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Application of gas and liquid chromatography–mass spectrometry to the evaluation of pirimiphos methyl degradation products in industrial water under ozone treatment

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Abstract

The organophosphorus compound pirimiphos methyl was oxidized in water under ozonolysis in the presence of formulating agents. A rapid sample handling procedure was developed based on liquid–solid extraction with nonporous carbon cartridges. This sorbent material allowed recovery of the polar degradation products (DPs). Analysis of oxidized solutions was performed with both GC–ion trap (IT)-MS using either electron impact or chemical ionization as ionization modes and LC–atmospheric pressure ionization (API)-MS using either an ionspray (ISP) or an atmospheric pressure chemical ionization (APCI) interface in order to confirm the presence of DPs. The performances of both technologies were evaluated for structure elucidation and quantitation by using pirimiphos methyl, 2,4-aminophenol and cyanuric acid as external standards of DPs. LC–API-MS techniques allowed the detection of six DPs, of which two were not detected by GC–IT-MS techniques, even after a derivatization procedure with BF_3–MeOH reagent. ISP was the most suitable ionization method for identifying the DPs, because sodium or potassium adduct ions were of great help in confirming the molecular mass of unknowns. APCI provided more fragmentation patterns than ISP. However unequivocal identification of all DPs was impossible and only a tentative degradation pathway of pirimiphos methyl in water under ozone is proposed. At the end of the reaction time, DPs accounted for between 70 and 85% of the initial concentration of methyl pirimiphos.

Keywords: Water analysis; Ozonation; Pesticides; Pirimiphos methyl; Organophosphorus compounds

1. Introduction

Water pollution by organophosphorus pesticide (OPs) is of great concern due to their acute toxicity toward aqueous environments [1]. Their fate has therefore led to several investigations: their degradation involves chemical hydrolysis particularly at basic pH [2] and photochemical transformation leading to the formation of s-methyl isomers [3] and oxon derivatives [4]. Photocatalytic oxidation by semiconductor oxides such as TiO_2 or by Fenton's reagent have been evaluated for reducing the toxicity of wastewaters contaminated by OPs [5,6]. Over the last decade, a growing interest has been paid to ozone reactivity in relation to the elimination of pesticide residues [7]. However, little data is available on the capability of this clean technology to degrade OPs [8]. Even though ozone is a strong oxidant agent (E^o=2.07 V), the total pesticide mineralization is usually insignificant, but the objective is to oxidize the nonbiodegradable compounds to biodegradable ones and afterwards subsequent bio-

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logical treatments can be carried out easily with this water treatment [9]. Numerous stable intermediates are formed during ozonation experiments [10]. Since there is a lack of degradation product (DP) standards, it is difficult to identify pesticide degradation pathways, and the major objective for the analytical chemist is to get evidence on the DPs structural characteristics (e.g. preservation of aromatic ring, nature of functional groups) in order to improve degradation processes further [11]. Possible toxic DPs can be formed at low concentration levels (ppb) and the use of mass spectrometry (MS) is needed in order to gather qualitative and quantitative information in a fast way. The analysis of OPs in water samples is generally performed by liquid–solid extraction (LSE) followed by gas chromatographic (GC)–MS techniques [12]. LSE is a more appealing extraction procedure than liquid–liquid extraction (LLE) for environmental water analysis since, using polymeric or carbon materials, selectivity can be introduced in the preconcentration step and extraction of more polar compounds can be achieved. However, analyte breakthrough volumes are strongly dependent on the nature and amount of interferences. Moreover, when dealing with wastewaters, the influence of formulating agents (e.g. detergents, nonvolatile organic solvents), which account for more than 50% in the commercial specialities, on the analyte recoveries has rarely been studied systematically [13]. GC–ion trap (IT)-MS technology exceeds the possibilities of quadrupole instrumentation in the field of degradation studies since its ability to use electron impact and chemical ionization and MS–MS modes yielding complementary information is very useful for DPs identification purposes [11]. However, pesticide DPs usually include polyfunctional compounds such as phenols or acidic compounds. This implies the necessary use of a time-consuming derivatization procedure in order to identify the less volatile or very polar DPs by GC–MS [14]. As a consequence, there is a clear tendency to use liquid chromatographic (LC)–MS techniques with atmospheric pressure ionization (API) interfaces in order to determine both parent compounds and their DPs [15]. Both ionspray (ISP) and atmospheric pressure chemical ionization (APCI) allowed limits of detection at the picogram level to be obtained for two groups of selected OPs [16,17]. The increase of the extraction potential values in API techniques provides no more than three different fragment ions making the DPs structure elucidation difficult [18]. Only tentative degradation pathways are usually proposed. Unequivocal identification of DPs has to be carried out by means of more complex and time-consuming techniques such as LC–MS–MS [19] and NMR after LC fraction collection or by performing the synthesis of the metabolites [20].

In this work, the ozonolysis of the formulated organophosphorus compound, pirimiphos methyl, in water was undertaken and the main objectives of our studies were:

1. To develop a rapid sample handling procedure for the analysis of the pirimiphos methyl DPs in industrial waters.
2. To evaluate the respective performances of LC–API-MS and GC–IT-MS techniques for carrying out degradation studies.
3. To propose a degradation pathway of pirimiphos methyl in water under ozonolysis.

2. Experimental

2.1. Chemicals

LC-grade water, methanol and BF_3–methanol reagent were obtained from Merck (Darmstadt, Germany). All the solvents were passed through a 0.45 μm filter from Scharlau (Barcelona, Spain) before use. Ammonium formate, formic acid, cyanuric acid anhydrous and 2,4-aminophenol were purchased from Fluka (Basel, Switzerland). Analytical-grade, technical (>95% purity) and formulated pirimiphos methyl with trade name Actellic 50E (50%, w/w), were a gift from Zeneca (Madrid, Spain). Pesticide-grade dichloromethane, ethyl acetate and chloroform were supplied by Panreac (Barcelona, Spain).

2.2. Chromatographic conditions

For GC analysis, a Varian 3400 gas chromatograph equipped with a 1093 septum programmable injector model and a 8200 autosampler was used. A 30 m×0.25 mm I.D. fused-silica capillary column coated with chemically bonded phenyl methyl DB-5

(J&W Scientific, Folsom, CA, USA) was programmed from 60°C to 130°C at 23 C°/min and from 130°C to 210°C at 4.7 C°/min, up to 280°C at 23 C°/min and introduced into the ion source via a transfer line, the temperature of which was set at 280°C. Helium was used as a carrier (11 p.s.i.; p.s.i.=6894.76 Pa). The injection volume was 2 μl and the injection mode was splitless.

For LC analysis, the eluent was delivered by a gradient HP1100 series pumping system (Palo Alto, CA). An analytical column 150×2.1 mm I.D. Hypersil DBS packed with 5 μm particle size (Shandom Scientific, Cheshire, UK) was used. For LC–ISP-MS experiments, gradient elution was performed with an eluent A [containing methanol–water (95:5) with 1% formic acid] and an eluent B (containing water with 1% formic acid). The LC eluent conditions varied from 98% of B (5 min isocratic conditions) to 100% of A in 35 min at 0.3 ml/min; back to initial conditions in 5 min. For LC–APCI-MS experiments, a buffer (ammonium formate–formic acid, pH 3) was added in B instead of 1% formic acid. The flow-rate was set at 0.4 ml/min.

2.3. MS analysis

A GC–IT-MS Saturn 3 system (Varian, Harbor City, CA, USA) was used for GC–MS analysis either in the electron impact (EI) mode at 70 eV or in the chemical ionization (CI) mode using acetonitrile as reagent gas. Operating parameters in EI and CI modes were optimized as described elsewhere [21].

A Hewlett–Packard Model G1946A (Palo Alto, CA, USA) LC–API-MS system with a quadrupole mass spectrometer and a Hewlett–Packard Model G2710AA instrument for data acquisition and processing were used. LC–MS interface conditions were:

1. APCI: source and probe temperatures were set at 200°C and 300°C, respectively. Corona discharge emission current was set at 6 μA. Fragmentor (extraction voltage) was optimized at 100 V. Nitrogen drying gas flow-rate and nitrogen nebulizer gas pressure were 4 l/min and 40 p.s.i., respectively.
2. ISP: capillary and fragmentor voltages were set at 4 kV and 100 V, respectively. Nitrogen drying gas flow-rate and nitrogen nebulizer gas pressure were 8 l/min and 40 p.s.i., respectively. Source temperature was set at 150°C.

2.4. Ozonation experiments

Ozone was generated by corona discharge in oxygen using an Ambiozon GMF-10 ozonizer (Madrid, Spain). The laboratory-made reactor which has a capacity of 60 l is described elsewhere [22]. The stream of air and ozone was continuously introduced at the bottom of the reactor at a flow-rate of 100 l/h with 2 mg/l of ozone. The temperature was kept in the range 21±2°C. Dissolved ozone concentration in water was determined by the indigo method reaching a value of 0.4 mg/l at the equilibrium. Sixty litres of distilled water were successively spiked with 20 mg/l or 200 mg/l of technical or formulated pirimiphos methyl.

2.5. Sample preparation

At different periods of time, three 100 ml water samples were gathered from the reactor. Samples were acidified at pH 2.5 with sulfuric acid and preconcentrated by means of either a dichloromethane LLE (2×20 ml) or a LSE using either disposable 6 ml Isolute ENV+ cartridges from International Sorbent Technology (Hengoed, UK) packed with 500 mg styrene–divinylbenzene (PS–DVB) sorbent or disposable 6 ml Supelclean ENVI-Carb cartridges from Supelco (Bellefonte, PA, USA) packed with 500 mg of nonporous carbon sorbent. For LSE experiments, sample preconcentration was carried out manually at a flow-rate of 5 ml/min. Isolute ENV+ cartridges were conditioned by passing through 2 ml ethyl acetate, 2 ml acetone and 2 ml of distilled water and with 5 ml of dichloromethane–methanol (80:20), acidified with formic acid and 5 ml of distilled water in the case of ENVI-Carb cartridges. After a drying step, polymeric cartridges were eluted by 5 ml of methanol, while carbon cartridges were eluted by 5 ml of dichloromethane followed by 5 ml of methanol with 1% formic acid. LLE and LSE extracts were carefully evaporated to dryness and the residues were dissolved in 1 ml of methanol and split into two 500 μl aliquots either for derivatization purposes or direct injection into LC systems. An esterification procedure by means of

BF_3–MeOH was performed as described elsewhere [22,23]. Briefly, a solution of 2 ml of BF_3–methanol was added to the 500 μl methanol extract and was heated at 100°C for 10 min. After immediate cooling on ice, 20 ml of ice cold distilled water was added and the mixture extracted with 2 ml of chloroform and the extract was preconcentrated to 500 μl before GC–MS analysis.

3. Results and discussion

3.1. Ozonation kinetics

Pirimiphos methyl is stable in acidified water and no loss via chemical hydrolysis was observed after 4 h in solutions kept in the dark at pH 2.5. Conversely, at basic pH 9 degradation strongly occurred after 30 min. Fig. 1 shows the degradation curves of pirimiphos methyl under ozone along with the evolution of the total organic content (TOC) of the solutions during the reaction time. When ozonation of the technical product at initial concentration of 20 mg/l was undertaken, 90% of the compound was depleted within 60 min. The use of formulated product resulted in a very similar kinetic profile. Similar results were obtained at the 200 mg/l concentration level so degradation was shown not to be dependent on the initial concentration. Degradation fitted a first order reaction with respect to pirimiphos methyl. Since no decrease in TOC values took place during the reaction, mineralization could be regarded as an insignificant process and the formation of DPs was expected.

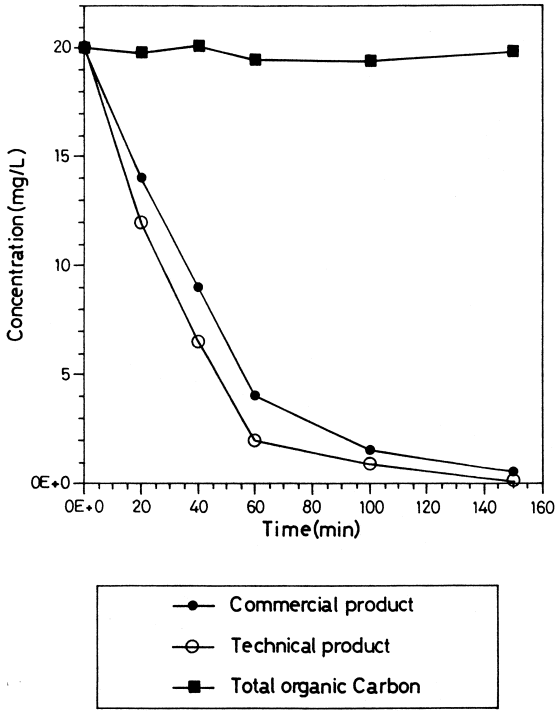

Fig. 1. Kinetics of disappearence of pirimiphos methyl as a function of ozonation time (in min) of (●) 20 mg/l of commercial product, (○) 20 mg/l technical product and (■) total organic carbon.

3.2. Identification of DPs

3.2.1. GC–IT-MS

At the end of the ozonation experiments, water pH values dropped to 4.2 suggesting the formation of ionic compounds. An esterification procedure was unavoidable before their detection by GC–IT-MS, although drastic experimental conditions might lead to the formation of artefact DPs as a consequence of their degradation. Pirimiphos methyl remained stable under this procedure which partly ensured the analytical integrity of the samples. Typical GC–IT-MS traces after 80 min of a treatment by ozone of a 20 mg/l formulated pirimiphos methyl solution are shown in Fig. 2. In Fig. 2a the EI mode was used while in Fig. 2b the CI mode was used. Both total ion chromatograms contain the parent compound (compound 6) together with 3 DPs (compounds 3,4,5) as a consequence of the oxidation process. Compounds were regarded as DPs provided that their concentration increased or decreased clearly as a function of the reaction time. Other peaks present in the chromatograms showed stable profiles versus time or a continuous decrease. Therefore, they were not considered involved in the pirimiphos methyl degradation process. These compounds were identified as phatalates exhibiting typical m/z 149 ions or linear alkyl compounds exhibiting typical losses of 14 a.m.u. They originated from the extraction procedure or surfactants present in the formulated product [24]. Identification of DPs was tentatively carried out on the base of their EI fragmentation patterns reported in Table 1. Their hypothetical

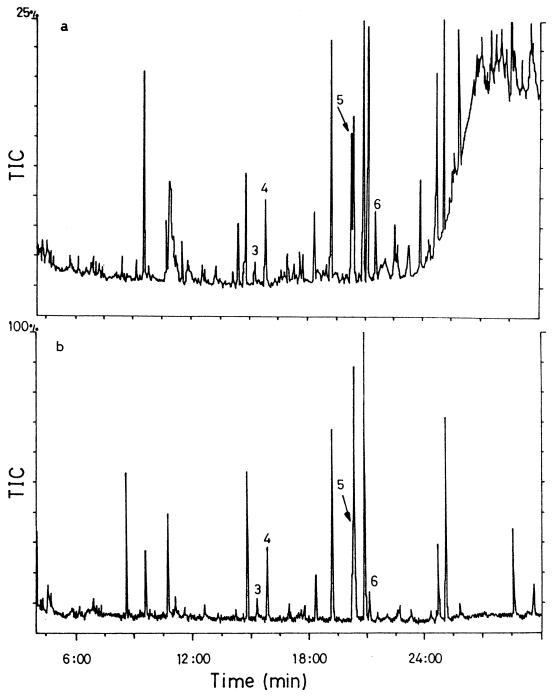

Fig. 2. GC–IT-MS total traces obtained after a nonporous carbon LSE of 100 ml of distilled water containing formulated compound, after 80 min ozone treatment and BF_3–MeOH derivatization procedure by using (a) EI and (b) CI as ionization modes. The numbers of the peaks refer to the compounds mentioned in Table 1. TlC=Total ion current.

structures are depicted in Fig. 3. The use of positive CI with acetonitrile as reagent gas, in an attempt to obtain the DPs molecular mass information, resulted in a strong increase in the selectivity for the analysis of the formulated pirimiphos methyl water samples. CI spectra of compounds 3 and 4 exhibited protonated molecular ions as base peaks, while the mass spectrum of compound 3 exhibited the $[M-31]^+$ ion as base peak which corresponds to the loss of a methoxy group. The use of different extraction procedures (LLE or LSE either with PS–DVB or nonporous carbon material) gave similar results with respect to selectivity and DP recovery values when GC–IT-MS is used. An issue poorly investigated in degradation studies is the reproducibility of the analytical method in the presence of formulated compound. Table 2 gives some insights in the recovery values of pirimiphos methyl and the coefficient of variation of the three extraction methods used. The major feature is that LLE performances are not affected by the presence of formulating agents while LSE reproducibility went up from 9% to values higher than 20% when switching from technical product to commercial product experiments. However, the results obtained for nonporous carbon sorbent were still acceptable for quantitation purposes.

3.2.2. LC–API-MS

Fig. 4 shows the chromatograms corresponding to the analysis of 100 ml of two water samples by LC–APCI-MS (positive mode) after 80 min of ozone treatment and carbon LSE. Fig. 4a represents the chromatogram corresponding to a solution of technical product and Fig. 4b the same treatment applied to formulated compound.

Fig. 5 represents the chromatograms corresponding to the analysis of 100 ml of two water samples by LC–ISP-MS (positive mode) after 80 min of ozone treatment by application of two different sample handling procedures. In Fig. 5a, the applied sample handling was dichloromethane LLE and in Fig. 5b nonporous carbon LSE was applied.

LC–API-MS techniques allowed the detection of two additional polar DPs (compounds 1 and 2) as compared to GC–IT-MS techniques. The main ions of the whole DPs detected under positive APCI or ISP and their relative abundances are reported in Table 1. Another advantage of LC–API-MS over GC–MS is that, with experiments at higher concentration levels (e.g. 200 mg/l), DP analysis can be carried out by directly injecting 20 μl of the treated water sample into the LC analytical column. Those experiments confirmed the presence of the same DPs in the aqueous medium. Besides, switching from experiments involving technical product to experiments involving formulated product did not result in a need for additional clean-up of sample extracts in order to analyse DPs. As shown in Fig. 4b, the interference background level was higher at the beginning of the chromatograms, but DPs detection was not hampered. Dichloromethane LLE is no longer a suitable method for the analysis of DPs since the more polar compounds 1 and 2 were not recovered at all (Fig. 5). In addition, a loss in selectivity was observed with respect to LSE experiments, as illustrated in Fig. 5a. The use of PS–DVB

Table 1
Main ions and their relative abundances (RA) of each degradation product detected after a 80 min ozone treatment of formulated pirimiphos methyl using either GC–IT-MS (positive CI or EI) after sample derivatization with BF_3–MeOH or LC–APCI-MS and LC–ISP-MS (positive mode)

Compound		Positive ISP ions	Positive APCI ions	El ions (RA%)	Positive Cl ions
No.	M_r				
1	157	$[M+H]^+$ (100) $[M+Na]^+$ (6) $[M+K]^+$ (5)	$[M+H]^+$ (100) $[M-41]^+$ (41) $[M-16]^+$ (11)	n.d.	n.d.
2	169	$[M+H]^+$ (100) $[M+Na]^+$ (5)	$[M+H]^+$ (100) $[M-41]^+$ (12) $[M-16]^+$ (15)	n.d.	n.d.
3	195	$[M+H]^+$ (92) $[M+Na]^+$ (6) $[M+K]^+$ (5)	$[M-H]^+$ (100) $[M-41]^+$ (51) $[M-69]^+$ (12)	178 (12); 149 (32); 135 (41); 121 (22); 77 (15)	$[M+H]^+$ (31) $[M-31]^+$ (100)
4	277	$[M+H]^+$ (100)	$[M+H]^+$ (18) $[M-27]^+$ (100) $[M-91]^+$ (21)	277 (100); 262 (61); 233 (31); 152 (43); 135 (49); 125 (15) 109 (13)	$[M+H]^+$ (100)
5	319	$[M+H]^+$ (100) $[M+Na]^+$ (7) $[M-41]^+$ (42)	$[M+H]^+$ (5) $[M-41]^+$ (100) $[M-73]^+$ (26)	319 (100); 305 (8); 290 (30) 276 (45); 151 (25); 125 (22); 109 (12)	$[M+H]^+$ (100)
6 (Pirimiphos methyl)	305	$[M+H]^+$ (100) $[M-141]^+$ (11)	$[M+H]^+$ (100) $[M-27]^+$ (15) $[M-141]+$ (92) $[M-169]+$ (23)	305 (31); 290 (100); 276 (72); 233 (51); 180 (42); 151 (25); 125 (22); 109 (11)	$[M+H]^+$ (100)

or nonporous carbon as LSE materials gave similar results with respect to the selectivity (results not shown). However, the latter sorbent allowed higher recovery values than the former one for compounds 1 and 2, provided that acidification of the eluting solvent was performed. The elution was tried in backflush mode following the data reported for the analysis of triazine metabolites [25], but the results did not improve in any way.

ISP, at extraction voltage value of 100 V, appeared to be the most suitable ionization technique for identification of DPs, since formation of Na^+ or K^+ adduct ions in ISP allowed a better confirmation of the DPs' molecular masses. $[M+H]^+$ ion was the base peak for the whole group of metabolites, except for compound 3 which exhibited more extensive fragmentation (see Table 1). Conversely, APCI, at an extraction voltage value of 100 V, provided more abundant fragmentation patterns than ISP, which was very useful for identification purposes. However, because unknown DPs may undergo thermal degradation during the vaporization of the mobile phase (300°C), the molecular mass assessment is not straightforward. Negative mode of ionization was applied as a means of confirmation of the results obtained with positive ionization mode. The negative mode only allowed the detection of compound 2 or compounds 2 and 3 under ISP or APCI, respectively. For both compounds, a strong signal of deprotonated molecular ion was observed.

In order to get more structural information, sample extracts were injected at a higher extraction voltage value (150 V). As a result of the high CID, fragment ions at low m/z values were observed for compounds 3, 4 and 5 and their identification was enhanced. For compounds 1 and 2, an increase of the extraction voltage value resulted in the recording of unuseful mass spectra, with high ion background level. The main difference between both groups of compounds is that compounds 3, 4 and 5 were clearly separated from matrix interferences in the LC chromatograms, whereas compounds 1 and 2 were eluted in the middle of interfering peaks. As a rule, extraction voltage collision induced dissociation

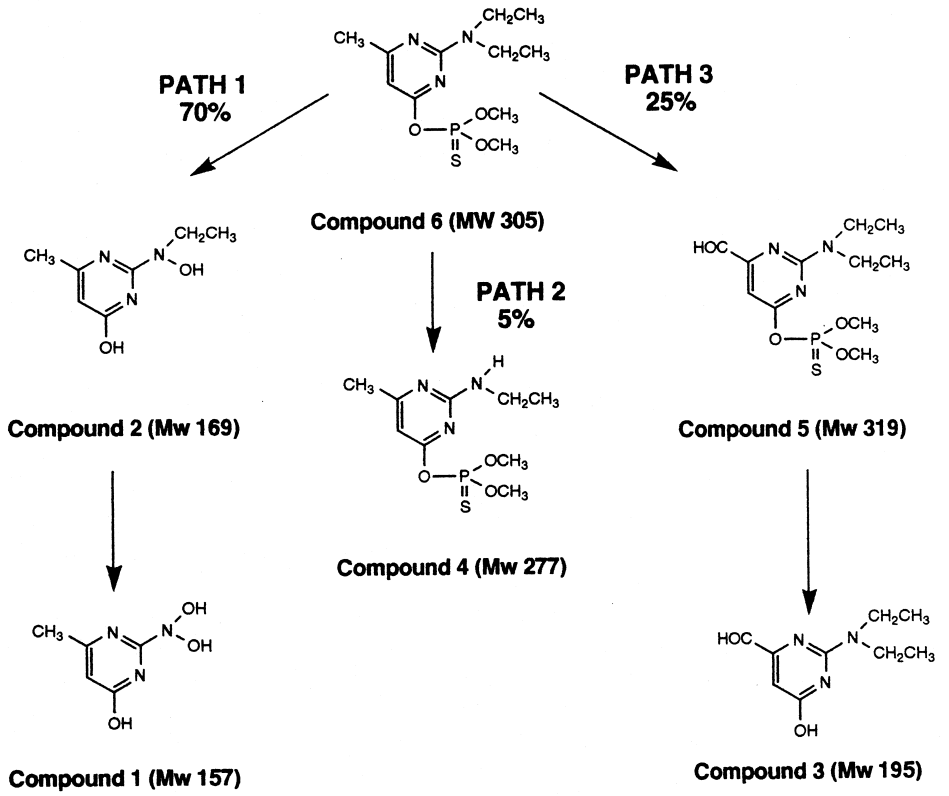

Fig. 3. Scheme of the proposed degradation pathway of formulated pirimiphos methyl under ozonolysis in water and estimation of the relative importance of the different routes of degradation. MW=Molecular mass.

(CID) is an useful tool for improving fragmentation patterns provided that efforts have previously been focused on the isolation of peaks of interest from impurities. Compounds 1 and 2 mass spectra were only characterized by two fragment ions at m/z $[M-41]^+$ and at m/z $[M-16]^+$ which may point out that pirimiphos methyl underwent a hydroxy addition. Assignation of definitive chemical structures was difficult. However, the nitrogen position of the diethylamino group is bound to be the most activated position for an hydroxy electrophilic addition following a molecular ozone attack and leading therefore to the formation of oxime derivatives.

3.3. Degradation pathway

Following structure identification of DPs, a tentative degradation pathway of formulated methyl pirimiphos in water under ozonolysis is proposed in Fig. 3. There are three major routes of degradation. One route (path 1) may involve the formation of a N-oxime (compound 1) together with the induced

Table 2
Mean recovery values (±R.S.D.; $n=5$) of pirimiphos methyl using LLE or different LSE cartridges (PS–DVB and nonporous carbon) and after preconcentrating 100 ml of water sample spiked with 20 mg/l of either formulated or technical product

Pirimiphos methyl	LLE (CH_2Cl_2)	LSE (PS–DVB)	LSE (carbon)
Technical product	85±7	88±6	92±9
Formulated product	79±8	71±22	86±19

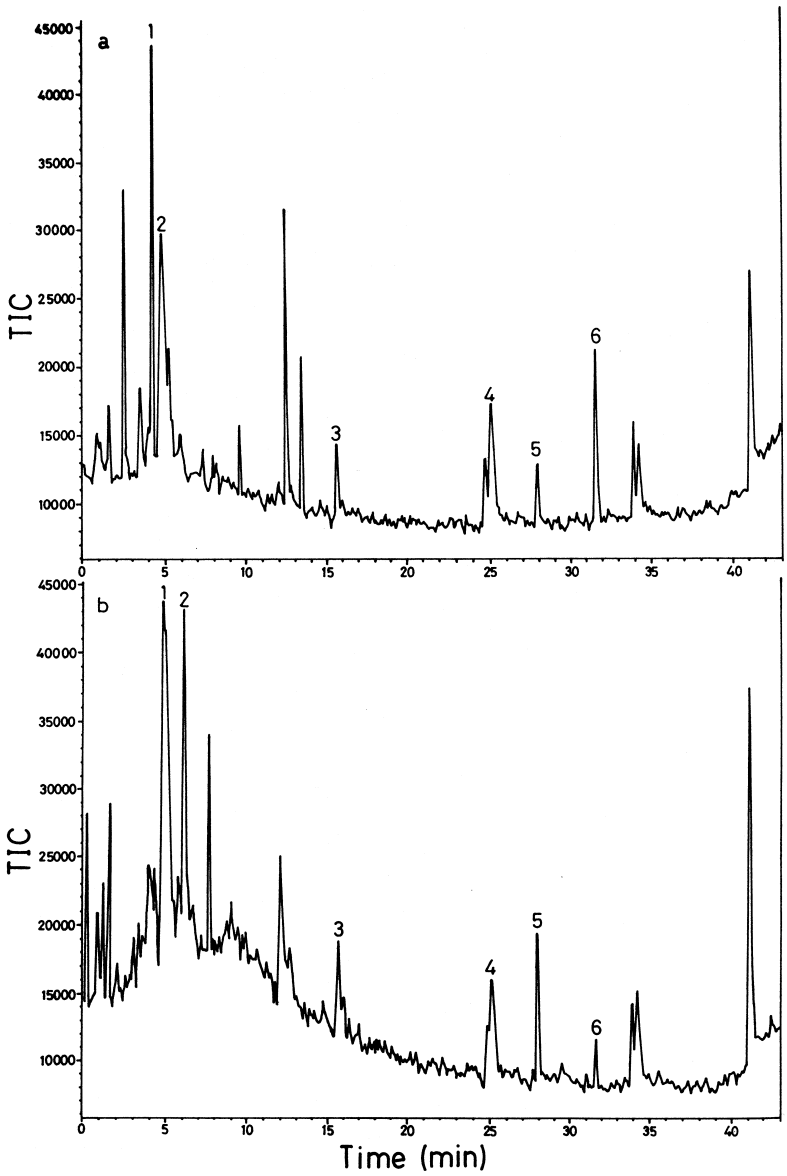

Fig. 4. LC–APCI-MS (positive mode) traces obtained after a nonporous carbon LSE of 100 ml of water and after 80 min ozone treatment of (a) 20 mg/l solution of technical compound and (b) 20 mg/l solution of formulated compound.

hydrolysis of the phosphoric ester function (compound 2). A second path is the result of a N-dealkylation which gives compound 4. A third route involves the oxidation of the methyl group into an aldehyde function (compound 5), followed by the induced hydrolysis of the phosphoric ester function (compound 3). The stability of an aldehyde in an oxidative medium was surprising, but it has been pointed out that aldehydes are oxidized only by radical oxidants and not by ozone, reflecting the slow generation of hydroxy radicals under acidic conditions [26]. In the absence of standards, the assessment of the relative importance of the different routes of degradation is the most problematic topic.

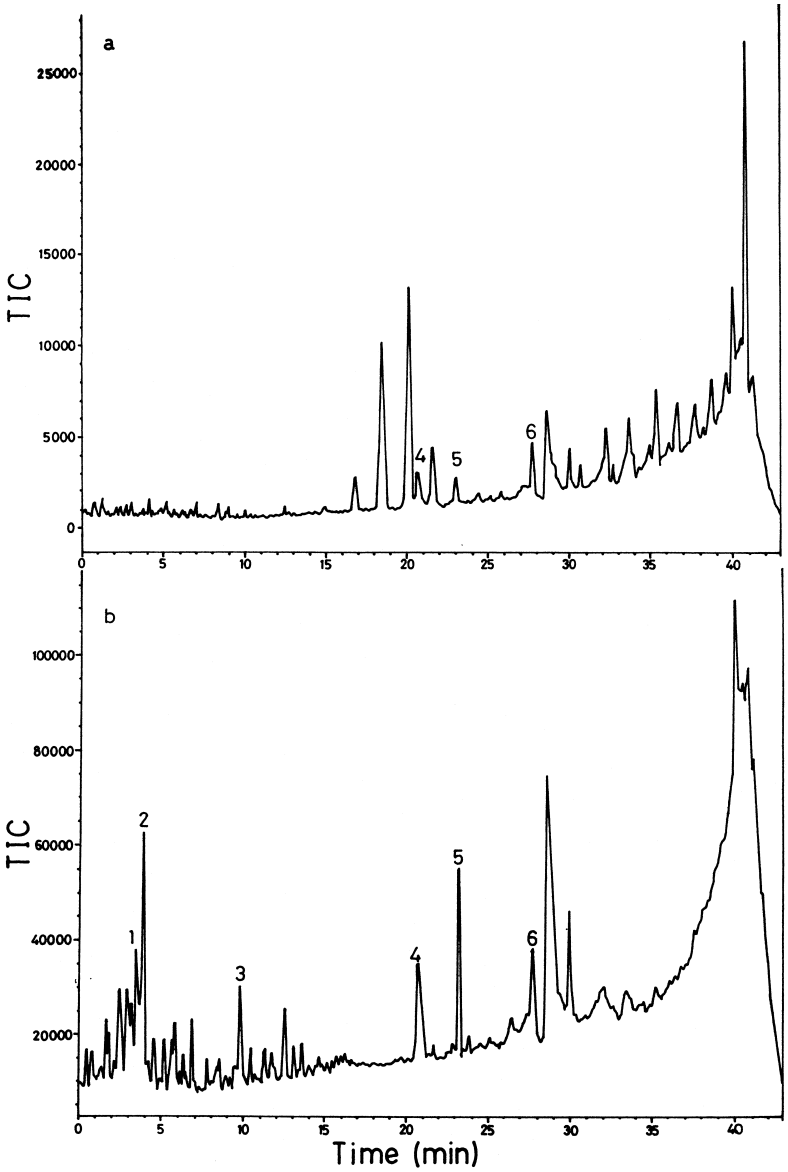

Fig. 5. LC–ISP-MS (positive mode) traces obtained after 80 min ozone treatment and (a) a dichloromethane LLE or (b) a carbon LSE of 100 ml of water sample containing formulated compound.

For DP quantitation purposes, the use of close structurally related compounds, as external standards can be regarded as a good solution. The response factor may vary over a limited range in EI, while a wider range is expected in APCI and ISP ionization modes. In this context, compounds 4 and 5 were arbitrary quantified under GC–IT-MS in the EI mode using pirimiphos methyl as internal standard, while compounds 1, 2 and 3 were quantified under LC–APCI-MS (positive mode) using two external standards: 2,4-aminophenol and cyanuric acid. The aim of using two different external standards was to obtain ''bracketing'' quantitative data of each DP in order to minimize errors. The mean recovery values

of pirimiphos methyl, 2,4-aminophenol and cyanuric acid were 92%, 54% and 68% with R.S.D. values of 9%, 15% and 18% ($n=3$) respectively, which made estimated quantitation feasible. At the end of the experiments (150 min), the sum of concentration of the DPs ranged from 70% (cyanuric acid as external standard) to 85% (2,4-aminophenol as external standard) of the pirimiphos methyl originally present. The first degradation route, which was not detected under GC–MS conditions accounted for the disappearance of 70% of the pirimiphos methyl originally present due to the low reactivity of the N–OH group [27] for BF_3–MeOH. LC–API-MS definitively exceeds the performances of GC–IT-MS in order to achieve a balance of the whole degradation process.

4. Conclusions

LSE involving nonporous carbon cartridges resulted in the only available method for extraction of the more polar DPs of pirimiphos methyl from water treated by ozone. Cleaner extracts and higher recoveries than those observed with LLE and polymeric LSE material were obtained. When experiments were carried out with the commercial speciality instead of the technical product, no additional clean-up steps were needed for the analysis of the DPs. GC–IT-MS using EI and CI modes yielded enough structural information to identify three DPs but failed in detecting two polar DPs, which were not amenable to the esterification reaction. Their detection could only be achieved by applying LC–API-MS. ISP exceeded the possibilities of APCI in pesticide degradation studies since the confirmation of the DPs' molecular masses was better achieved thanks to the formation of adduct ions. Both techniques did not provide enough structural information for unequivocal structure elucidation. However, enough structural characterization was obtained to evaluate the results of the ozone treatments in a fast way, which will permit, in the future, selection of further appropriate biological treatments. It was stated that oxidation of pirimiphos methyl by ozone mainly occurred through the formation of polar phenol derivatives. At the end of the oxidative reaction, the DPs concentration accounted for 70% to 85% of the initial concentration of pirimiphos methyl. LC–API-MS techniques exceed the performances of GC–IT-MS in order to perform a balance of the whole degradation process.

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