Investigation on the Behavior of Pesticides in Atmosphere

Pasquale Avino[1], Giuseppe Cinelli[2], Ivan Notardonato[2], Mario V. Russo[2*]

[1] *DIPIA, INAIL (ex-ISPESL), via Urbana 167, 00184 Rome, Italy*
[2] *Faculty of Agriculture, University of Molise, via De Sanctis, Campobasso, Italy*

ABSTRACT

Although pesticides are widely used in agriculture, they and in particular the relative residues in foodstuffs, water and atmosphere, may cause remarkable sanitary problems due to the harmful effects (carcinogenic and mutagenic effects) on the human health. In fact, their spread in waters and atmosphere can produce undesired effects on various organisms and/or water contamination.

This paper shows an analytical approach based on XAD-2 adsorbent and GC analysis for evaluating the pesticide trend in atmosphere: in particular, the pesticides investigated are omethoate, dicrotofos, disulfoton, dimethoate, parathion methyl, formothion, paraoxon ethyl, malaoxon, parathion ethyl, iodofenfos and triazofos. For the analytical methodology a linearity response was obtained ($r^2 = 0.9988$) in GC-NPD whereas the limits of detection range between 2 and 5 pg/µL in GC-NPD with a Relative Standard Deviation below 9.5. Finally, this approach has been successfully applied to real samples: the results show that dimethoate concentration decreases with increasing distance from the sampling site but it is still persistent in atmosphere after few days from the pesticide spraying.

Keywords: Pesticides; XAD-2 adsorbent; GC analysis; Atmosphere; Air quality.

INTRODUCTION

Pesticides, mainly comprising plant protection products (PPP) and biocidal products, are designed to influence fundamental processes in living organisms. They may have the potential to kill or control harmful organisms such as pests, but can also cause unwanted adverse effects on non-target organisms (Russo *et al.*, 2002), human health and the environment (Lacorte *et al.*, 1993; Juhler, 1997; Hyotylainem *et al.*, 1998; Dogheim *et al.*, 2001; Lentza-Rizos *et al.*, 2001; Zohair, 2001; Xu *et al.*, 2005; He *et al.*, 2009; Rudel *et al.*, 2010). Among the different types of pesticides, the organophosphorous pesticides (OPs) are widely used in agriculture and their properties provide numerous benefits in terms of production and quality increase, but they simultaneously may cause sanitary problems due to the harmful effects on the human health. The OPs exhibit a large degree of persistence in the environment, which causes various health and safety problems (Jelinek, 1985; Kosikowska and Biziuk, 2010): this degree depends also on the stability/instability of atmospheric conditions investigated by Radon measurements (Avino *et al.*, 2003; Papastefanou,

2009). One of the most important OP reactions is water hydrolysis. This reaction can take place at the P atom or in the alkylic chain and in general induces a loss of pesticide action. The phosphorodithionate conversion into their O-homologues, i.e., the phosphates, strongly increases the toxicity for insects and mammals. The typical reaction with O-phosphorothioates is the thiol-thiol isomerization induced by light and temperature. In this way, the O-phosphorothioates are transformed into S-phosphorothioates, which are more toxic than the parent compounds. The OPs inhibit the phosphorylate esterases, particularly the enzyme acetylcholinesterase, thus causing an accumulation of the neurotransmitter acetylcholine (Marrs, 1993). The cholinesterase inactivation by OPs involves a reaction in which one substituent group (i.e., the leaving group) produces a dialkylphosphoryl enzyme. The vast majority of insecticides produce a dimethylphosphorylate enzyme or a diethylphosphorylate enzyme, and the reactivation kinetics are the same for each derivative regardless of the OP leaving group structure. The dimethylphosphorylate enzyme reactivation is (considerably) quicker than that one of the diethyl equivalent and it occurs in few hours (Krenzelok, 1984). Acute intoxication with OPs can cause major effects such as convulsions, respiratory failure, and cardiac arrhythmias, all of which can result in anoxia. It is hardly surprising that major intoxication is sometimes associated with long-term central nervous system changes. A number of studies on this problem have shown

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* Corresponding author. Tel.: -39-0874-404-631;
  Fax: -39-0874-404652
  E-mail address: mvrusso@unimol.it

behavioral and psychological alterations, and others have failed to demonstrate any effect (Ferrer and Cabral, 1989). It should never be forgotten that OPs may have other properties entirely independent of their anticholinesterase effects, including mutagenicity and carcinogenicity as well as specific organ toxicity to heart, liver, kidney, and other organs (Concon, 1988).

From a legislative point of view pesticides have been regulated for a long time in most EU Member States and the Community. Unwanted amounts of pesticides can however still be found in environmental media (in particular soil and water) and residues exceeding regulatory limits still occur in agricultural production. The risks to human health and the environment from pesticide use are therefore being closely evaluated. Exposure to pesticides should be minimised or, where possible, eliminated. The Community regulatory framework concerning pesticides focuses particularly on the placing on the market and the end of the life cycle of such products. The legislative gap regarding the use-phase of pesticides should be filled in. Also, the research and development of less harmful, including non-chemical, alternatives should be further encouraged.

The main scope of this study is the identification of the presence, the concentration levels and the behavior of organophosphorous pesticides such as omethoate, dicrotofos, disulfoton, dimethoate, parathion methyl, formothion, paraoxon ethyl, malaoxon, parathion ethyl, iodofenfos and triazofos, in atmosphere also taking into account the water and soil environment which are considered as final receptors of the fate of each pesticide. In fact, a direct consequence of the continuous and massive use of pesticides is the possibility that a certain amount of these substances can be transferred from agricultural use to the river surface through the phenomena of overland flow (i.e., runoff) or reach the groundwater through infiltration (i.e., leaching) or disperse into the atmosphere through diffusion and transport phenomena reaching settlements or industrial. The pesticide diffusion in water and air may produce undesirable effects on non-target and determine the contamination of drinking and/or irrigation water. For this aim we set up a specific analytical methodology and investigated it using dimethoate as a proof-test.

METHODS

Sampling Site

The two sampling sites were located near Campobasso, in the Molise region (Center of Italy, about 300 km far from Rome, South-East direction): the first location (site 1: San Martino in Pensilis, 41°52′0″N 15°1′0″E, 281 m a.s.l.) was an agricultural location cultivated at sugar beet whereas the second position (site 2: Larino, 41°48′0″N 14°55′0″E, 341 m a.s.l.) was an area of olive trees and vineyards surrounded by an industrial settlement.

Materials

A personal pump (Zambelli srl, Milan, Italy) was used for air sampling (rate 2 L/min). Pyrex glass tubes (12 cm ×

0.6 mm) were used for packing XAD-2 adsorbent (Sanders *et al.*, 2001). Amberlite XAD-2 polymeric adsorbent is a hydrophobic crosslinked polystyrene copolymer resin, supplied as 20–60 mesh size white insoluble beads. Each bead consists of an agglomeration of many very small microspheres, giving a continuous gel phase and a continuous pore phase. For storing the water and soil samples the sterile glass box were employed.

Standards of omethoate, dicrotofos, disulfoton, dimethoate, parathion methyl, formothion, paraoxon ethyl, malaoxon, parathion ethyl, iodofenfos, triazofos and M20 (used as Internal Standard, I.S.) were furnished by Riedel-de Haen (Seelze, Germany). The methylene chloride, acetonitrile, hexane, acetone, methanol, toluene, carbon disulfide, diethylether, anhydrous sodium sulfate and pure reagents for pesticides were furnished by Carlo Erba (Milan, Italy).

Equipment

The gas-chromatography (GC) analysis was performed by means a gas chromatograph mod. 86.10 HT (Dani, Monza, Italy) equipped with a PTV (programmed temperature vaporizer) injector, a fused silica capillary column (25 m × 0.20 mm × 0.20 μm of stationary phase SE 54, Hewlett Packard, Palo Alto, CA, USA) and nitrogen-phosphorous (NPD) and an Electron Capture (ECD) Detectors.

The experimental conditions were: PTV from 60°C to 280°C at 800 °C/min; NPD temperature at 290°C; column temperature at 90°C (1 min in isotherm) and after up to the final temperature of 280°C at 10 °C/min. Hydrogen as carrier gas at linearity velocity of 38 cm/s.

The confirmation of both dimethoate and omethoate were performed by means of gas chromatograph series II mod. 5890 connected to a mass spectrometer model 5889A and interfaced to a data system "Chemstation 58940A" (Hewlett Packard) operating in Negative Chemical Ionization (NCI) and Selected Ion Monitoring (SIM) modes (typical fragment ions used, abundance 100%: m/z 157 corresponding to $[(CH_3O)_2PS]^-$ for dimethoate and m/z 141 corresponding to $[(CH_3O)_2PSO]^-$ for omethoate) (Avino *et al.*, 2010).

Sample Collection

During May the sites were subjected to pesticide treatment with copper oxychloride and Rogor (dimethoate).

Intensive sampling campaigns were performed in springtime: before the pesticide treatment samples of soil, sugar beet leaves, irrigation water and air were randomly sampled in both sites. After the treatment, samples were collected at different hours and distance. Two hours after the treatment 12 air samples were collected for 1 h-long at the following distances: a) 4 samples at 100 m far from the point; b) 4 air samples at 200 m; c) 4 air samples at 300 m. Further, three hours after the treatment, samples of soil, leaves and water river were randomly collected. Finally, air samples were collected 10, 20 and 30 days after the treatment. All the samples were stored at –5°C.

For analyzing the air samples, the glass fiber filter and the 270 mg (XAD-2) "sampling section" were transferred

into 4 mL-vial and 2 mL of methanol, 5 μL of M20 (I.S.) were added: the solution were mixed for 90 min. The organic phase was recovered, concentrated (100–200 μL) and analyzed by means of GC-NPD.

The passive samplers (3 g of XAD-2) collected for 10 days: they were extracted through CS2 (5 mL × 2) and, after IS addition, the solution was dried and recovered with 100–200 μL of methanol. A few μL were used for the GC-NPD analysis.

After collection, leaves, soil and water samples were washed with hot water (50°C). After NaCl (12 g/L) addition (Russo *et al.*, 1993), the aqueous phase was extracted with methylene chloride (leaves and soil) or diethyl ether (water) (3 × 20 mL) and the organic phase was concentrated (100–200 μL) under nitrogen flow and analyzed by GC-NPD (and by GC-MS for confirmation).

Standardization of the Analytical Methodology

The analytical procedure was reported in detail in Avino *et al.* (2010); here, a brief summary of the main information is given. The analytical evaluation regarded dimethoate and omethoate and afterwards applied to the OPs investigated.

About the desorption efficiency, 270 mg of XAD-2 and about 10 mm of glass fibers were introduced into 9 vials of 4 mL. The vials were divided into three groups; 9.5, 19 and 38 μL of dimethoate (5.15 μg/mL in toluene) were added. The dimethoate amount is 48.925 μg, 97.85 μg and 195.7 μg, respectively. The vials were hermetically sealed

and kept overnight at room temperature. The adsorbent spiked with dimethoate, was desorbed with 2 mL of methanol, concentrated under nitrogen flow, and analyzed by GC-NPD, after IS addition. The average desorption efficiency was of 97.1%. Table 1 shows the results obtained.

For evaluating the breakthrough volume (Russo *et al.*, 1993), five glass tubes filled with XAD-2 adsorbent (270 mg sampling section and 140 mg backup section) were prepared. After addition of 1.9 μL of dimethoate (5.15 μg/mL in toluene) in the sampling section of each vial, the tubes were sealed and stored overnight at room temperature. Then, 50, 100, 150, 200 and 250 L of air (about 90–85% relative humidity) drawn with a personal pump (2 L/min), were flown through them. Then, the glass fiber and 270 mg of XAD-2 of the sampling section were put in 5 vials and 2 mL of methanol were added: the solution was recovered and concentrated till to 100–200 μL. The same operation was performed on the adsorbent (140 mg) of the backup section. Some μL of methanol solutions were analyzed by GC-NPD (and GC-MS/NCI for confirmation). Table 2 shows the results obtained.

For assessing the retention efficiency (Russo *et al.*, 1999), three sampling tubes were used. 1.9 μL of dimethoate (5.15 μg/mL in toluene) were added to each tube and kept overnight at room temperature; then, 250 L of air were flown. The XAD-2 adsorbent (270 mg) and the fiberglass were extracted with 2 mL of methanol, concentrated under nitrogen flow and analyzed by GC-NPD (and GC-MS/NCI for confirmation). Table 3 reports the results.

Table 1. Descriptive statistics of the MTBE and BTEX measured at four night markets and a background location during night market activity periods.

Sample	Dimethoate added (ng)	Dimethoate found (ng)	Recovery (%)
A1	48.9	46.8	95.7
A2	48.9	47.9	98.0
A3	48.9	50.2	102.3
A4	97.9	93.5	95.5
A5	97.9	92.8	94.8
A6	97.9	98.2	100.3
A7	195.7	186.1	95.1
A8	195.7	189.0	96.6
A9	195.7	187.3	95.7
Backup section	0.0	0.0	n.d.
Average value			97.1

Table 2. Recovery (%) of dimethoate after sample storage at –5°C and 25°C for 7 days (n.d.: not detected).

Time/Temperature (day/°C)	Dimethoate added (ng)	Dimethoate found (ng)	Recovery (%)
7/–5	9.79	9.65	98.5
7/–5	9.79	9.61	98.2
7/–5	9.79	9.67	98.8
7/–5	0.0	0.0	n.d.
7/25	9.79	9.57	97.8
7/25	9.79	9.55	97.6
7/25	9.79	9.63	98.4
7/25	0.0	0.0	n.d.

Table 3. Retention time, linearity range, correlation coefficient and LOD with Relative Standard Deviation of the OPs investigated in this study by means of GC-NPD. RSD is calculated from three determinations.

Peak	Compounds	RT (min)	Linearity range (pg/μL)	r^2	LOD (pg/μL)	RSD
1	Omethoate	14.57	10–500	0.9985	5	9.5
2	Dicrotofos	16.16	10–500	0.8980	2	8.5
3	Disulfoton	18.94	10–500	0.9985	2	7.8
4	Dimethoate	19.18	10–500	0.9988	2	7.5
5	Parathion methyl	23.38	10–500	0.9978	2	8.1
6	Formothion	23.64	10–500	0.9987	2	7.2
7	Paraoxon ethyl	23.80	10–500	0.9978	5	9.0
8	Fenitrotion	25.12	10–500	0.9982	5	9.1
9	Malaoxon	25.43	10–500	0.9980	2	8.5
10	Parathion ethyl	27.02	10–500	0.9984	2	7.8
11	Iodofenfos	31.40	10–500	0.9979	5	8.8
12	Triazofos	38.29	10–500	0.9980	2	7.4
13	M20	39.08				

Finally, it was studied the sample storage using six sampling tubes. 1.9 μL of dimethoate (5.15 μg/mL in toluene) were added to each tube and 250 L of air (2 L/min) were flown. After storage at room temperature and in freezer at –5°C for seven days, they were analyzed by the method described above. Table 5 shows the results obtained.

Fig. 1 shows the gas chromatogram of a standard solution of organophosphate pesticides investigated in this study (1 ng/μL of each pesticide). As it can be noted, the peaks are well resolved and separated. Using the analytical conditions described above, some analytical parameters such as linearity range, correlation coefficient, limit of detection (LOD), and percentage recovery were investigated.

RESULTS AND DISCUSSION

Validation of Analytical Procedure

The validation of the analytical procedure was performed on dimethoate pesticide: the choice depended on its large use for agricultural activities. Table 1 shows the results concerning the dimethoate desorption efficiency from XAD-2 adsorbent using methanol. The absolute amount of dimethoate considered for this test, were between 48.9 and 195.7 ng while the average desorption efficiency obtained was 97.1%.

First of all, the breakthrough volume and the retention efficiency were investigated. The measures performed by XAD-2 for determining the breakthrough volumes, showed clearly the XAD-2 to be a very good material for air dimethoate sampling. The breakthrough volume was higher than 250 L (sampling rate of 2 L/min) and the dimethoate recovery was > 98.0% whereas the evaluation of the retention efficiency indicated a recovery around 98%. For confirming this, experiments performed on XAD-2 adsorbent varying the air sampling volume (from 50 to 250 L), allowed to reach recovery between 98.2% and 99.2%. All the experimentation was performed sampling air 250 L-volume.

Experimental tests performed after a week (Table 2) demonstrated no differences to be between the results obtained analyzing air samples stored at room temperature

(97.9%) and in freezer (98.5%).

Finally, the investigated analytical procedure was applied to the total OP standard mixture (50 pg). Table 3 shows the retention time (RT), linearity range and limit of detection (LOD) with the Relative Standard Deviation (RSD) for each pesticide investigated in this study. In particular, for studying the linearity range, the calibration curve was investigated by adding 1.0, 4.0, 8.0 and 21.0 μL of a solution of dimethoate (1.2 μg/mL) and omethoate (1.3 μg/mL) in toluene to 12 vials of 4 mL, divided into four groups of three vials, respectively. After a night at room temperature, 2 mL of methanol and 5 μL I.S. were added to each vial under mixing for about 30 minutes. The organic liquid phase was recovered, concentrated to small volume (100–200 μL) and analyzed by GC-NPD (and by GC-MS/NCI for confirmation). The results obtained were plotted in a graph quoting the ratio between Adimeth/AI.S. vs. the dimethoate concentration (or Aomethate/AI.S. vs. omethoate) in ng/mL. The LODs of the OPs analyzed ranged between 2 and 5 pg/μL with RSD ≤ 9.5%. These values were determining according to Knoll's definition (Knoll, 1985), i.e., an analyte concentration that produces a chromatographic peak equal to three times the standard deviation of the baseline noise. Table 4 reports the percentage recovery with the RSD for each OP. The recoveries noted were satisfactory: the average recovery was 96.2% ranging between 91.8% for iodofenfos and 99.1% for dicrotofos and parathion ethyl whereas the average RSD was 5.7 varying between 9.1 for paraoxon ethyl and 3.7 for dicrotofos. These consideration allowed us to apply the analytical procedure above investigated to real air sample for investigating the presence and the levels of all the OPs.

Analysis of Real Samples

Fig. 2 shows the gas chromatogram obtained from analysis of an air sample collected at 300 m from the point of sampling site 1 a few hours after pesticide spraying. As it can be seen, the only pesticides present were omethoate and dimethoate. Table 5 reports the pesticide concentration level. The table shows that the dimethoate concentration
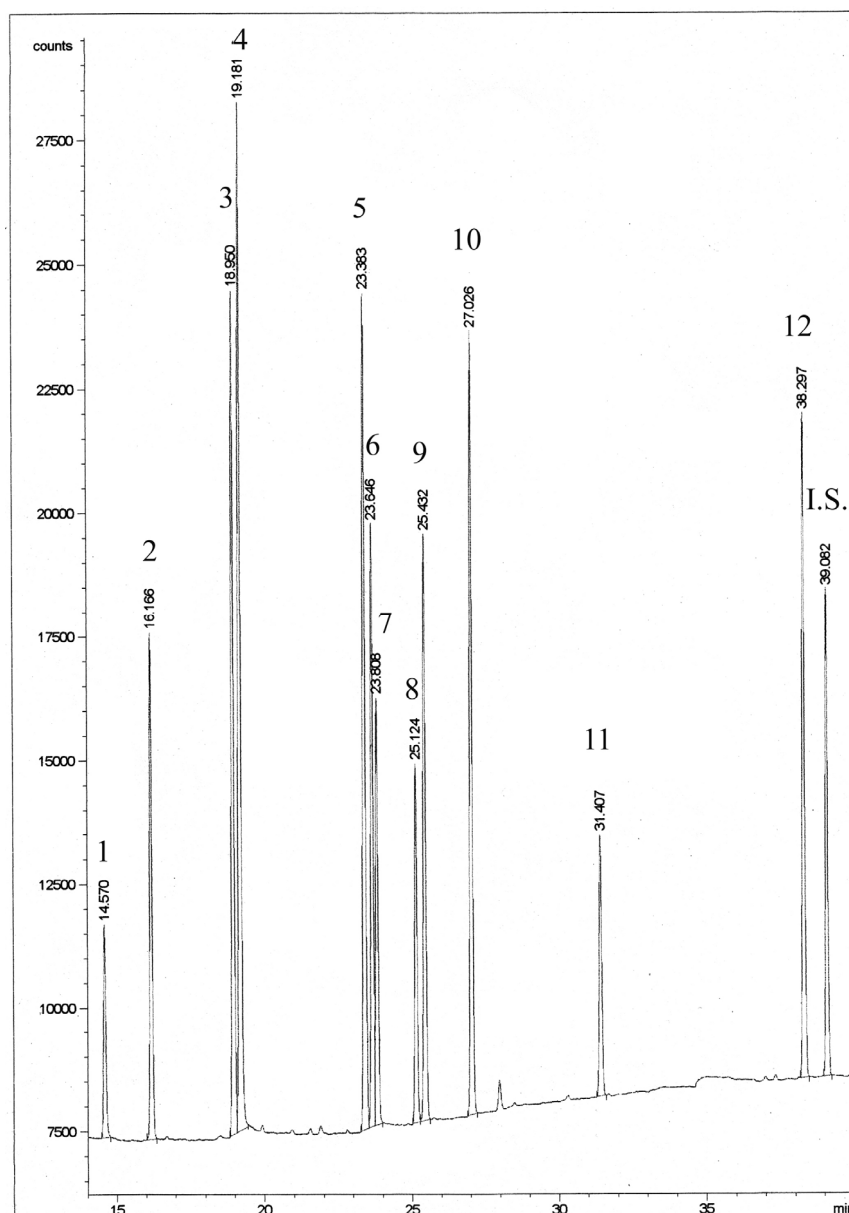
Fig. 1. Gas chromatogram of a OP standard mixture (1 ng/µL of each pesticide). See text for experimental conditions and Table 4 for peaks.

Table 4. Recovery of each pesticide (50 pg) after air sampling of 250 L and storage for 7 days at –5°C. RSD is calculated from three determinations.

Peak	Compounds	Pesticide added (pg)	Pesticide found (pg)	Recovery (%)	RSD
1	Omethoate	50	48.1	96.2	4.8
2	Dicrotofos	50	49.6	99.1	3.7
3	Disulfoton	50	46.3	92.6	8.2
4	Dimethoate	50	49.3	98.6	6.7
5	Parathion methyl	50	48.9	97.8	6.8
6	Formothion	50	47.6	95.1	7.2
7	Paraoxon ethyl	50	46.8	93.6	9.1
8	Fenitrotion	50	48.1	96.2	3.8
9	Malaoxon	50	47.7	95.3	5.1
10	Parathion ethyl	50	49.6	99.1	3.9
11	Iodofenfos	50	45.9	91.8	5.1
12	Triazofos	50	49.2	98.4	4.2
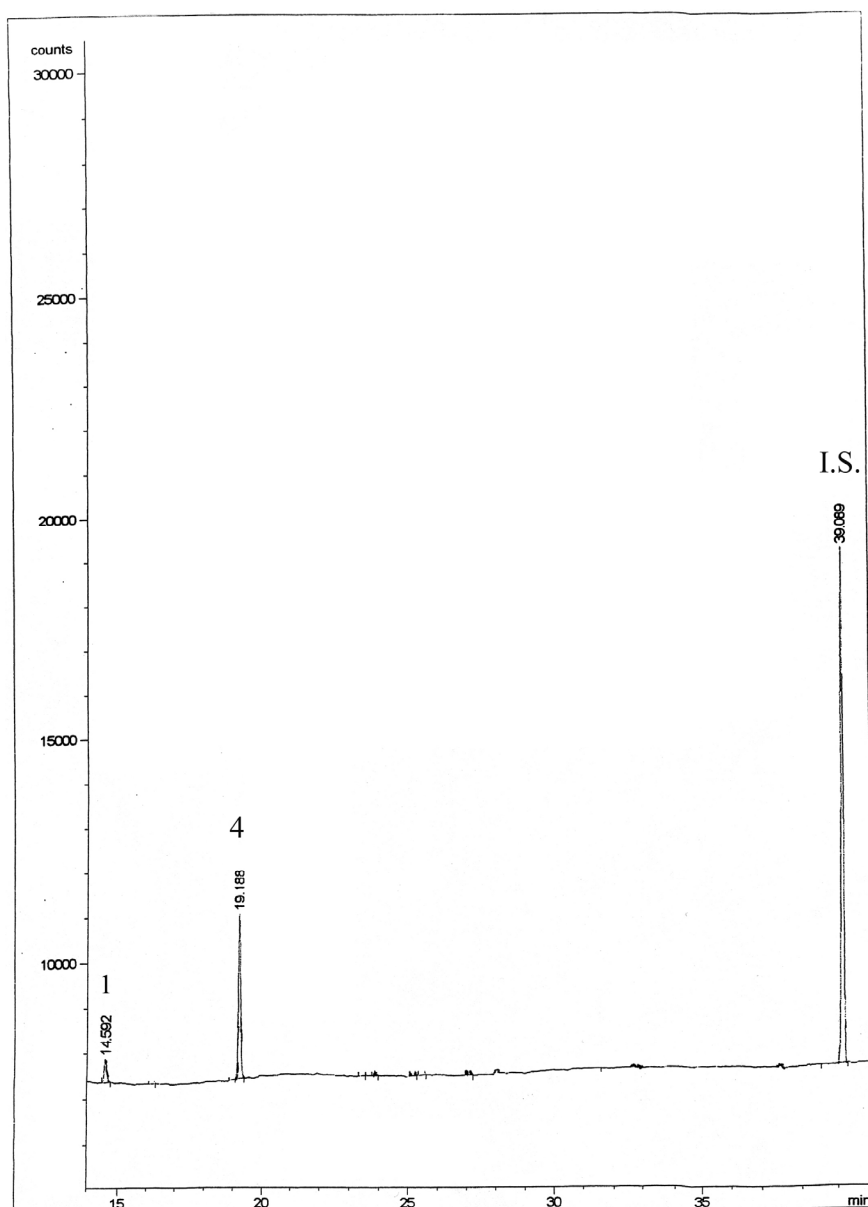
Fig. 2. Gas chromatogram of a real air sample collected in the site 1 at 300 m far from the sampling point after pesticide spraying. See text for experimental conditions and Table 1 for peaks.

decreased with increasing distance from the sampling site in both cases, even if for the site 2 this decreasing was more pronounced than for the site 1. Maybe, this decrease was due to the presence of olive trees making a natural barrier: this occurrence prevents the transport of dimethoate, although the wind speed at the site 2 was higher than at site 1. Moreover, it should be considered the different amount of active ingredient sprayed (0.3–0.5 kg/ha for site 1; 0.7–0.8 kg/ha for site 2).

An interesting issue regards the significant amount of omethoate found in air samples collected at longer distances: in site 1 at a distance of 300 m, it was equal to 0.007 µg/m. The omethoate, compound having a P atom replaced by an O atom, is more toxic than dimethoate: the transformation is due to the reaction of dimethoate with oxygen in particular conditions of temperature, humidity

and pH. It is important noting that this homologous is formed already after a few hours the spraying.

Further, analyzing the data reported in Table 5 it can be evidenced that different behavior of dimethoate considering the wind direction and the presence of natural barrier. In fact, at site 1 dimethoate was detected till to 300 m-far from the sampling point, while in the air samples collected at site 2 the concentration was considerably lower.

There are very interesting additional values shown in Table 5: the dimethoate concentration relate to air samples collected at the sites 1 and 2 days after pesticide spraying (10 and 20 days later). These data show the dimethoate persistence for a long period in the vicinity of the site, regardless of wind speed, meaning a slow but steady spread along all the directions. Once again, the analytical data of site 2 are more significant than ones determined at

Table 5. Dimethoate levels (μg/m^3) determined in air samples collected at sites 1 and 2 at different distance and at different time after pesticide spraying (LOD: limit of detection). a: detection of omethoate at concentration level of 0.007 μg/m^3.

Distance (m)	North	South	East	West
Site 1				
After spraying, wind direction E, wind speed 0.4 m/s				
100	< LOD	0.20	< LOD	< LOD
200	< LOD	0.06	< LOD	< LOD
300	< LOD	0.03[a]	< LOD	< LOD
After 10 days, wind direction SE, wind speed 0.2 m/s				
50	0.007	0.02	0.01	0.008
100	< LOD	< LOD	< LOD	< LOD
200	< LOD	< LOD	< LOD	< LOD
After 20 days, wind speed 0 m/s				
50	0.005	0.006	0.009	0.004
100	< LOD	< LOD	< LOD	< LOD
200	< LOD	< LOD	< LOD	< LOD
Site 2				
After spraying, wind direction E, wind speed 0.4 m/s				
100	< LOD	< LOD	0.07	< LOD
200	< LOD	< LOD	0.02	< LOD
300	< LOD	< LOD	<LOD	< LOD
After 10 days, wind speed 0 m/s				
50	0.003	0.002	0.005	0.002
100	< LOD	< LOD	< LOD	< LOD
200	< LOD	< LOD	< LOD	< LOD
After 20 days, wind direction N, wind speed 0.6 m/s				
50	0.001	< LOD	LOD	LOD
100	< LOD	< LOD	< LOD	< LOD
200	< LOD	< LOD	< LOD	< LOD

site 1. In this site, the dimethoate concentration was higher and its distribution is more uniform than the site 2. The results also demonstrate that, after twenty days from the sites pesticide spraying, the dimethoate in atmosphere is totally absent or at least its concentration is below the instrumental limit of detection (LOD), at least for distances over 50 meters from the site.

Table 6 shows the values of dimethoate determined in passive samplers located along the cardinal points. Even if these values are no high, they are interesting: in fact, they demonstrate that, after ten days from the spraying, the active ingredient reaches considerable distances (in this case 500 m) dependent on the wind direction.

Regarding the concentration of dimethoate in samples of leaves of sugar beet and soil (site 1) collected immediately after spraying, it amounted to 0012 μg/cm and 0.003 μg/g, respectively (in such soil, pH < 7, dimethoate undergoes degradation to form phosphoric acid).

It should be underlined that in air, soil, water and leaf (site 1) and air (site 2) samples collected before spraying, pesticides, particularly dimethoate, are absent while traces of linear hydrocarbons, phthalates and carbamate were detected in river water. A special consideration should be given to the two passive samplers set close the rural town and the industrial settlement (site 2): in these two samples were determined, respectively, 0.006 and 0.004 μg of dimethoate.

Table 6. Dimethoate levels (μg/m^3) determined in passive samplers collected for 10-days at sites 1 and 2 at different distance after pesticide spraying (LOD: limit of detection). a: detection of omethoate at concentration level of 0.002 μg/m^3.

Distance (m)	North	South	East	West
Site 1				
500	< LOD	0.006[a]	< LOD	< LOD
800	< LOD	< LOD	< LOD	< LOD
1000	< LOD	< LOD	< LOD	< LOD
Site 2				
500	0.003	< LOD	< LOD	< LOD
800	< LOD	< LOD	< LOD	< LOD
1000	< LOD	< LOD	< LOD	< LOD

CONCLUSIONS

The results reported show interesting information on pesticide concentration and behavior in air considering the distance from the spraying point and the residence time in atmosphere. Further, the pollution level depends on wind speed and wind direction as well as on tree presence considered as natural barrier to atmospheric dispersion.

Finally, the omethoate and dimethoate concentration values in atmosphere necessitate particular attention with regard to the concept of "vulnerable zone" (the area where

dimethoate and/or omethoate can be present by means of spreading or wind transport). Indeed, the persistence of the active ingredient in atmosphere can generate serious problems for the personnel working in that agricultural areas sprayed, because dimethoate such as the other organophosphorous pesticides, is toxic and interferes with the enzyme cholinesterase.

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