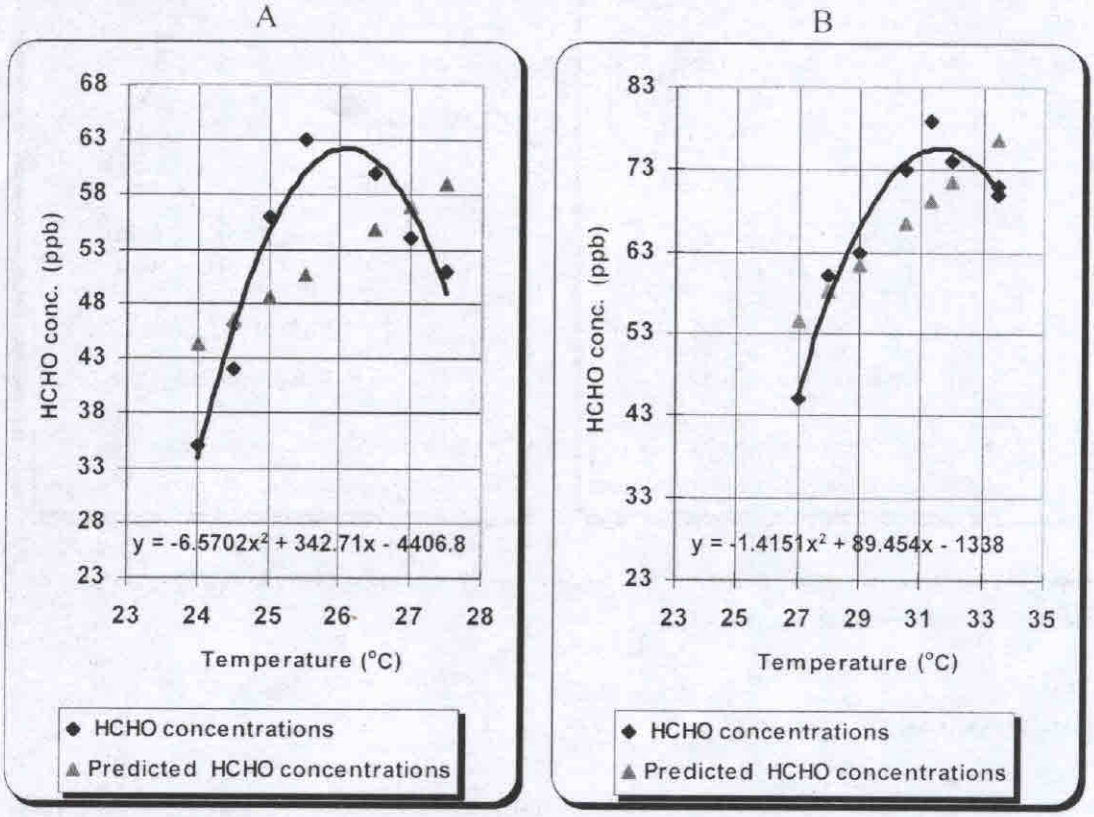

Fig. 5. HCHO concentrations vs. ambient temperature on the 2nd day of the spring (A) and 1st summer (B) experiments

On the other hand, the formaldehyde concentration had a significant and negative correlation with the corresponding relative humidity values before and after PSP. In Experiment 1 and 2, the predominant relationships between them were represented by cubic equations in the background, spray, 2nd and 3rd after spray days. The correlation coefficients averaged –0.78 –0.88, –0.77 and –0.78, respectively, in the spring PSP and –0.93, –0.93, –0.94 and –0.91 in 1st summer PSP, respectively. *Fig. 6* (A and B) represent this relationship including the predicted formaldehyde concentrations too, obtained in Experiments 1 and 2, respectively.

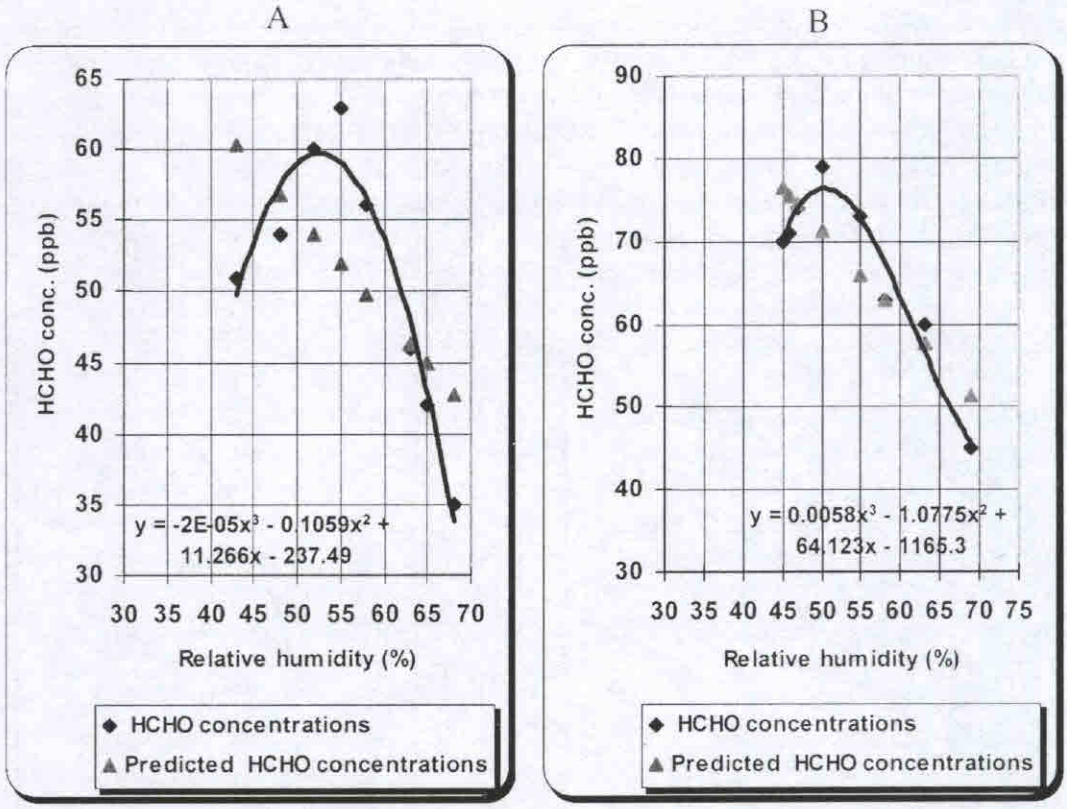

Fig. 6. HCHO concentrations vs. relative humidity on the 2nd day of the spring (A) and 1st summer (B) experiments

DISCUSSION

In Egypt, mainly two factors underlie formaldehyde formation: *i)* most of the pesticides used are the organic hydrocarbon and organophosphorous systemic insecticides (Rizk et al., 2002) and *ii)* the air pollution levels in Cairo are among the highest in the world (Nasrala, 2001 and USAID, 2001). In summer, aldehydes are produced by photo-oxidation of gas-phase hydrocarbons (Williams et al., 1996) or they are generated in the polluted air oxidation products due to various free radicals formed by photochemical reactions (Finlayson-Pitts and Pitts, 1986). In this way, formaldehydes may be primary pollutants and/or oxidation products of hydrocarbons. They are of great significance to atmospheric chemistry due to the strong influence on the formation of nitric acid, peroxyacetyl nitrate (PAN) and other smog components (Seinfeld, 1986; De Andrade et al., 1998).

In detail, it could be supposed that, the after-sunrise photolysis of ozone produces OH^- radical that oxidizes the organic compounds of the pesticide producing organic peroxy radical (RO_2) which in its turn, reacts with NO to produce alkoxy radical and NO_2. The alkoxy radical reacts with atmospheric oxygen to produce

formaldehyde. The appearance of the maximum concentrations of formaldehyde in the 2nd after-spray day indicates that the peak of the substrate presentation to the degrading reaction is reached with a day's delay after PSP.

The relative high background formaldehyde concentrations measured could be attributed to the location of the investigated farm being downwind of one of the biggest industrial areas of Greater Cairo (Shubra El-Kheima) and surrounded by heavy traffic density from the east and west side (Rizk et al., 2002). Accordingly, the ambient formaldehyde concentration and the level of primary pollutants had to be high due to vehicle exhaust (Cleveland et al., 1977; Corrêa et al., 2003).

The present study revealed that the average HCHO concentrations measured in background days were, in agreement with other studies (Khoder et al., 2000; Possanzini et al., 2002), higher (about 1.3 times) in the summer than in the spring. In all likelihood, it is the consequence of higher summer solar flux and UV radiation.

As for the pesticide Courakron, the rise of the daily average of HCHO concentration after the 2nd summer PSP was even higher (about 1.6 times) than the corresponding average after spring PSP. This surplus, however, might be caused by the 1st summer PSP with a blend of pesticides that had occurred three days before.

Comparing with the concentrations of formaldehyde obtained at other sites of the world it was found that the concentration of formaldehyde for 30 min in ambient air was limited to 30, 50, and 70 ppb in Romania, Chechoslovakia, and Hungary (for vegetation), respectively (Stern, 1986). HCHO concentrations in urban areas tend to be higher, typically 5–40 ppb as reported by some investigators (Graedel et al., 1986; Grosjean et al., 1990, 1993, 1996; Ball et al., 1991). In Rome, then hourly formaldehyde concentrations ranged from 8 to 28 ppb in summer and from 7 to 17 ppb in winter (Possanzini et al., 2002). Concentrations of formaldehyde in outdoor air at residential houses located in suburban area of New Jerseys equaled 12.53 ppb (Zhang et al., 1994). About 54% of the formaldehyde concentrations, measured in ambient air in day-time in a high traffic street of Rio de Janeiro in Brazil were ≤ 5 ppb, 71% of them were ≤ 11 ppb, 75% ≤ 20 ppb, and 90% ≤ 30 ppb throughout a study expanded more than two years (Corrêa et al., 2003). It is clear that in the present study the average of formaldehyde concentrations of 2nd and 3rd days after spring and 2nd summer PSP were several times higher than the values given above.

Poor air quality due to pollution is a serious environmental problem in most urban areas. Actually, ambient air quality can be considered as an indicator that used to reflect these complexities between the outdoor air quality and the true population exposure (WHO, 1987). In Cairo the level of air pollution is among the highest in the world (Nasrala, 2001; USAID, 2001), therefore, it was necessary to evaluate the background ambient air quality at the treated farm. Unfortunately, the Egyptian legislation has not prescribed any value for outdoor concentration of formaldehyde (EEAA, 1995). Based on the results of the authors mentioned above we set a level of 53 ppb as an estimated guideline value of the 30-minute formaldehyde concentration in ambient air of Egypt.

In conclusion, to replace hazardous pesticides by using natural antagonists in the biocontrol of fungal plant diseases and biological control of soil-borne plant pathogens is highly desirable.

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