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Applications of thermospray liquid chromatography–mass spectrometry in photochemical studies of pesticides in water

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ABSTRACT

Thermospray liquid chromatography–mass spectrometry (TSP-LC–MS) in the positive- and negative-ion modes (PI and NI, respectively) was used for the characterization of the pesticides aldicarb, carbaryl, cyanazine, fenitrothion, linuron and parathion-methyl, including the corresponding photodegradation products. The LC analyses were performed on RP-18 columns using methanol–water (70:30 or 50:50) + 0.05 *M* ammonium acetate or 0.05 *M* ammonium formate. Photodegradation studies of pesticides in distilled water were performed using a suntest apparatus, except for fenitrothion, for which a high-pressure mercury lamp was used because of slow photodegradation. The main photodegradation pathways corresponded to dealkylation, deamination, dehalogenation and hydroxylation. Photodegradation experiments were carried out using solutions of the different pesticides at 10–200 ppm in distilled water. For carbaryl photolysis is very slow in distilled water, so 5% of acetone was needed as photosensitizer. When PI-mode TSP-LC–MS was employed, aldicarb sulphoxide, monolinuron, hydroxysimazine and fenitrooxon could be identified as breakdown products of aldicarb, linuron, cyanazine and fenitrothion, respectively. In NI-mode TSP-LC–MS aldicarb sulphoxide, 1-naphthol and *p*-nitrophenol could be identified as the main degradation products of aldicarb, carbaryl and parathion-methyl, respectively. As all the pesticides were dissolved in methanol for solubility reasons, methoxy analogues of the degradation products of cyanazine were also identified. In the PI mode of operation the base peak generally corresponded to $[M+H]^+$ for cyanazine and its photodegradation products and to $[M+NH_4]^+$ for linuron, aldicarb and fenitrothion and their corresponding degradation products. For carbaryl $[M+NH_4]^+$ was also the base peak, but its main photodegradation product, 1-naphthol, could only be identified under NI conditions. In the NI mode of operation different processes such as proton abstraction, (dissociative) electron capture and anion attachment, take place. Fragment ions such as $[M]^{\cdot -}$ for aldicarb sulphoxide, the main photodegradation product of aldicarb, $[M-H]^-$ for 1-naphthol and $[M-CONHCH_3]^-$ for carbaryl and anion attachment ions corresponding to $[M+CH_3COO]^-$ for aldicarb sulphoxide and 1-naphthol and to $[M-CONHCH_3+CH_3COOH]^-$ for carbaryl were formed. A tentative photodegradation pathway for the different pesticides in water is postulated.

INTRODUCTION

Polar pesticides such as carbamates, chlorotriazines, phenylureas and organophosphorus compounds are being used in many agricultural applications [1–3] and residue levels varying between 7 ng/l and 5 μg/l have been detected in different types of water [4–6]. After application, their environmental fate is poorly understood, depending upon several degradation pathways such as hydrolysis, photolysis and mi-

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crobial transformation. In this respect, *e.g.*, atrazine is degraded by soil microorganisms by mechanisms involving dealkylation, deamination, dehalogenation and hydroxylation [5]. As a consequence, atrazine, carbaryl and aldicarb and their corresponding degradation products such as dealkylated atrazines, 1-naphthol and aldicarb sulphoxide, respectively, have also been detected in soil and water samples [2,4,7,8].

For establishing the aquatic photolysis processes under field conditions, prior identification of the different photodegradation products formed in laboratory experiments is needed. Previous photolysis experiments under laboratory conditions have been reported for a variety of pesticides, including carbamates [9–11], phenylureas [12,13], organophosphorus compounds [12,14] and triazines [12,15]. The formation of photolysis products such as oxo derivatives of organophosphorus pesticides [16], hydroxyatrazine [17], 1-naphthol [10,11] and aldicarb sulphoxide [18] is of concern because of their toxicity. Difficulties are often compounded because most of these breakdown products are involatile and/or polar and so not readily amenable to direct gas chromatography (GC) and GC–mass spectrometric (MS) determinations and as a consequence isolation of the reaction products is required [10,11,13,14]. Thermospray liquid chromatography–mass spectrometry (TSP-LC–MS) has been demonstrated to be a valuable technique for the identification of several pesticides and their polar metabolites, such as the oxo derivatives of organophosphates [19], *p*-nitrophenol [20], hydroxytriazines [12,15] and 1-naphthol, metabolite of carbaryl [21], and aldicarb sulphoxide and sulphone [22,23]. TSP-LC–MS–MS has also been employed for the identification of triazine [24] and aldicarb and its metabolites [23,25].

This paper presents results on aquatic photodegradation studies of pesticides of four different groups, carbamates, chlorotriazines, organophosphorus compounds and phenylureas, *viz.*, aldicarb, carbaryl, cyanazine, fenitrothion, linuron and parathion-methyl. TSP-LC–MS in the positive-ion (PI) and negative-ion (NI) modes of operation together with co-elution using authentic photodegradation standards, when available, were used for the unequivocal identification of the different photodegradation products. This work is a sequel to previous research using TSP-LC–MS for the characterization of the photolysis products of atrazine and simazine [12,15] and diuron [12] in water.

EXPERIMENTAL

Chemicals

HPLC-grade water from Riedel-de Haën (Seelze-Hannover, Germany) and methanol and acetonitrile from Merck (Darmstadt, Germany) were passed through a 0.45-μm filter (Scharlau, Barcelona, Spain) before use. Ammonium acetate and ammonium formate were obtained from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland), respectively. Analytical-reagent grade aldicarb, carbaryl and cyanazine were from Polyscience (Niles, IL, USA), 1-naphthol from Merck, linuron from Riedel-de Haën and parathion-methyl, fenitrothion and monolinuron from Promochem (Wesel, Germany). Fenitrooxon and aldicarb sulphoxide were gifts from Sumitomo Chemical (Osaka, Japan) and Rhône-Poulenc (Research Triangle Park, NC, USA), respectively, and hydroxysimazine (HSIM) and deisopropylhydroxyatrazine (DIHA) were gifts from Ciba-Geigy (Basle, Switzerland).

Chromatographic conditions

Eluent delivery was provided by two Model 510 high-pressure pumps coupled with a Model 680 automated gradient controller (Waters Chromatography Division, Millipore, Bedford, MA, USA) and a Model 7125 injection valve with a 20-μl loop from Rheodyne (Cotati, CA, USA). Cartridge columns of 12.5 cm × 4.0 mm I.D. from Merck and of 22 cm × 4.6 mm I.D. from Brownlee, Applied Biosystems (Santa Clara, CA, USA) were packed with 5-μm LiChrospher 100 RP-18 and 5-μm Spherisorb ODS, respectively, from Merck. A Polyglosil 500-7 C_{18} semi-preparative column (40 × 0.7 cm I.D.) from Macherey, Nagel & Co. (Düren, Germany) was employed for fractionation of UV-irradiated fenitrothion solutions.

The LC mobile phase compositions were methanol–water (50:50) + 0.05 *M* ammonium acetate for the analysis of aldicarb, carbaryl and linuron photodegraded solutions and methanol–water (70:30) + 0.05 *M* ammonium formate for the analysis of cyanazine and fenitrothion photodegraded solutions. Parathion-methyl photodegraded solution was analysed using acetonitrile–water (50:50) + 0.05 *M* ammonium acetate during 5 min with gradient elution up to 90% of acetonitrile in 20 min. The flow-rate was 1 ml/min.

Mass spectrometric analysis

A Hewlett-Packard (Palo Alto, CA, USA) Model 5988A quadrupole mass spectrometer and a Hewlett-Packard Model 59970C instrument for data acquisition and processing were employed. The temperatures of the TSP were stem 100°C, tip 188°C and vapour and ion source 270°C; the electron multiplier voltage was 2700 V and the electron energy was 255 eV. Full-scan spectra from *m/z* values of 150 and 180 in the PI and NI mode, respectively, were obtained. For parathion-methyl photodegradation products, the vapour and ion source temperatures were 200°C. In all the experiments the filament-on mode (ionization by an electron beam) was used. In the PI mode under full-scan conditions the sensitivity for the carbamates and organophosphorus compounds, chlorotriazines and phenylureas and their photolysis products was in the range 1–20 ng. The NI mode was used for the identification of *p*-nitrophenol, paraoxon-methyl and carbamate photolysis products as the sensitivity varied from 5 to 50 ng under full-scan conditions [12,15,19–21].

Photolysis experiments

In order to obtain stable and reproducible results in the photodegradation studies, a suntest apparatus from Heraeus (Hanau, Germany) equipped with a xenon lamp was used. This xenon arc lamp has been demonstrated to be equivalent to natural sunlight for conducting aqueous photolysis studies of several compounds, *e.g.*, carbaryl [26]. The wavelength range varies from 300 to 800 nm, which represents radiation very close to natural sunlight, and the temperature was set at 44°C. Distilled water samples, previously spiked at 0.1 ppm with aldicarb, carbaryl, cyanazine, linuron and parathion-methyl in methanolic solution and kept in a quartz reaction reservoir, were subsequently introduced into the suntest apparatus. At different periods of time, 20 μl of the solution were analysed by TSP-LC–MS. The identification of the different photolysis products was confirmed from retention index and spectral data using PI and NI modes of operation (when feasible, depending on the response of the compound) and matching with authentic standards (when available). For carbaryl,

5% of acetone was added as a photosensitizer, as done previously for organophosphorus and carbamate pesticides [12,27,28].

Fenitrothion showed slow photodegradation in distilled water when using the suntest apparatus and without the use of a photosensitizer [12]. As a consequence, in order to identify the possible photodegradation products, fenitrothion solution was irradiated in an HPK 125-W high-pressure mercury lamp fitted with a quartz filter (a gift from M. Mansour, GSF, Munich, Germany). A water–methanol (5:1) solution of 200 ppm of fenitrothion was kept in a 600 ml round-bottomed Quartz flask, attached to the high-pressure mercury lamp. In order to eliminate any effects from the heat which the mercury lamp emitted, the vessel was cooled with circulating distilled water provided by a cooling machine. The temperature of the test solution was kept at 25°C in a water-bath. After 7 h of irradiation, fenitrothion solution was injected onto a semi-preparative reversed-phase LC columns, from which six fractions were obtained by elution with methanol–water (60:40) at a flow-rate of 2 ml/min and UV detection at 254 nm. The collection times for each fraction were 0–12 min (fraction 1), 12–20 min (fraction 2) , 20–24 min (fraction 3), 24–27 min (fraction 4), 27–30 min (fraction 5) and 30–40 min (fraction 6). Fraction 1, the most polar, corresponded to fenitrooxon, and dimethylphosphoric acid and the last fraction, fraction 6, which is the least polar, corresponded to fenitrothion.

RESULTS AND DISCUSSION

Carbamates

Fig. 1 shows the amount of aldicarb and carbaryl degraded in distilled water after different periods of UV irradiation. Owing to the slower photodegradation of carbaryl than aldicarb, 5% of acetone was added to the carbaryl solutions as photosensitizer. A half-life of 50 min for carbaryl (without acetone) was obtained, 1-naphthol being the main breakdown product [11]. Previous results on the photodegradation of carbaryl using lake water and a medium-pressure mercury lamp showed a

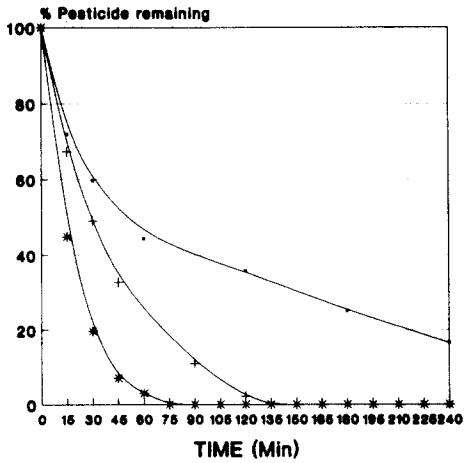

Fig. 1. Percentage of remaining pesticides aldicarb and carbaryl after UV irradiation as a function of time. ● = Carbaryl + 2% methanol; + = carbaryl + 5% of acetone; * = aldicarb + 4% of methanol.

half-life of 60 min. In general, when N-methylcarbamates are subjected to UV irradiation, the carbamate group is preserved after photolysis, although carbaryl is one of the exceptions to this rule, giving 1-naphthol [10,11]. When carbaryl is irradiated with a xenon arc lamp in an aqueous buffer solution at pH 5.5, which stabilizes the carbaryl, the photodegradation is much slower, giving a half-life of 200 h [26]. Also, when other types of water, *e.g.*, lake and sea water, were employed, quenching effects have been observed for carbaryl, thus retarding the photodegradation [11], similarly to what was observed with diuron [12].

A solution of carbaryl +5% acetone after 30 min of UV irradiation was injected directly into the TSP-LC–MS system and the total ion currents (TIC) obtained in the PI and NI modes are shown in Fig. 2. Of the different chromatographic peaks, only carbaryl (peak 1) and 1-naphthol (peak 2) could be unequivocally confirmed by TSP-LC–MS. Here carbaryl ions $[M + H]^+$ and $[M + NH_4]^+$ corresponded to *m/z* 202 and 219 with relative intensities of 10 and 100%, respectively [21]. Other workers have reported similar intensities [25,29]. As 1-naphthol does not give any signal under PI conditions [21], NI conditions were used. The $[M - H]^-$ and $[M + CH_3COO]^-$ ions, at *m/z* 143 and 203, for 1-naphthol and $[M - CONHCH_3 + CH_3COOH]^-$, at *m/z* 203, for carbaryl were obtained. The ion formation in the PI and NI modes in TSP-LC–MS and the differences in sensitivity between the PI and NI mode of operation for carbaryl and 1-naphthol were reported in previous papers [21,30].

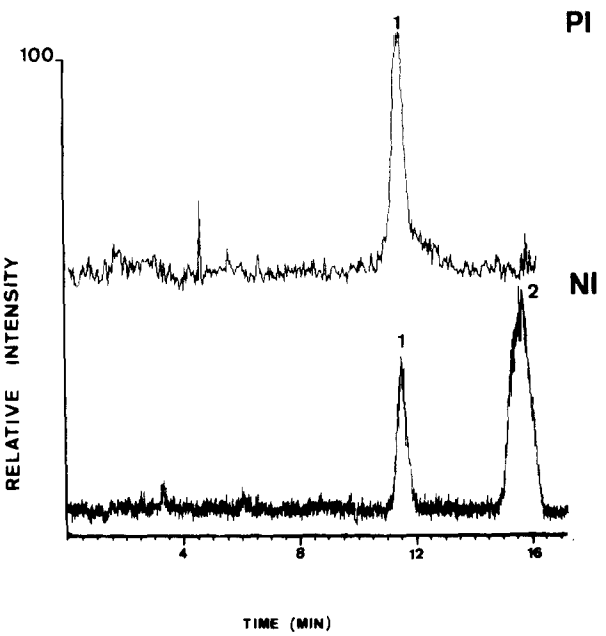

Fig. 2. TIC chromatogram obtained by TSP-LC–MS in PI and NI modes of a 9 ppm degraded solution of carbaryl (+ 5% acetone) after 30 min of photodegradation with the suntest apparatus. For carbaryl (peak 1), the ions identified corresponded to $[M + H]^+$ and $[M + NH_4]^+$ and $[M - CONHCH_3]^-$ in the PI and NI modes, respectively, whereas those for 1-naphthol (peak 2) corresponded to $[M - H]^-$ and $[M + CH_3COO]^-$ in the NI mode. The structures of both compounds are given in Fig. 3. LC mobile phase: methanol–water (50:50) + 0.05 *M* ammonium acetate at 1 ml/min. LC packing: 5-μm LiChrospher 100 RP-18.

The use of the NI mode for carbamate identification is not a common practice in MS, as indicated previously [31], as it gave poor sensitivities, close to 4–5 orders of magnitude lower than the PI mode [29]. The good sensitivity for carbaryl under NI conditions was attributed to its 1-naphthol structure, which can easily stabilize the negative charge under NI conditions [21]. The structures of carbaryl and its photodegradation product 1-naphthol are shown in Fig. 3.

Concerning the degradation of aldicarb, it has been reported that aldicarb sulphoxide and sulphone are the main degradation products of aldicarb under microbial degradation [32], hydrolysis [9] and chlorination of water at pH in the neutral to alkaline range [33]. Sulphoxide and sulphone metabolites are obtained when photooxidation is applied to a variety of organophosphates [14] and this was also expected to occur with aldicarb [10], but so far no data are available. Selected-ion monitoring (SIM) chromatograms obtained in the PI and NI modes for aldicarb sulphoxide are shown in Fig. 4, corresponding to an aldicarb solution after 180 min of UV irradiation. Fig. 3 shows the structures of aldicarb and aldicarb sulphoxide. Other

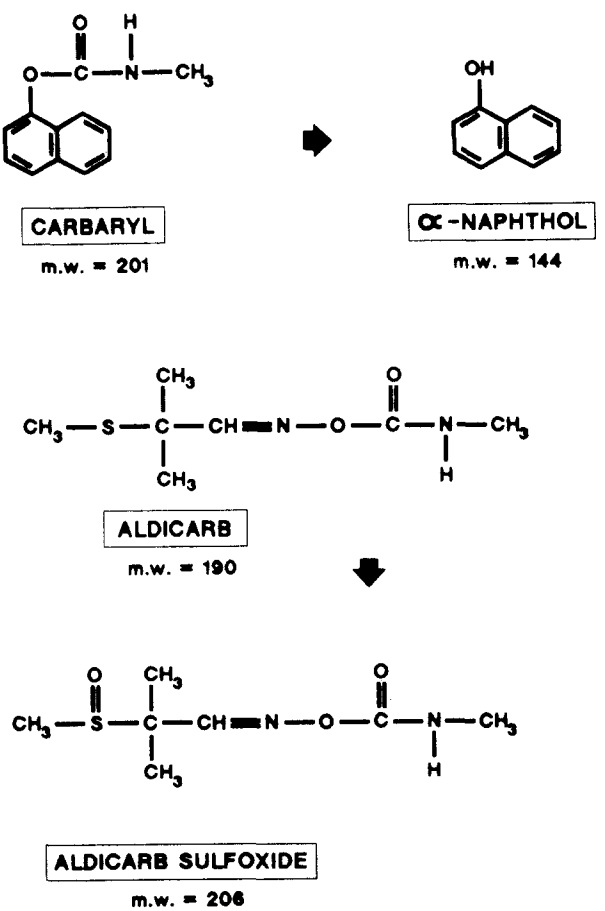

Fig. 3. Main photodegradation products of carbaryl and aldicarb in water. m.w. = Molecular weight.

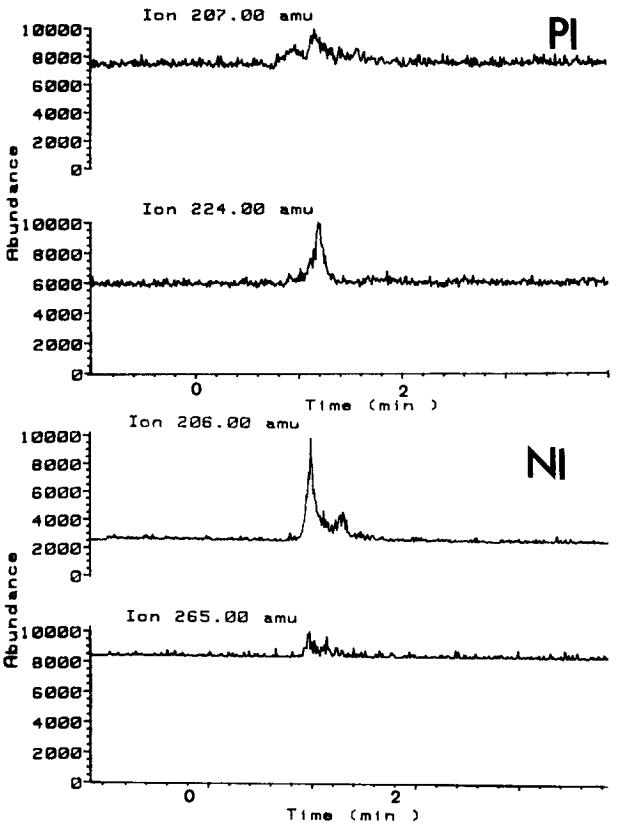

Fig. 4. SIM chromatograms obtained by TSP-LC–MS in PI and NI modes of a 15 ppm μg/l degraded solution of aldicarb after 180 min of photodegradation with the suntest apparatus. Aldicarb sulphoxide was identified by the $[M + H]^+$ and $[M + NH_4]^+$ ions and $[M]^-$ and $[M + CH_3COO]^-$ ion in PI and NI modes, respectivey. The structure of aldicarb sulphoxide is given in Fig. 3. Other experimental conditions as in Fig. 2.

peaks were observed in the chromatographic traces, but only aldicarb sulphoxide could be positively identified. In the PI mode of operation, aldicarb sulphoxide $[M + H]^+$ and $[M + NH_4]^+$ ions corresponded to *m/z* 207 and 224 whereas in the NI mode $[M]^{\cdot -}$ and $[M + CH_3COO]^-$ ions corresponded to *m/z* 206 and 265. The PI mode showed $[M + NH_4]^+$ as the base peak, as reported for aldicarb sulphoxide [22,23,25], whereas the NI TSP-LC–MS results are reported here for the first time. The different adduct ions obtained in the PI and NI modes of operation for the carbamate insecticides and their photolysis products are indicated in Table I.

Aldicarb sulphoxide and sulphone showed a 1.5 order of magnitude lower sensitivity in the NI than in the PI mode. Aldicarb sulphone was not detected in all the experiments performed, even with the use of SIM. This could be attributed to the fact that the formation of aldicarb sulphone may need the addition of a photosensitizer, such as acetone. In this respect, it has been reported that for the detection of aldicarb sulphone acetone is needed as a photosensitizer in postcolumn indirect photolysis [28].

TABLE I

IMPORTANT FRAGMENTS AND RELATIVE INTENSITIES OBSERVED IN TSP-LC–MS IN PI AND NI MODES AND FILAMENT-ON MODE OF OPERATION

Mol. wt.	Compounds and ions (m/z and tentative identification)		PI mode	NI mode
Carbamate pesticides + photolysis products				
144	Naphthol			
	143	$[M - H]^-$		100
	203	$[M + CH_3COO]^-$		50
201	Carbaryl			
	202	$[M + H]^+$	10	
	203	$[M - CONHCH_3 + CH_3COOH]^-$		100
	219	$[M + NH_4]^+$	100	
206	Aldicarb sulphoxide			
	206	$[M]^{\cdot -}$		100
	207	$[M + H]^+$	40	
	224	$[M + NH_4]^+$	100	
	265	$[M + CH_3COO]^-$		50
Chlorotriazine herbicides + photolysis products				
155	Deisopropylhydroxyatrazine			
	156	$[M + H]^+$	100	
	215	$[M + CH_3COONH_4 + H - H_2O]^+$	10	
183	Hydroxysimazine			
	184	$[M + H]^+$	100	
	243	$[M + CH_3COONH_4 + H - H_2O]^+$	10	
240	Cyanazine			
	241	$[M + H]^+$	100	
	300	$[M + CH_3COONH_4 + H - H_2O]^+$	10	
Organophosphorus pesticides + photolysis products				
126	Dimethylphosphoric acid			
	144	$[M + NH_4]^+$	100	
139	*p*-Nitrophenol			
	198	$[M + CH_3COO]^-$		100
247	Paraoxon-methyl			
	232	$[M - CH_3]^-$		100
261	Fenitrooxon			
	262	$[M + H]^+$	20	
	279	$[M + NH_4]^+$	100	
277	Fenitrothion			
	278	$[M + H]^+$	30	
	295	$[M + NH_4]^+$	100	
Phenylurea herbicides + photolysis products				
214	Monolinuron			
	215	$[M + H]^+$	20	
	232	$[M + NH_4]^+$	100	
248	Linuron			
	249	$[M + H]^+$	20	
	266	$[M + NH_4]^+$	100	

Chlorotriazines

Photodegradation studies carried out with the chlorotriazine atrazine have shown that hydroxyatrazine is one of the main degradation products formed in various water samples [12,27]. Further photolysis breakdown products such as 2-H, 2-H-deisopropylhydroxyatrazine and 2-methoxydeisopropyl analogues have been reported for atrazine and simazine in distilled water solution [15] and using particulate titania as a photocatalyst [34]. A solution of cyanazine degraded after 4.5 h was injected into the TSP-LC–MS system and the selected ion chromatograms obtained in the PI mode are shown in Fig. 5. By using this mode of operation, $[M + H]^+$ is obtained as base peak with no adduct formed with NH_4^+, which was attributed to a higher proton affinity of the chlorotriazines than ammonia [4,15,21]. As the second most abundant ion $[M + CH_3COONH_4 + H - H_2O]^+$ was formed with a relative abundance between 5 and 10%, which is not indicated in the Fig. 5 owing to its poor signal but it has been reported elsewhere [21].

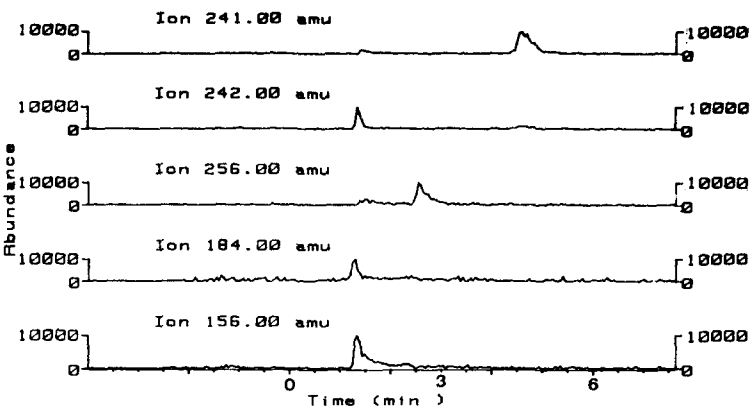

Fig. 5. Selected ion chromatograms obtained by TSP-LC–MS in the PI mode of a 200 ppm degraded solution of cyanazine after 300 min of photodegradation with the suntest apparatus. The ions identified correspond to $[M + H]^+$ and their structures are given in Fig. 6.

The tentative identification of the different photodegradation products is shown in Fig. 6. Hydroxysimazine (HSIM) (mol. wt. 183) and deisopropylhydroxyatrazine (DIHA) (mol. wt. 155) were positively identified and correspond to the degradation of the 2-chloro position of the triazines to its corresponding 2-hydroxy analogues together with a dealkylation process. These two breakdown products were previously identified for simazine [15] and are expected to be formed when chlorotriazines are subjected to UV irradiation [35].The formation of the methoxy analogue (mol. wt. 255) due to the photolysis in the presence of a small amount of methanol and the transformation of the cyano group into a carboxylic group (mol. wt. 241) are also expected behaviour in the degradation of chlorotriazines and it has been described elsewhere [35]. The ions and relative intensities of the main photolysis products are given in Table I.

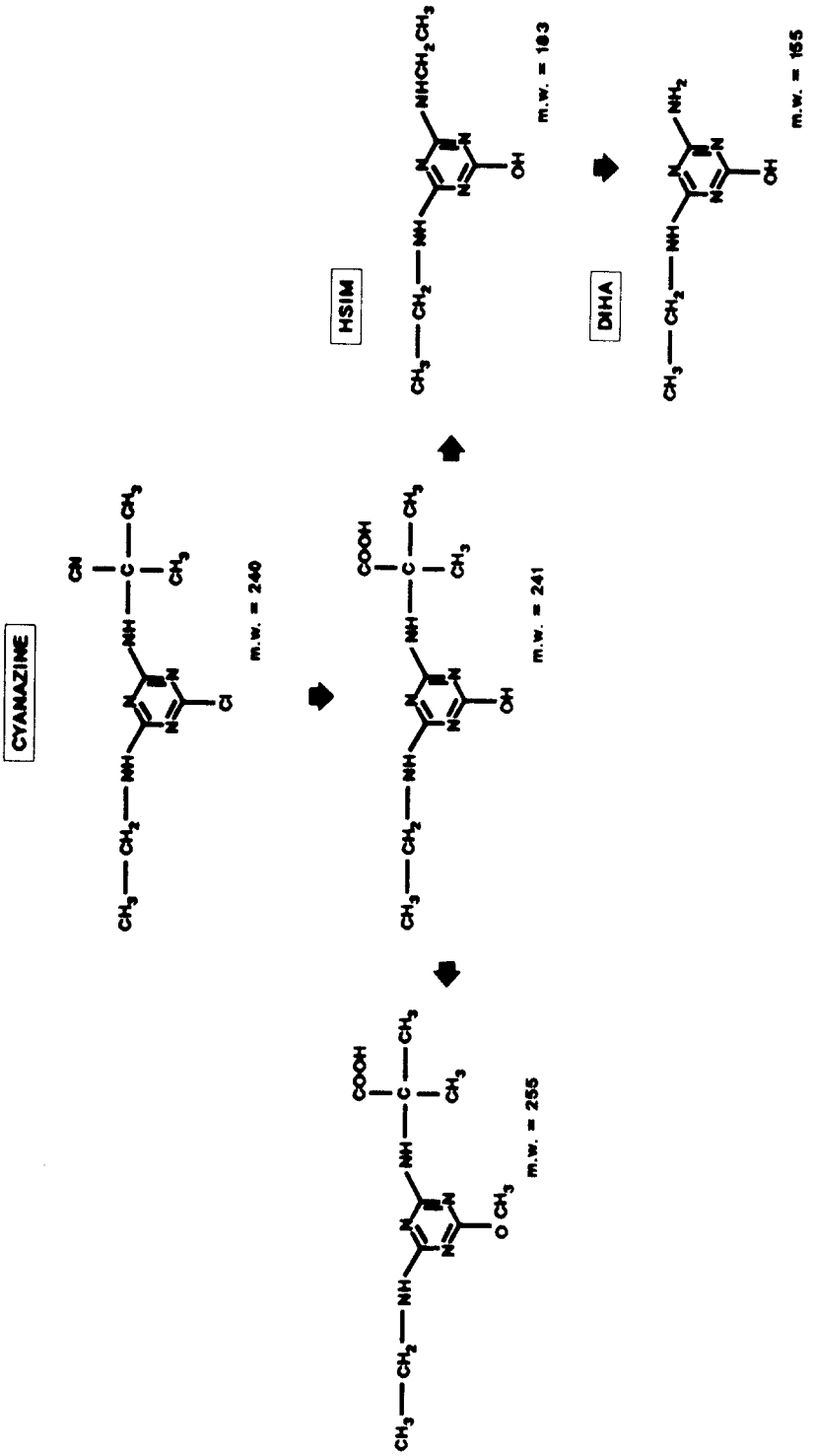

Fig. 6. Tentative photodegradation pathway of cyanazine (mol. wt. 240) in water containing 3–4% of methanol.

Organophosphorus compounds

Photodegradation studies in water using either sunlight [14] or UV irradiation [14,27,36] have shown a variety of photoalteration products, *e.g* oxo derivatives and different phenols. When solutions of fenitrothion in water were irradiated with a xenon lamp using the suntest apparatus [12], it has been shown that after 3 h of irradiation virtually no breakdown product was observed with 50% degradation of the parent compound. As a consequence, in the present experiments a solution of fenitrothion in water was irradiated with a high-pressure mercury lamp, which provides stronger UV irradiation than the xenon lamp. In this way, we still were able to identify some of the breakdown products formed. Fenitrothion solutions were irradiated for 7 h and subsequently the irradiated solution was injected onto a semi-preparative LC column from which six fractions were collected and analysed directly by

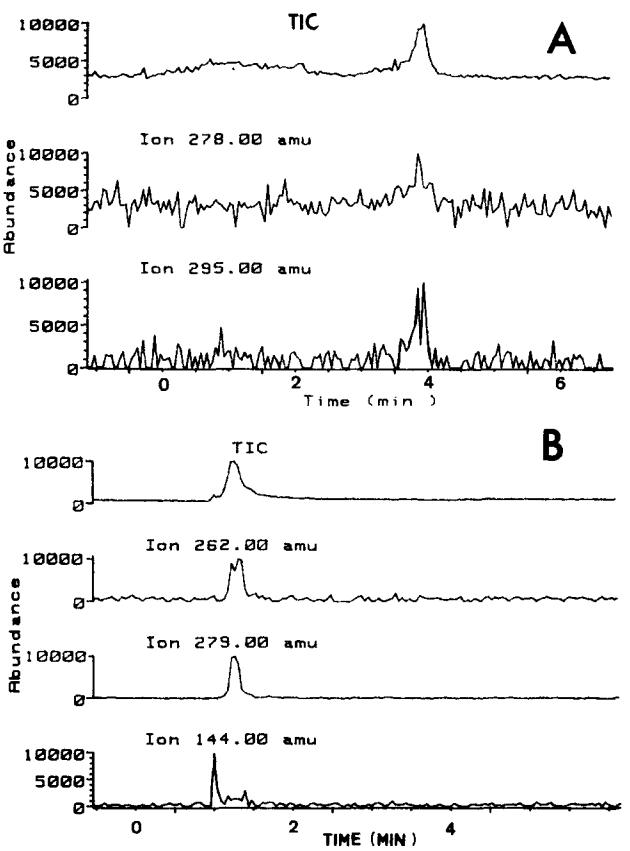

Fig. 7. TIC and selected ion chromatograms obtained by TSP-LC–MS in the PI mode of a 200 ppm degraded solution of fenitrothion after 420 min of irradiation with a high-pressure mercury lamp. Fractions 1 and 6 of the fenitrothion degraded solution were separated in a semi-preparative Polyglosil 500-7 C_{18} HPLC column and injected into the TSP-LC–MS system. In fraction 6 the ions of fenitrothion identified corresponded to $[M + H]^+$ and $[M + NH_4]^+$. In fraction 1 fenitrooxon was identified also by the $[M + H]^+$ and $[M + NH_4]^+$ ions, whereas dimethylphosphoric acid could be identified only by its $[M + NH_4]^+$ ion. The photodegradation scheme of fenitrothion is given in Fig. 8. LC mobile phase: methanol–water (70:30) + 0.05 *M* ammonium formate at 1 ml/min. LC packing: 5-μm LiChrospher 100 RP-18.

TSP-LC–MS. In the most polar fraction, fraction 1, fenitrooxon and dimethylphosphoric acid, could be identified, whereas fenitrothion was identified in the least polar fraction, fraction 6. Other compounds have been detected in the other fractions that may correspond to different photolysis products of fenitrothion, *e.g.*, carbometoxyfenitrothion [36]. Such fractions are still under investigation and future work will consider the identification of the different photolysis products of fenitrothion.

Fig. 7 shows the TIC and selected ion chromatograms obtained by TSP-LC–MS in the PI mode. Fenitrothion and fenitrooxon gave $[M + H]^+$ and $[M + NH_4]^+$ corresponding to *m/z* values of 278 and 295 for fenitrothion and *m/z* 262 and 279 for fenitrooxon. As the scan started at *m/z* 140 the $[M + H]^+$ ion could not be obtained for dimethylphosphoric acid and it was identified only by its $[M + NH_4]^+$ ion, corresponding to *m/z* 144. In all instances $[M + NH_4]^+$ was the base peak [19,37] and the identification of the two breakdown products was matched with authentic standards.

The identification of dimethylphosphoric acid was feasible as this compound was obtained during the synthesis of fenitrooxon and it is formed by hydrolysis [19] and matches the results obtained for this compound in TSP-LC–MS [38]. The tentative photodegradation pathway of fenitrothion is indicated in Fig. 8. The formation of the photoalteration products identified by us agrees with the photodegradation products which are expected to be formed for fenitrothion when using a low-pressure mercury lamp [36].

The photodegradation of parathion-methyl was carried out in aqueous solution and using the suntest apparatus. Fig. 9 shows the TIC chromatogram corresponding to a solution containing 0.1 ppm of parathion-methyl after 2 h of irradiation. In Fig. 9 the selected ions at *m/z* values of 198 and 232 corresponded to $[M + CH_3COO]^-$ and $[M - CH_3]^-$ of *p*-nitrophenol and paraoxon-methyl, respectively. Both metabolites have already been reported in photolysis experiments with parathion-methyl [14,27].

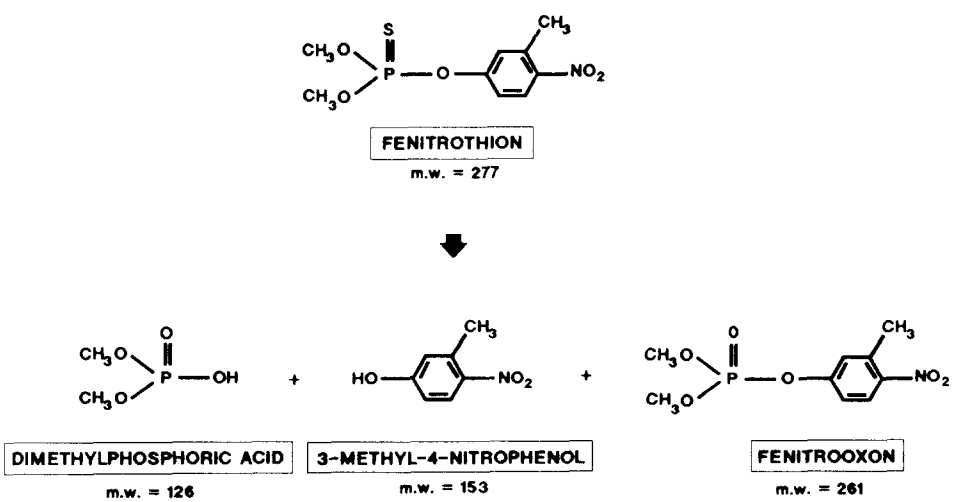

Fig. 8. Tentative photodegradation pathway of fenitrothion (mol. wt. 277) in water containing 3–4% of methanol.

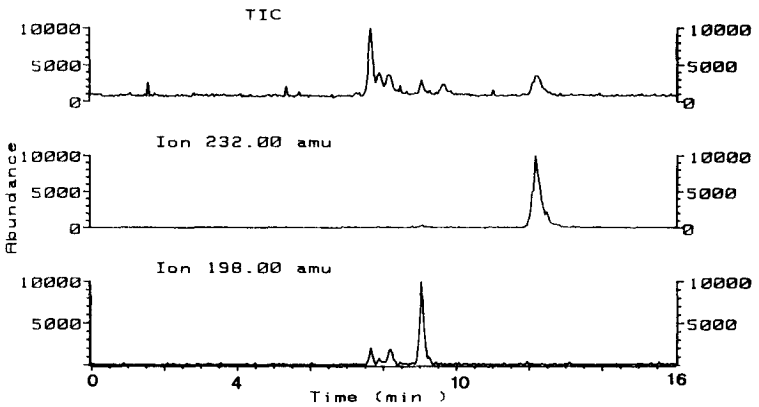

Fig. 9. TIC and selected ion chromatrograms obtained by TSP-LC–MS in the NI mode of a 50 ppm degraded solution of parathion-methyl after 120 min of photodegradation with the suntest apparatus. The ions identified correspond to $[M + CH_3COO]^-$ and $[M - R]^-$ for *p*-nitrophenol and paraoxon-methyl, respectively. The photodegradation pathway is given in Fig. 10. LC mobile phase: acetonitrile–water (50:50) + 0.05 *M* ammonium acetate for 5 min with a gradient elution up to 90% of acetonitrile in 20 min. LC packing: 5-μm LiChrospher 100 RP-18. Flow-rate, 1 ml/min.

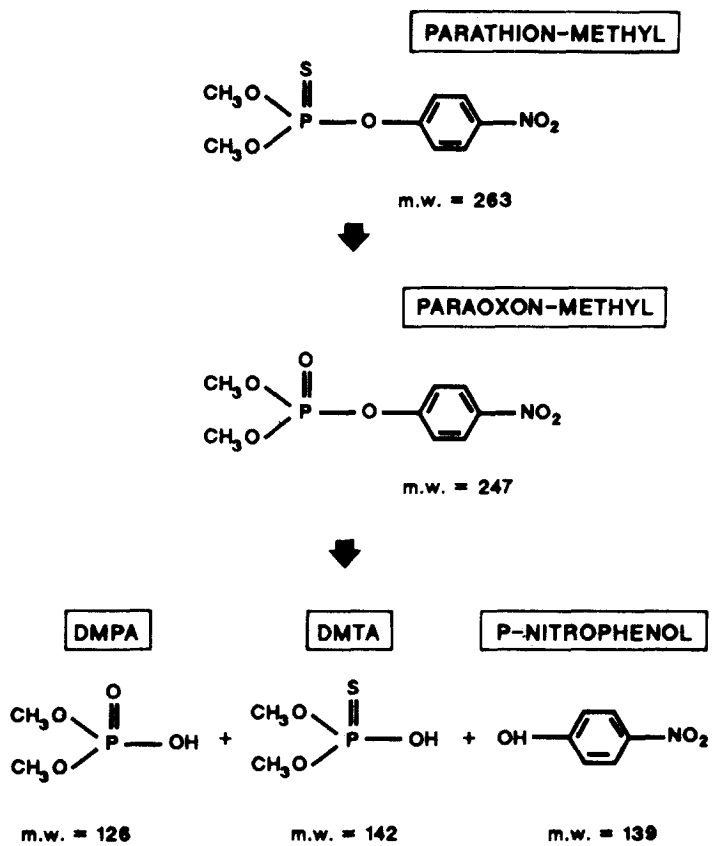

Fig. 10. Tentative photodegradation pathway of parathion-methyl (mol. wt. 263) in water containing 3–4% of methanol.

Identification of *p*-nitrophenol was reported previously under NI conditions [20] when hydrolysis experiments on parathion-methyl were carried out. As *p*-nitrophenol can only be detected under NI conditions but parathion-methyl in both modes of operation [19,37], the NI mode was preferred for the simultaneous identification of both compounds. The $[M - CH_3]^-$ ion was monitored instead of $[M]^{\cdot -}$ for parathion-methyl, because during these experiments we were working at lower vapour and source temperatures (200°C) instead of 270°C. At lower temperatures the $[M - CH_3]^-$ peak decreases whereas at higher temperatures $[M]^-$ is the base peak as a consequence of the better electron-capture mechanisms at these higher temperatures [19]. The tentative photodegradation pathway of parathion-methyl is indicated in Fig. 10. The ions and relative abundances of the different photolysis products of organophosphorus pesticides are given in Table I.

Under the experimental conditions used, parathion-methyl was not detected after 2 h of irradiation, which indicates a much stronger photodegradation than fenitrothion. This corresponds to a much shorter half-life than that reported [27], where degradation of 80% of the pesticide occurred after 5 h of irradiation. Such a

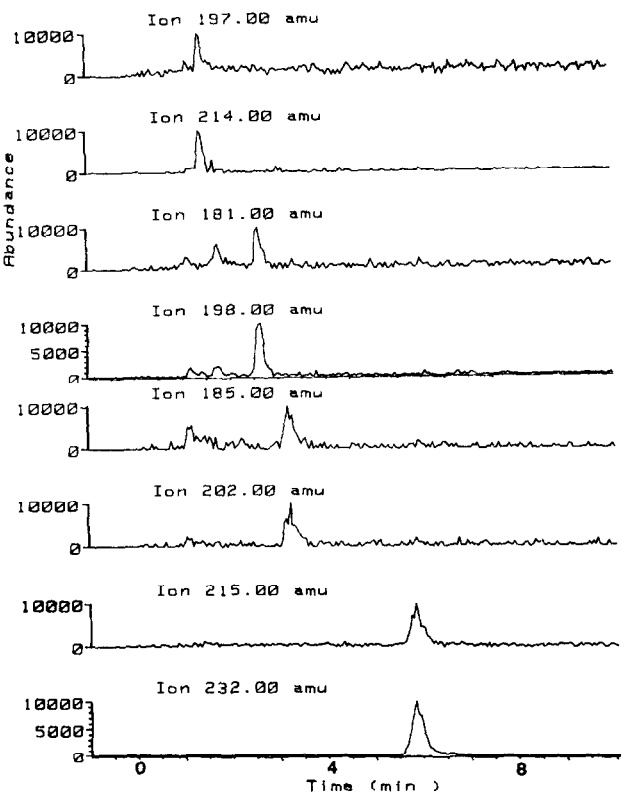

Fig. 11. Selected ion chromatograms obtained by TSP-LC–MS in the PI mode of a 100 ppm degraded solution of linuron after 300 min of photodegradation with the suntest apparatus. Each breakdown product was identified by $[M + H]^+$ and $[M + NH_4]^+$ ions and the corresponding photodegradation pathway is given in Fig. 12. LC mobile phase: methanol–water (50:50) + 0.05 *M* ammonium acetate. LC column, Brownlee. Flow-rate, 1 ml/min.

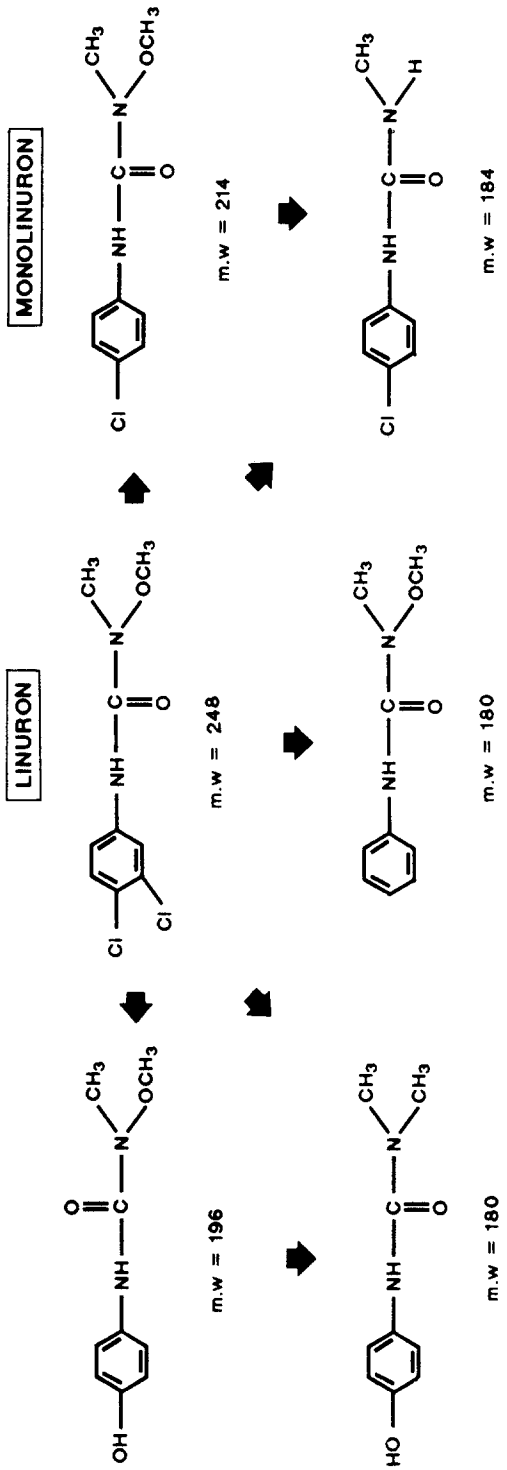

Fig. 12. Tentative photodegradation pathway of linuron (mol. wt. 248) in water containing 3–4% of methanol.

discrepancy can be explained by the different suntest photolysis temperature (44°C in our experiments *versus* 20°C).

Phenylureas

Previous photodegradation studies carried out with phenylurea herbicides showed that dechlorination is one of the main degradation pathways of diuron [12], linuron [13], buturon and monolinuron [39]. Further photodegradation products reported corresponded to OH, CHO and H derivatives [13,39]. In most of the examples cited [13,39], identification of the different photoproducts was carried out off-line, after isolation of the different reaction products and injection into a gas chromatograph.

Linuron solutions in distilled water were irradiated in the suntest apparatus and subsequently injected directly into the TSP-LC–MS system. A half-life of 2 h has been found for this compound. This is much shorter than the photodegradation under sunlight conditions, which has been reported to be very slow, 69% of the compound remaining after 2 months [13]. A solution of linuron after 4.5 h of irradiation was injected into the TSP-LC–MS system in the PI mode and the selected ion chromatograms obtained are shown in Fig. 11. The PI mode of operation was preferred to the NI mode [40] as the sensitivities are 30% better and the information obtained corresponds to $[M + NH_4]^+$ as the base peak and the second most abundant ion, varying from 10 to 25%, corresponds to $[M + H]^+$. In Fig. 11 each of the metabolites identified was monitored using both ions. Linuron could only be identified in the SIM mode, because after 4.5 h of irradiation of a linuron solution only 6% of the parent compound remained. The tentative degradation pathway of linuron is shown in Fig. 12, monolinuron being one of the main breakdown products. The ions and relative abundances of monolinuron and linuron are indicated in Table I.

At a molecular weight of 180 two possible photoproducts of linuron are indicated in Fig. 12. These two compounds are likely to be formed [13] but at present we do not know which one predominates in photolysis experiments. However, considering the retention times and structures of these two metabolites, it is feasible to consider that the dehydroxylated metabolite has been identified as it elutes later than the compound of mol. wt. 196, as can be observed in Fig. 11.

CONCLUSIONS

The combination of PI and NI modes of TSP-LC–MS has allowed the identification of different photolysis products of carbamate, chlorotriazine, organophosphorus and phenylurea pesticides in water by direct injection of the photodegradation solutions into the LC system. The method is much simpler than those currently used, which require various steps prior to the MS characterization of the breakdown products. By using PI and NI modes of operation and co-elution with authentic standards, different polar photodegradation products were identified, such as 1-naphthol and aldicarb sulphoxide for carbaryl and aldicarb, respectively, hydroxysimazine and deisopropylhydroxyatrazine for cyanazine, fenitrooxon and dimethylphosphoric acid for fenitrothion, paraoxon-methyl and *p*-nitrophenol for parathion-methyl and monolinuron for linuron.

Although aldicarb does not give any signal when 1 μg is injected into the TSP-

LC–MS, system in the NI mode, aldicarb sulphoxide could be unequivocally identified in this mode of operation for the first time, thus indicating the usefulness of utilizing both modes of operation in the detection of polar pesticide metabolites.

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