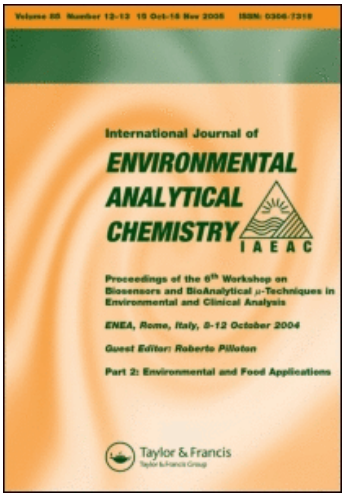

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Identification of Carbofuran And Methiocarb and their Transformation Products in Estuarine Waters by On-line Solid Phase Extraction Liquid Chromatography—Mass Spectrometry

S. Chiron[a]; J. A. Torres[b]; A. Fernandez-alba[b]; M. F. Alpendurada[c]; D. Barcelo[cd]
[a] Dept. of Environmental Chemistty, CID-CSIC, Barcelona, Spain [b] Dept. Analytical Chemistry, Faculty of Sciences, Almeria, Spain [c] Lab. of Hydrology, Faculty of Pharmacy, University of Porto-R. Anibal Cunha, Porlo, Portugal [d] Dept. of Environmental Chemistry, CID-CSIC, Barcelona, Spain

To cite this Article Chiron, S. , Torres, J. A. , Fernandez-alba, A. , Alpendurada, M. F. and Barcelo, D.(1996) 'Identification of Carbofuran And Methiocarb and their Transformation Products in Estuarine Waters by On-line Solid Phase Extraction Liquid Chromatography—Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 65: 1, 37 — 52
To link to this Article: DOI: 10.1080/03067319608045542
URL: http://dx.doi.org/10.1080/03067319608045542

Intern. J. Environ. Anal. Chem., Vol. 65, pp. 37–52
Reprints available directly from the publisher
Photocopying permitted by license only

IDENTIFICATION OF CARBOFURAN AND METHIOCARB AND THEIR TRANSFORMATION PRODUCTS IN ESTUARINE WATERS BY ON-LINE SOLID PHASE EXTRACTION LIQUID CHROMATOGRAPHY—MASS SPECTROMETRY

S. CHIRON[1], J. A. TORRES[2], A. FERNANDEZ-ALBA[2], M. F. ALPENDURADA[3] and D. BARCELÓ[3]*

[1]*Dept. of Environmental Chemistry, CID-CSIC, c/Jordi Girona 18–26, 08034 Barcelona, Spain;* [2]*Dept. Analytical Chemistry, Faculty of Sciences, Almeria Campus, 04071 Almeria, Spain;* [3]*Lab. of Hydrology, Faculty of Pharmacy, University of Porto-R. Aníbal Cunha, 164, 4000 Porlo, Portugal*

(Received, 15 October 1995; in final form, 10 March 1996)

The degradation of the carbamate insecticides carbofuran and methiocarb in distilled and natural waters was determined. Degradation studies were carried out both under a xenon arc irradiation and natural sunlight at pesticide concentrations of 50–100 μg/L. 50–100 mL water sample were preconcentrated using automated on-line solid phase extraction (SPE) followed by liquid chromatography (LC), UV detection or post column fluorescence detection (EPA method 531.1 for carbamate insecticides). Structure identification was carried out by on-line SPE-LC-MS either with thermospray and/or high flow pneumatically assisted electrospray interfaces. Half-lives varying between 4–12.5 days for carbofuran and methiocarb were determined under natural sunlight exposure, being chemical hydrolysis the major degradation pathway. When using xenon arc lamp irradiation both pesticides degraded very rapidly with half-lives varying from 0.3–1.7 hours. The various degradation products identified were: methiocarb sulfoxide, 4-methylthio-3, 5-dimethylphenol, 3-hydroxy-7-carbofuranphenol and 2-hydroxy-3-(2-methylprop-1-enyl)-phenyl-*N*-methylcarbamate.

KEY WORDS: Carbofuran, methiocarb, degradation products, photochemical degradation, solid phase extraction, liquid chromatography-mass spectrometry.

INTRODUCTION

Carbofuran (2,3-dihydro-2, 2-dimethyl-7-benzofuranyl methylcarbamate) and methiocarb (4-methylthio-3, 5-xylyl methylcarbamate) are both broad spectrum insecticides belonging to the *N*-methyl carbamate group. Carbofuran is used in rice culture, where it is applied in the form of granule[1]. Carbofuran was detected in surveys of

* To whom correspondence should be addressed. Permanent address: Dept. of Environmental Chemistry, CID-CSIC, Barcelona, Spain.

well water monitoring programs in Central Maine (USA)[2], in ground waters from Wisconsin, Long Island and Maryland[3] and in the estuarine water from San Francisco Bay[4]. During our current ground water monitoring in Almeria area (Andalucia, Spain) carbofuran, 3-hydroxycarbofuran, methiocarb and methiocarb sulfone were detected at concentration levels up to 0.4 μg/L[5]. The presence of 3-keto and 3-hydroxycarbofuran was detected in soil and water from flooded rice culture[1,6,7]. The decline of carbofuran in water was pH dependent and the complete hydrolysis of carbofuran to 3-hydroxycarbofuranphenol was reported to occur in 5 days after application in rice ecosystems[8]. Half lives varied from 7[7] to 18[1] days in paddy water being hydrolysis the major degradation pathway observed with little contribution of volatilization and photodegradation[1]. Methiocarb was completely degraded in river water at pH = 7.3 under natural sunlight exposure after one week period and its major degradation product was 4-methylthio-3, 5-dimethylphenol[10].

It is known that sunlight degradation of pesticides plays an important role in environmental chemistry, e.g., the photolysis of carbofuran in water was published[11,12]. However, these studies were carried out in pure organic or aqueous/organic solvents and at relatively high concentration of pesticide (μg/mL), far from the real environmental situations[13]. In order to make a better comparison with real environmental data, degradation studies in lake or pond water were conducted for metolachlor[14] and for carbofuran[15] either using natural sunlight or xenon arc irradiation. For methiocarb scarce data is available and it is known that in soil methiocarb is oxidized to methiocarb sulfoxide and then to sulfone[16]. The sunlight irradiation of methiocarb sorbed on soil surface led to a rapid conversion to the sulfoxide analog[17].

Xenon arc lamps with an emission spectrum which closely matches that of the sunlight are adequate for conducting photodegradation studies of pesticides in water[15,18]. Metabolites obtained under natural sunlight irradiation[19] were similar to those obtained after xenon arc lamp irradiation[20]. Local environmental conditions contributed to the fast degradation of fenitrothion, with a half life of 12 h, mainly attributed to natural temperatures of above 30°C and photolysis, which was partly associated with its quantum yield of 1%[21].

Automated on-line solid phase extraction (SPE) LC postcolumn fluorescence detection (EPA method 531.1) is a sensitive and selective method for the determination of *N*-methyl carbamates and their main transformation products in environmental waters[22]. Automated on-line SPE-LC thermospray mass spectrometry (TSP-MS) is a powerful system for the analysis and confirmation of pesticides and their metabolites in water matrices[22,23]. The on-line SPE LC-MS techniques were previously used for the identification of the more polar transformation products in water with limits of detection (L.O.D.) below 0.1 μg/L. This technique was applied to degradation studies of organophosphorus pesticides and alachlor at concentration as low as 20–100 μg/L, close to environmental levels[23,24].

Our aims in this work were as follows: (i) To study the degradation of carbofuran and methiocarb at 50–100 μg/L level using distilled and estuarine river water by using formulated or analytical grade pesticide (ii) To compare the degradation behavior of carbofuran and methiocarb under laboratory studies (using a xenon arc lamp) and under natural sunlight (iii) To provide for both carbamate insecticides the identification of the major transformation products by means of LC-MS techniques. The combination of automated solid-phase extraction procedures with the recently introduced high-flow pneumatically assisted electrospray mass spectrometry should be useful for such identification purposes with a sensitivity of approximately 100 times lower as compared to thermospray LC-MS interfacing systems[26,27].

EXPERIMENTAL SECTION

Chemicals

Analytical-grade methiocarb, carbofuran and methiocarb sulfoxide were purchased from Promochem (Wesel, Germany). LC-grade water, methanol were obtained from J. T. Baker (Deventer, Holland) and were passed through a 0.45 μm filter before use. Ammonium formate was obtained from Merck (Darmstadt, Germany). Mesurol (50% of methiocarb) was obtained from Bayer (Leverkusen, Germany).

The phenolic compounds were obtained by hydrolyzing the corresponding carbamate esters in alkaline solutions. Pesticide dissolved in methanol (1 mg/mL; 1 ml) was mixed with 0.5 N NaOH solution (1 mL). The mixture was heated at 70°C for 5 h and then neutralized with 1 N HCl solution and it was analyzed by LC-UV-Visible spectrophotometry and LC-TSP-mass spectrometry.

LC-diode array detection

The eluent was delivered by two high pressure pumps coupled to a model 715 automated gradient controller (Gilson, Villier le Bel, France) and a 1000S Applied Biosystems diode array detector (Foster City, CA, USA). In the laboratory experiments, a Lichrocart cartridge column 60 RP-8 select B (25 cm × 4.6 mm i.d.) packed with 4 μm Supersphere material from Merck (Darmstadt, Germany) was used. Gradient elution was performed from an eluent containing 0% of A (methanol/water, 90 : 10) and 100% of B (water) to 100% of A in 35 min at a flow rate of 0.9 mL/min. In case of field experiments, a C-18 column (125 × 4 mm i.d.) packed with 5 μm Lichrospher material from Merck was used. Gradient elution was performed from an eluent containing 25% of A (acetonitrile) and 75% of B (water) to 90% A and 10% B in 15 min at a flow rate of 1 mL/min.

LC-Postcolumn fluorescence detection (PCR-FD)

The eluent was delivered by a Model 250 binary LC pump from Perkin Elmer (Norwalk, CT, USA) coupled to a PCX 5000 carbamate postcolumn analysis module from Pickering Laboratories (Mountain View, CA, USA). Post column reaction was carried out as described elsewhere[22]. A Model LC-240 fluorescence detector from Perkin Elmer (Buckinghamshire, UK) was used at excitation and emission wavelengths of 330 and 465 nm, respectively. The same elution gradient conditions as in UV detection were applied.

Thermospray LC-MS detection

A Hewlett-Packard (Palo Alto, CA, USA) Model 5988 Thermospray LC-MS quadrupole mass spectrometer and a Hewlett-Packard Model 35741B instrument for data acquisition and processing were employed. The thermospray tip and stem temperatures were programmed from 190°C to 180°C and from 90°C to 80°C, respectively. The filament-on was used in all experiments, with conventional positive and negative ion chemical ionization modes. The same LC chromatographic conditions as in UV detection were applied with the addition of 50 mM ammonium formate in the mobile phase. For more experimental details, see ref. 23 and 24.

Electrospray LC-MS detection

A VG Platform ESP from Fisons Instruments (Manchester, UK) equipped with a Megaflow ESP probe was used. Optimum values of drying nitrogen gas flow rate and ESP nitrogen nebulizing gas flow rate were set at 300 and 15 L/h, respectively. Focus and extraction voltages were set at 55 and 62 V, respectively. The source temperature was set at 150°C. Other experimental conditions have been described elsewhere[26]. The analysis involved a Lichrocart cartridge column (125 × 3 mm i.d.) packed with Lichrospher 60 RP select B material from Merck (Darmstadt, Germany). Gradient elution was accomplished by using a eluent containing 5% of solvent A (methanol) and 95% of solvent B (water) to 100% of A in 35 min at a flow rate of 0.3 mL/min.

Light sources

Irradiation experiments were carried out using a Suntest apparatus from Heraeus (Hanau, Germany) equipped with a low pressure, air cooled xenon arc lamp. The light source equipped with an inner borosilicate filter guarantees a constant low wavelength UV cut-off at 286 nm. The light intensity was measured with an OMA II multichannel spectroradiometer (EG and G, Princeton, New Jersey) as described elsewhere[27]. Measurements of Almeria spectral solar irradiance (Latitude 37°N) taken over one day was achieved using a precision spectroradiometer LICOR 1800. Figure 1 shows the comparison of spectral irradiances of both lights used in the experiments. In addition we need to consider that in the natural sunlight experiments that the sunlight intensity of the sun may vary during the day. Clouds were not present during all the days of the experiments, so no appreciable fluctuations of the light intensity were expected.

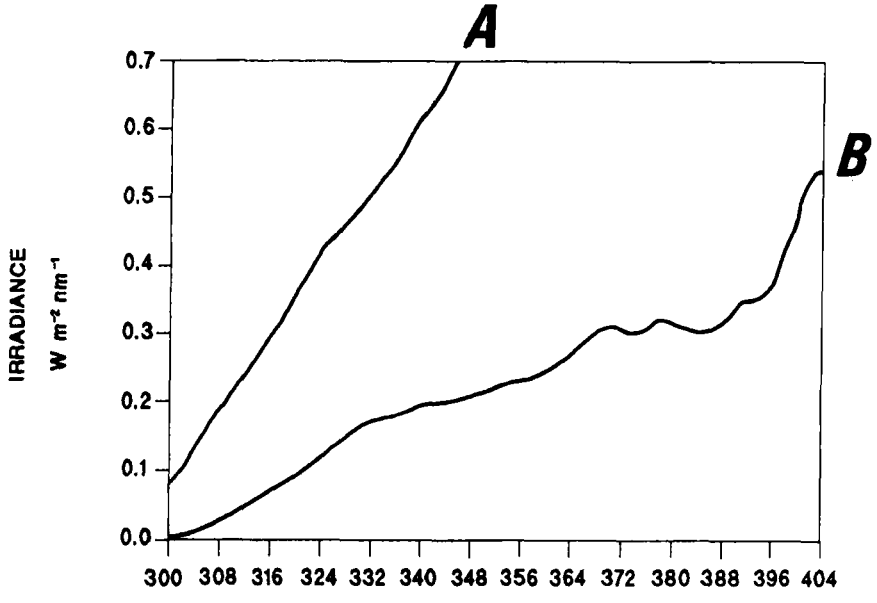

Figure 1 Comparison of the spectral irradiances between 286 and 400 nm of (A) xenon arc lamp and (B) Almeria sunlight.

Kinetic experiments

All of the outdoor tests were performed in quartz reaction reservoirs which contained distilled or estuarine river water sample spiked at 50–100 μg/L of pure methiocarb/carbofuran. Two reservoirs of methiocarb/carbofuran aqueous solution in distilled water were prepared. One reservoir was wrapped with aluminium foil and kept in the dark and was served as a blank. The exposures took place September-October 94. Solution temperatures were controlled not to exceed 35°C, with an average of 24°C (night time) and 32°C (day time). As regard to laboratory experiments, 500 mL of distilled water and 500 mL river water samples were spiked with 50 μg/L of either formulated or analytical grade carbofuran/methiocarb. River water samples were filtered through a 0.45 μm membrane filter (Millipore, Bedford, MA, USA). Since the water solubility of carbofuran and methiocarb is 350 and 30 mg/L, respectively, no addition of organic solvent took place to ensure the pesticide solubility. Irradiation experiments were carried out in a quartz reaction reservoir and solution temperature was set at 30°C using a cooling circuit (for Suntest apparatus). Similar reaction vessels were wrapped in aluminium foil to serve as the dark control. All experiments were performed in triplicate for quantitation purposes.

Sample handling

At different periods of time, 20 μl of the solution were directly analyzed by LC-PCR-FD. Additionally, an OSP-2 autosampler from Merck (Darmstadt, Germany) was connected on-line to a LC-UV, LC-TSP-MS and/or LC-ESP-MS detectors. A L-6200A intelligent pump (Merck) delivered the water sample containing the pesticides. OSP-2 cartridge Lichrospher 100 RP-18 of 10 μm particle size were first conditioned by flushing 5 mL of methanol and then 5 mL of HPLC water at a flow rate of 1 mL/min. Water sample volume of 50 mL was preconcentrated through the precolumns at a flow rate of 4 mL/min. Following the preconcentration step the OSP-2 valve was switched and the analytes were separated on an analytical column in a similar way as described elsewhere[22–24].

RESULTS AND DISCUSSION

General remarks

Samples were kept in the reservoirs and wrapped in aluminium foil, stored at room temperature with biologically inhibited water at pH 7.6. Under these conditions 90% to 80% conversion was observed for methiocarb and carbofuran, respectively, after 20 days of natural sunlight exposure. For both compounds the corresponding phenols were detected by LC-TSP-MS in NI mode of detection and were attributed to chemical hydrolysis. Previous studies from us[22] showed up to 100% loss for methiocarb sulfoxide after 20 days in well water maintained at pH 4.8 and stored at 4°C. Published literature about these two compounds indicates that for carbofuran a decline in water is very much pH dependent, with values of 10 or 0.58 days when the pH raises from 7 to 8.7[8]. Less than 1% of the pesticide was detected in water exhibiting a pH 8.1 after 10 days[9] being the half-life in paddy rice of 7 days[21]. With regard to the formation of metabolites, 3-keto and afterwards 3-hydroxycarbofuran were detected in flooded rice culture after one day of pesticide application[6]. The formation of 3-hydroxy-7-carbofuranphenol was determined after 5 days of application and it was attributed to the water pH of 8 in a rice

ecosystem[8]. Soil microorganisms and rice plants were also the cause of the enhanced degradation in flooded and unflooded rice ecosystems[8]. In the case of methiocarb, the formation of 4-methylthio-3, 5-dimethyl phenol and carbamic acid after natural sunlight exposure of methiocarb spiked in river water (pH = 7.3) indicated that hydrolysis was the main degradation pathway in natural systems. This degradation was very fast and all methiocarb disappeared after one week but the phenol metabolite slowly degraded and it was present after three weeks[10].

Form these results, it seems clear that the two pesticides selected are easy to hydrolyze under natural conditions because of the pH of the estuarine water used in many experiments (pH = 7.8) and the content of dissolved organic matter (7 mg/L). In a previous paper from us it was shown that the degradation of carbofuran in pond water was twice rapid as compared to distilled water[15] similarly as reported by Seiber *et al.*,[7] that showed a remarkable decrease in half-life of carbofuran when using paddy water instead of distilled water.

Qualitative information. Identification of methiocarb metabolites

Figure 2 shows that two metabolites were detected under xenon arc irradiations in river water. These compounds contained the carbamate group necessary for postcolumn

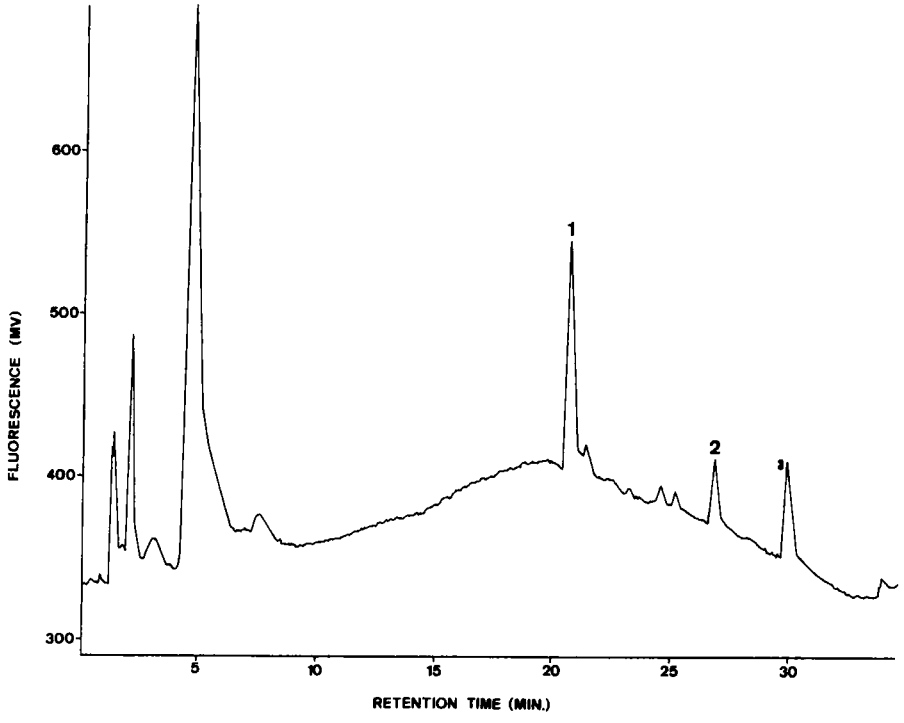

Figure 2 LC-PCR-FD chromatogram obtained after direct injection of 20 µL of a estuarine river water spiked with 1000 µg/L methiocarb irradiated 30 min under xenon arc lamp. Excitation and emission wavelength were set at 330 and 465 nm, respectively. Compound numbers: methiocarb sulfoxide (compound 1), 3, 5-dimethylphenyl-*N*-methylcarbamate (compound 2) and methiocarb (compound 3). Other conditions see experimental part.

fluorescence detection and $CONHCH_3$ moiety was preserved under xenon arc lamp irradiations. By using LC-UV detection (Figure 3a) also two metabolites were found. The on-line SPE-LC-TSP-MS methodology using negative and positive chemical ionization afforded the unequivocal characterization of two photoproducts in distilled water,

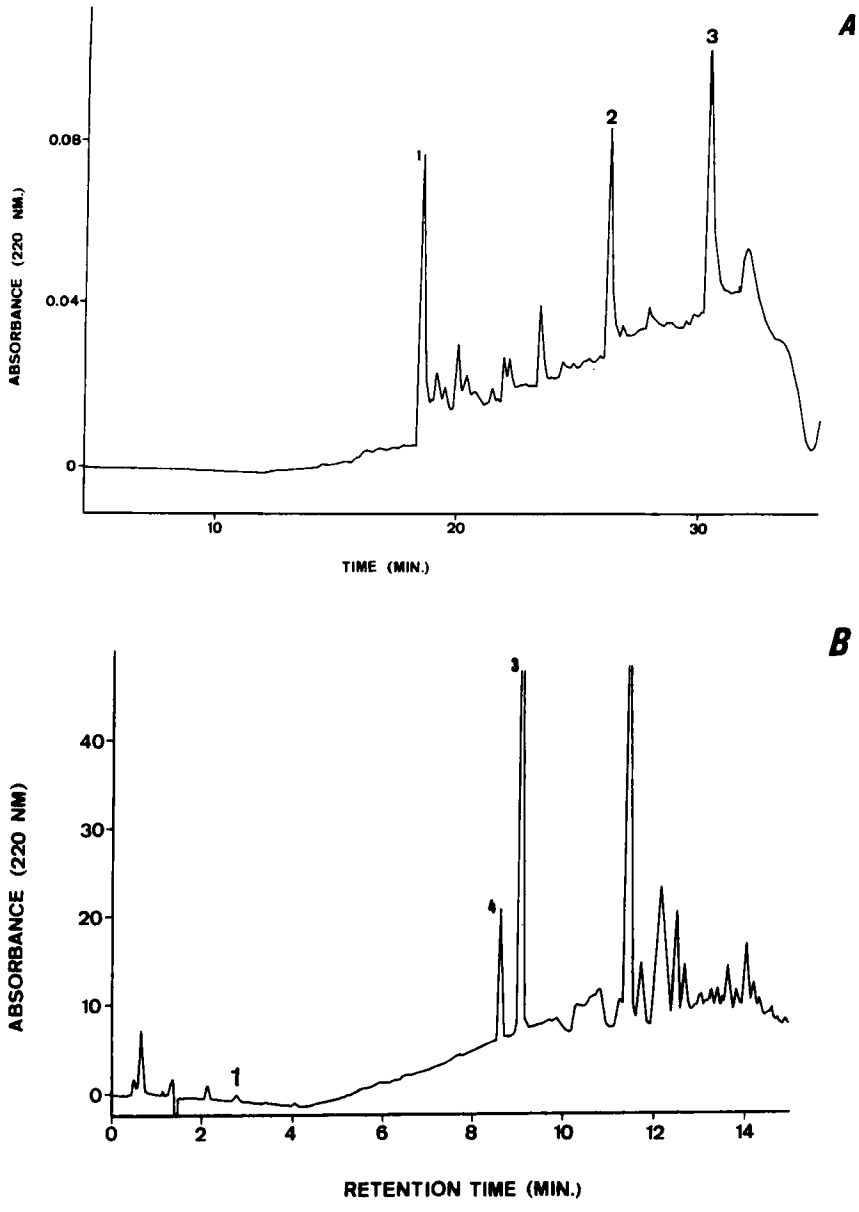

Figure 3 On-line SPE-LC-UV chromatogram obtained at 220 nm after preconcentration of 50 mL of distilled water spiked at 50 μg/L methiocarb a) irradiated 30 min under xenon lamp irradiation b) irradiated 4 days under Almeria sunlight. Compound numbering as in Figure 2. Compound 4 is 4-methylthio-3, 5-dimethylphenol. Other conditions, see experimental part.

methiocarb sulfoxide (compound 1) and 3, 5-dimethylphenyl-*N*-methylcarbamate (compound 2). As regards to the formation of the sulfoxide it is probable that this process is self-sensitized singlet oxygen reaction at the sulfur. Their molecular weights (Mw), main ions and their relative abundances under TSP-MS are reported in Table 1 and the tentative degradation pathways of methiocarb in water is described in Figure 4a. The main ions identified for methiocarb and methiocarb sufoxide agreed with previous paper using the LC-TSP-MS system[29]. The different compounds identified in full scan traces, when using distilled water were confirmed in river water using the selected ion monitoring mode. Each compound was characterized by two diagnostic ions. Identification of methiocarb sulfoxide was obtained by matching its TSP-MS spectra in PI and NI mode with those of a commercially available standard. Methiocarb sulfoxide was unstable and its degradation led to compound 2. After 3 h of irradiation only compound 2 was left in water samples. No significant fragmentation patterns of compound 2 were given by LC-TSP-MS but the support for structural identification was provided by the fact that the presence of carbamate group (confirmed by LC-PCR-FD).

Only when using natural sunlight irradiation (see Figure 3b), the major metabolite was 4-methylthio-3, 5-dimethylphenol (compound 4) which has been previously identified by thin layer chromatography following natural sunlight exposure[10]. Under natural sunlight methiocarb sulfoxide was only detected after 4 days of irradiation. Compound 4 with a Mw 168 was fully identified by matching its NI TSP-MS spectrum with that of a synthetic standard (see experimental part). Hydrolysis is the major pathway following natural sunlight irradiation whereas using the xenon irradiation, methiocarb sulfoxide is formed and the degradation of methiocarb follows another route that does not involve hydrolysis as major pathway.

Table 1 Methiocarb photodegradation products molecular weight (Mw), retention time (RT in min), main ions and their relative abundances (RA) using on-line SPE-LC-TSP-MS and under positive or negative ionization modes.

Compound	*RT*	*Mw*	*Main ions*	*RA (%) PI mode*	*NI mode*
1	18.7	241	242 $[M + H]^+$	22	
			259 $[M + NH_4]^+$	8	
			283 $[M + H + CH_3CN]^+$	11	
			185 $[M - CH_3NCO + H]^+$	100	
			226 $[M - CH_3NCO + H + CH_3CN]^+$	9	
			183 $[M - CH_3NCO - H]^-$		12
			229 $[M - CH_3NCO + HCOO]^-$		100
2	26.6	179	180 $[M + H]^+$	13	
			197 $[M + NH_4]^+$	100	
			238 $[M + CH_3CN + NH_4]^+$	9	
4	28.2	168	167 $[M - H]^-$		32
			213 $[M + HCOO]^-$		100
3	30.3	225	226 $[M + H]^+$	15	
			243 $[M + NH_4]^+$	100	
			284 $[M + CH_3CN + NH_4]^+$	12	

LOD of methiocarb: 20 ng/L when preconcentrating 50 mL water sample

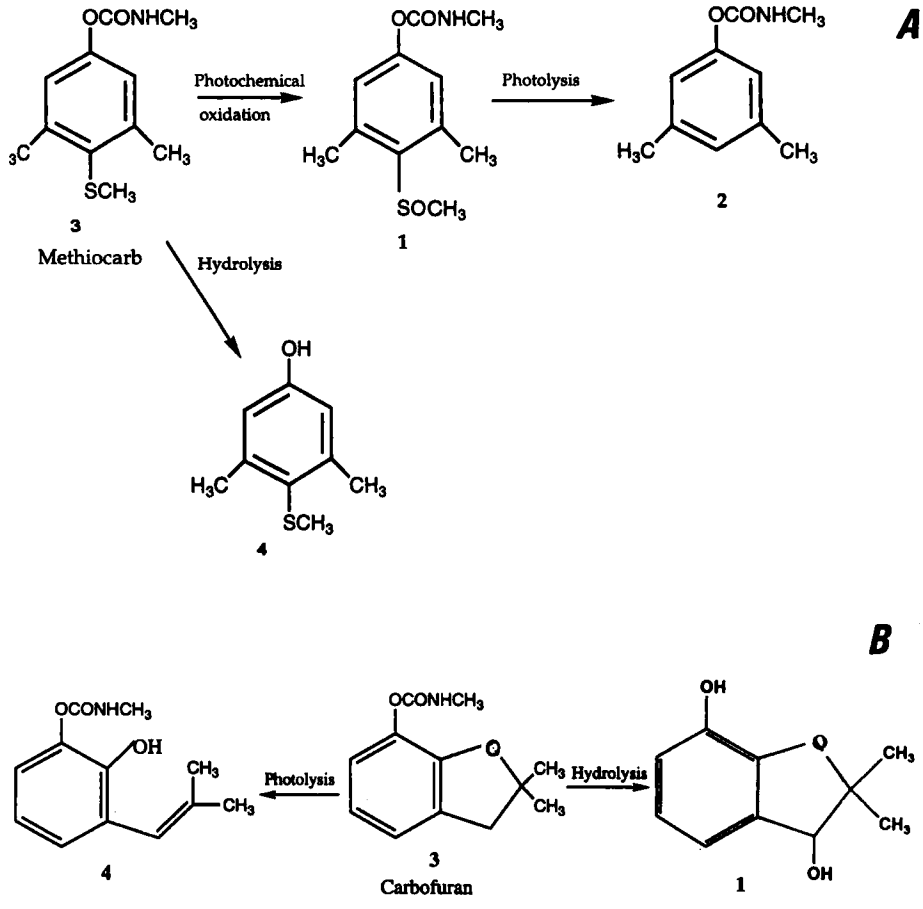

Figure 4 Tentative degradation pathway of a) methiocarb and b) carbofuran in natural waters.

Identification of carbofuran metabolites

Figure 5 shows that three metabolites were formed under xenon arc lamp irradiation. By using on-line SPE-LC-TSP-MS method, only compound 4 could be detected as isomer of carbofuran. Under PI mode, compound 4 showed a strong ammonium adduct $[M + NH_4]^+$ ion at m/z 239 as base peak and the protonated molecular $[M + H]^+$ ion at m/z 222 with a relative abundance of 23%, similarly as previously reported by us[29]. However, it was also reported that the use of the powerful approach on-line SPE-LC-TSP-MS was not sensitive enough for the detection of the carbofuran metabolites 3-hydroxycarbofuran and 3-hydroxy-7-carbofuranphenol at ug/L level[29]. Electrospray interface (ESP) was successfully used for the determination of carbamate insecticides in LC-MS[30]. Sensitivity of high flow ESP results 100 times higher than that of TSP as reported in two previous articles[26,27]. The combined use of on-line SPE-LC-high flow-ESP-MS, is a powerful analytical technique for the trace determination of pesticides in waters[27]. By using this approach it was possible to identify all the metabolites of carbofuran present in the water

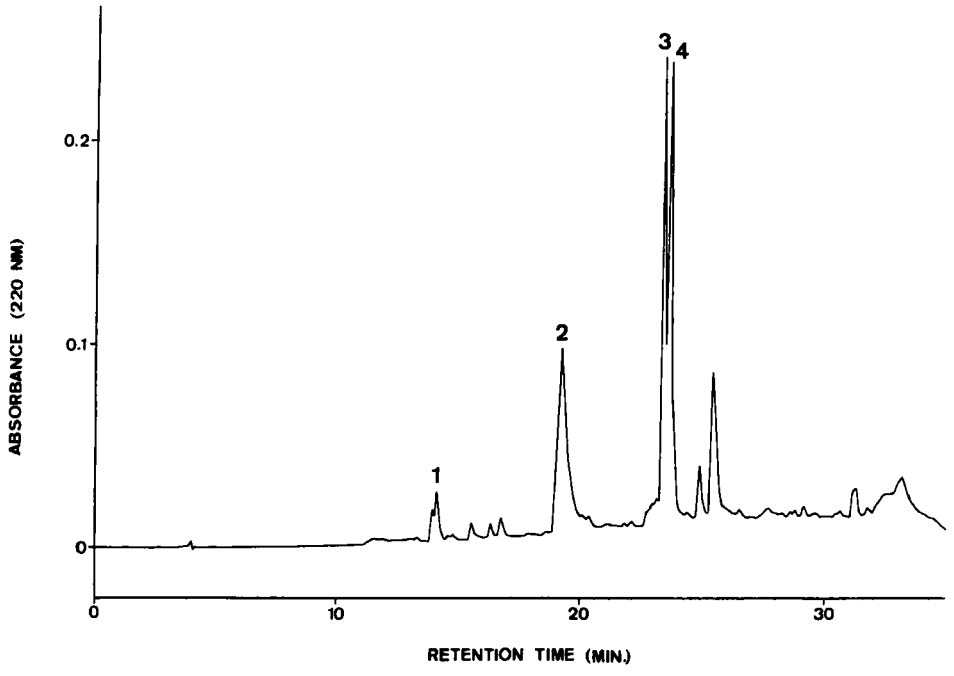

Figure 5 On-line SPE-LC-UV chromatograms obtained at 220 nm after preconcentration of 50 mL of a distilled water sample spiked with 50 µg/L pure carbofuran irradiated 2 h under xenon arc lamp. Compound identified were: 3-hydroxy-7-carbofuranphenol (compound 1), carbofuran (compound 3) and 2-hydroxy-3-(2-methylprop-1-enyl)-phenyl-*N*-methylcarbamate. (compound 4). Other conditions see experimental part.

samples. Figure 6a shows a TIC obtained after preconcentration of 50 mL of river water spiked with 50 µg/L of pure carbofuran after 5 h of xenon arc lamp irradiations. Besides, ESP provides in addition to the molecular weight information abundant fragment ions at extraction voltage values higher than 40 V (see Table 2) which are very useful for structure identification. In this regard the losses of CH_3CNO and H_2O are common for *N*-methyl carbamates and for 3-hydroxy-7-carbofuran phenol[31]. Compound 1 was unequivocally identified by coelution with an authentic standard as 3-hydroxy-7-carbofuranphenol. It could only be identified and detected due to the much higher sensitivity of ESP as regards to TSP (around 100 times better). This compound was tentatively identified by GC-MS during the sunlight degradation of carbofuran[11] and as one of final hydrolysis products in water and soils samples[8]. However, in both cases the concentrations applied were much higher (around 100 times more). The two other photoproducts contained the carbamate group, since they were detected under LC-PCR-FD. Compound 4 was identified as 2-hydroxy-3-(2-methylprop-1-enyl)-phenyl-*N*-methylcarbamate. Compound 4 was the major metabolite and may be formed by rearrangement[32] under UV irradiations. No structure could be attributed to compound 2 with a Mw 152 but it probably corresponds to a loss of water from 3-hydroxy-7-phenolcarbofuran. A tentative degradation pathway in natural waters is given in Figure 4b. When experiments were carried out upon sunlight irradiation, the same metabolites (see Figure 6b) were detected. This differs for methiocarb degradation, that different compounds were formed after sunlight and xenon arc irradiation.

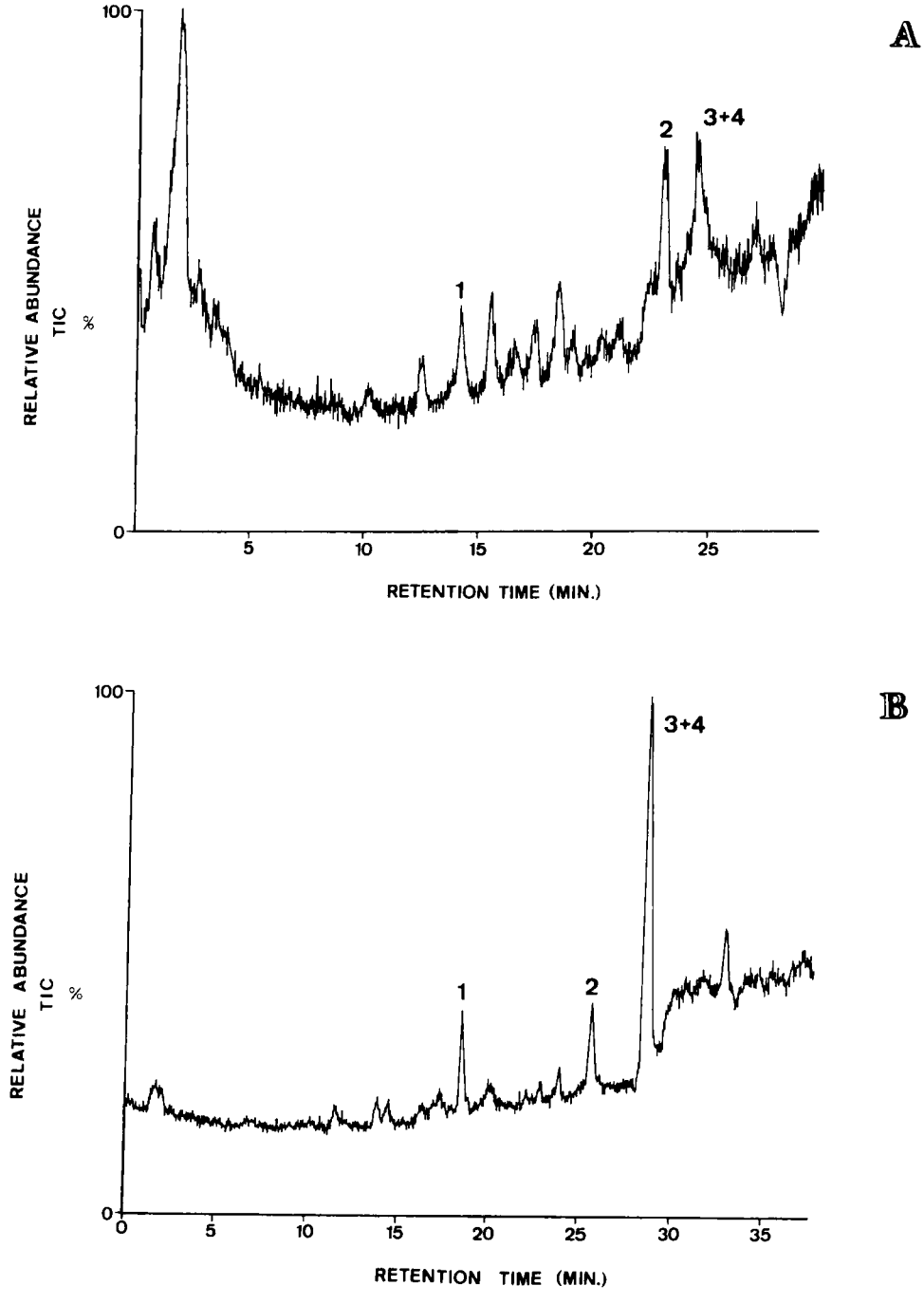

Figure 6 On-line SPE-LC-ESP-MS chromatograms obtained under full scan conditions after preconcentration of 50 mL spiked with 50 µg/L carbofuran of estuarine river water a) irradiated 2 h under xenon arc lamp b) after 30 h natural sunlight. Other conditions, see experimental part. Compound numbering as in Figure 5.

Table 2 Carbofuran degradation products molecular weight (Mw), retention time (RT in min), main ions and their relative abundances (RA) using on-line SPE-LC- high flow pneumatically assisted ESP-MS and positive ionization mode. Analytical separation is shown in Figure 5. All spectra were recorded with an extraction voltage value of 62 V.

Compound	*RT*	*Mw*	*Main ions PI mode*	*RA (%)*
1	14.4	180	181 $[M + H]^+$	11
			203 $[M + Na]^+$	100
			235 $[M + CH_3OH + Na]^+$	7
			163 $[M - H_2O + H]^+$	8
2	23.2	152	153 $[M + H]^+$	31
			175 $[M + Na]^+$	100
			207 $[M + Na + CH_3ON]^+$	12
			118 $[M - CH_3NCO + Na]^+$	18
			96 $[M - CH_3NCO + H]^+$	8
3	24.4	221	222 $[M + H]^+$	13*
			244 $[M + Na+]^+$	100*
			260 $[M + K]^+$	7*
			276 $[M + CH_3OH + Na]^+$	7*
			203 $[M - CH_3NCO + K]^+$	2*
			165 $[M - CH_3NCO + H]^+$	8*
			123 $[M - CH_3NCO - CO - CH_2 + H]^+$	49
4	24.4	221	222 $[M + H]^+$	13*
			244 $[M + Na]^+$	100*
			260 $[M + K]^+$	7*
			213 $[M - NH_2CH_3 + Na]^+$	31
			276 $[M + Na + CH_3OH]^+$	7*
			203 $[M - CH_3NCO + K]^+$	2*
			165 $[M - CH_3NCO + H]^+$	8*

* common ions between compounds 3 and 4.
LOD of carbofuran: 1-2 ng/L when preconcentrating 50 mL water sample.

Degradation kinetics. Artificial light

Carbofuran and methiocarb slightly absorb radiation in the solar region. In the case of xenon irradiation, still hydrolysis predominates for carbofuran whereas for methiocarb oxidation process is dominant. For methiocarb hydrolysis, under these conditions, is too slow to compete under artificial light irradiance, so photolysis alone must account for the rapid loss observed. Table 3 indicates also the values of k, the first-order constant rate calculated as the negative slope of the regression line where ln of % of the compound remaining is plotted against time (h^{-1}). Half-lives ($t_{1/2}$) are calculated according to the relationship $t_{1/2} = \ln 2/k$. For comparison purposes, the half-lives obtained for carbofuran in distilled and paddy water in ref. 7 are reported.

Degradation of carbofuran and methiocarb are fast and both pesticides were depleted within 3h and 5h, respectively. Both reactions fit pseudo first order kinetic from plots of ln C/C_0 versus time and using PCR-FD detection for quantitation purposes. Half-lives in distilled waters were estimated around 0.31 and 1.3 hours, for methiocarb and carbofuran, respectively. When experiments were carried out in river water, a slight

Table 3 Half-lives (hours) of carbofuran and methiocarb in two water types A) under xenon arc lamp, B) Half lives of the total toxic compounds (methiocarb + methiocarb sulfoxide) under xenon arc lamp. C) under sunlight irradiations D) data from ref. 7, using natural sunlight irradiation. Calculated rate constant, k, (h^{-1}) when using xenon arc lamp.

Water-type	*Carbofuran*				*Methiocarb*			
	A	*k*	*C*	*D*	*A*	*k*	*B*	*C*
Distilled water + pure compound	1.3	0.53	360	660	0.31	2.22	0.95	192
River water + pure compound	1.7	0.40	134	173	0.38	1.80	1.0	100
Distilled water + Mesurol*					0.60	1.15	1.50	216

n.d. not determined.
Half lives were estimated using LC-PCR-FD analysis (see experimental part).
Mesurol* = commercial formulation of methiocarb.
D = data obtained from ref. 7.

increase in half-life of carbofuran was observed whereas for methiocarb the effect of dissolved organic matter (DOM) is very small (from 0.31 to 0.38 hours increase in half-life). This slight difference is considered to be not significant. What happens is a rapid photolysis of the compounds. Although HO radicals from DOM are present in the solution, their concentration is very low and will not have any effect on these rates. Indeed the oxidation by HO, $^1O_2$ and RO_2 are all too slow to compete.

To give an explanation to the fast degradation observed under artificial xenon arc lamp, quantum yield were calculated according to previous work[33], assuming that quantum yield are wavelength independent and taking into account the irradiation spectrum of the xenon arc lamp (see Figure 1) and the UV spectra of both compounds shown in Figure 7. From the spectra of the compounds studied, the wavelength distribution, intensity of the artificial light used (Figure 1 and 7) and the degradation rate of the two pesticides studied (see table 3) these data are usually required by the US Environmental Protection Agency for the stability testing of a compound. These three parameters were demonstrated to be sufficient to calculate an average quantum yield directly, without the recourse to actinometry, as recently reported[33]. Quantum yields for carbofuran and methiocarb were ca 0.1%, which indicated that of the photons absorbed by both pesticides only such small percentage cause degradation. There is still some overlap between the solar irradiance spectrum and the absorption spectrum of both compounds studied and it would explain why there is still some photodegradation observed.

Natural sunlight

Figure 1 provides a comparison of the xenon arc lamp and Almeria sunlight spectral outputs between 286 and 400 nm. UV emission contribution is more significant for laboratory experiments and the irradiance is between 5 to 10 times higher according to

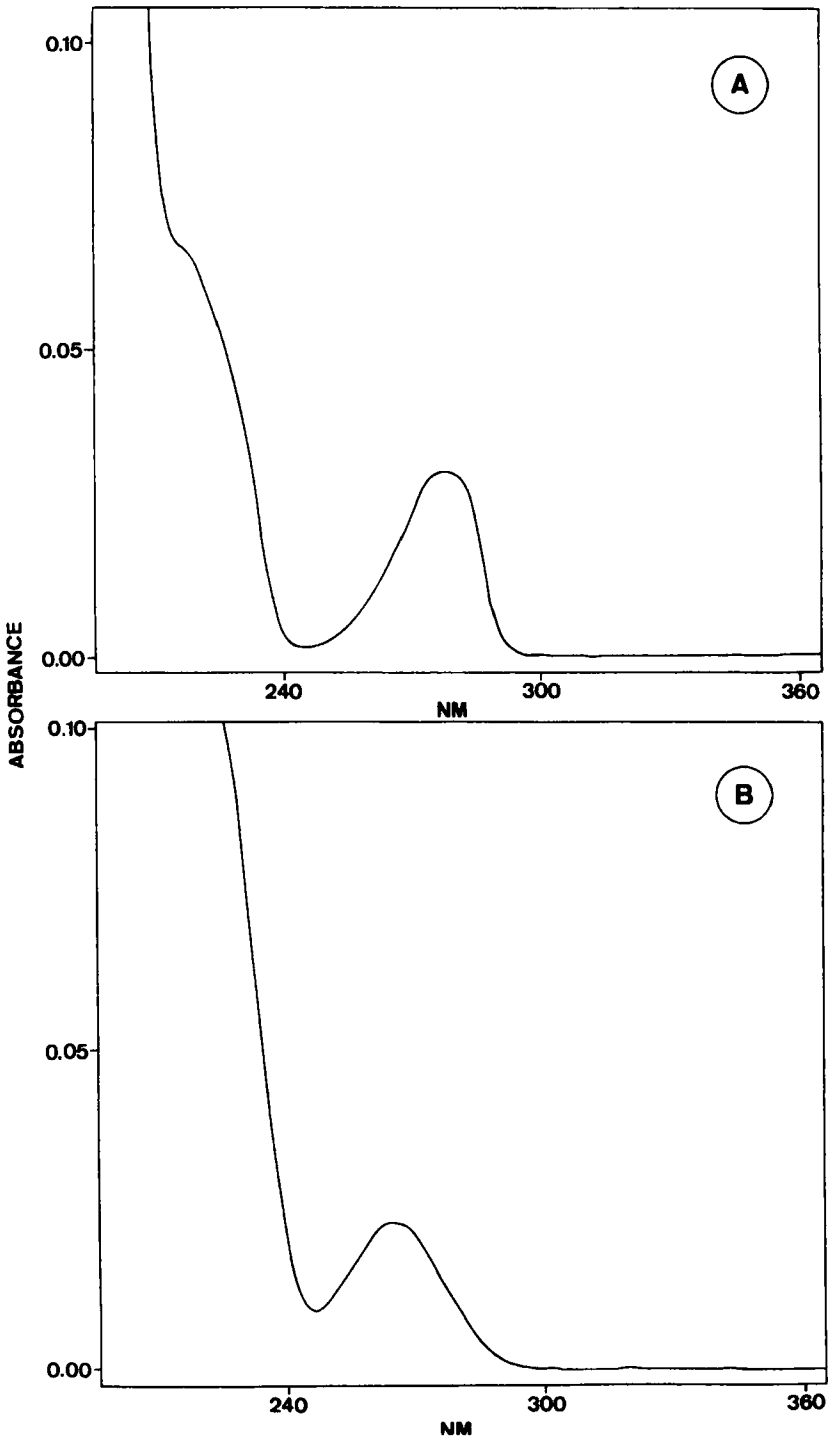

Figure 7 UV spectra of (A) carbofuran and (B) methiocarb recorded at 20 µg/mL.

the wavelength with xenon arc lamp as regards to sunlight. Carbofuran and methiocarb degraded more slowly in outdoor conditions, being their half lives of 5.5 and 12.5 days, respectively. The difference on half lives between laboratory and field data is attributed to the lamp intensity, as indicated above, but also to the lower wavelength used (from 286 nm) in the case of xenon arc irradiation. Under natural sunlight irradiation, the degradation of both carbofuran and methiocarb is mainly attributed to hydrolysis. This is caused by the water pH and previous experiments reported by other authors, corresponding to the natural sunlight irradiation of methiocarb showed that completely disappeared after one week of exposure. Probably the fact that in this previous work a faster degradation of methiocoarb was observed can be attributed to an enhanced microbial degradation due to a different river water composition, which contained high content of salts and dissolved organic matter[10]. Comparing the values of Table 3, we can also notice that in the case of estuarine river water, much shorter half-lives are obtained, which agrees with these statements.

The composition of salts and organic matter enhances degradation of pesticides in natural water as reported[34] and it can be noticed in Table 3 when comparing distilled water and natural river water degradation studies. The formation of major hydrolysis products such as 4-methylthio-3, 5-dimethylpehnol (metabolite 3 of methiocarb) and 3-hydroxy-7-phenolcarbofuran (metabolite 1 from carbofuran) are attributed to hydrolysis. Microbial degradation can also be of importance, as reported for carbofuran[8]. Under natural conditions, the half-live were much lower being 100 hours (4 days) for methiocarb and 134 h (5.5 days), which indicates that microbial degradation and/or hydrolysis affect the degradation of both pesticides (as compared to distilled water).

CONCLUSIONS

In summary, this study confirms and extends earlier findings that carbamate insecticides, carbofuran and methiocarb are not persistent. Half-lives in natural waters varied from 4–12.5 days, depending on the water type and the compound studied. Major degradation pathways under natural sunlight exposure were hydrolysis and microbial degradation, being photolysis of much less importance. Different degradation rates were observed when using natural sunlight irradiation and xenon arc lamp which indicate that it is difficult to correlate both irradiation procedures and in any case the dissipation process cannot be compared. The comparison can only be useful for the degradation products formed, that in the case of carbofuran were similar. In the case of methiocarb when using xenon irradiation the photolysis metabolite predominate over the hydrolysis.

Automated on-line SPE-LC-ESP-MS appeared to be a powerful tool in order to identify the more polar degradation products and exceeded the TSP performances in this field by providing (i) more sensitivity and (ii) more structural informations. In these conditions tentative degradation pathways could be formulated in natural waters for methiocarb and carbofuran together with the unequivocal identification of metabolites.

Acknowledgements

This work was supported by a grant from PRAXIS XXI-BCC-4347-1994. S. Malato is thanked for providing data on emmission sunlight spectrum. Financial support from CICYT (AMB95-0075-(03)) is acknowledged.

References

1. S. Nicosia, N. Carra, D. A. Gonzales and N. K. Orr, *J. Environ. Qual.*, **20**, 532–539. (1991).
2. R. J. Bushway, H. J. Hurst, L. B. Perkins, L. Tian, C. Cabanillas, B. E. S. Young, B. S. Ferguson and H. S. Jennings, *Bull. Environ. Contam. Toxicol.*, **49**, 1–9 (1992).
3. W. F. Ritter, Pesticide contamination of ground water in the United States. A review. *J. Environ Sci. Health, B*, **25**, 1–29 (1990).
4. J. L. Domagalski and K. M. Kuivila, *Estuaries*, **16 3A**, 416–426 (1993).
5. S. Chiron, A. Valverde, A. Fernandez-Alba and D. Barceló, *J. Assoc. Off. Anal. Chem.*, **78**, 1346–1352 (1995).
6. G. W. Johnson and T. L. Lavy, *J. Environ. Qual.*, **24**, 487–493 (1995).
7. J. N. Seiber, M. P. Catahan and C. R. Barril, *J. Environ. Sci. Health*, **B13**, 131–148 (1978).
8. E. D. Magallona, in *Ecotoxicology and Climate* (Ed., by F. Bordeau, J. A. Haines, W. Kelin and C. R. Krishna Marti, John Wiley and Sons, N. York, 1989) pp 265–297.
9. G. W. Johnson and T. L. Lavy, *J. Environ. Qual.* **23**, 556–562 (1994).
10. J. W. Eichelberger, and J. Lichtenberg, *Environ. Sci. Technol.*, **5**, 541–544 (1971).
11. P. Raha and A. K. Das, *Chemosphere*, **21**, 99–106 (1990).
12. A. Bhattacharya, P. Raha and N. Adityachaudhury, *Chemosphere*, **29**, 155–162 (1994).
13. H. M. Dung and P. W. O'Keefe, *Environ. Sci. Technol.*, **28**, 549–554 (1994).
14. J. Kochany and J. Maguire, *J. Agric. Food Chem.*, **42**, 406–412 (1994).
15. N. De Bertrand and D. Barceló, *Anal. Chim. Acta.*, **254**, 235–244 (1991).
16. J. Strankowski and C. Stanley, *J. Agric. Food Chem.*, **29**, 1034–1037 (1981).
17. K. Gohre and G. Miller, *J. Agric. Food Chem.*, **34**, 709–713 (1986).
18. J. E. Yager and C. D. Yue, *Environ. Toxicol. Chem.*, **7**, 1003–1011 (1988).
19. S. Lacorte and D. Barceló, *Environ. Sci. Technol.*, **28**, 1159–1163 (1994).
20. G. Durand, J. L. Abad, F. Sanchez-Baeza, A. Messeguer and D. Barceló, *J. Agric. Food Chem.*, **42**, 814–821 (1994).
21. H. B. Wan, M. K. Wong and C. Y. Mok, *J. Agric. Food Chem.*, **42**, 2625–2630. (1994).
22. S. Chiron, A. Fernandez Alba and D. Barceló, *Environ. Sci. Technol.*, **27**, 2352–2359 (1993).
23. S. Lacorte, S. Lartigues, Ph. Garrigues and D. Barceló, *Environ. Sci. Technol.*, **27**, 2352–2359 (1993).
24. S. Chiron, J. Abian, M. Ferrer, F. Sanchez-Baeza, A. Messeguer and D. Barceló. *Environ. Toxicol. Chem.*, **14**, 1287–1298 (1995).
25. R. D. Voyksner *Environ. Sci. Technol.*, **28**, 118A–127A (1994).
26. C. Molina, M. Honing and D. Barceló, *Anal. Chem.*, **66**, 4444–4449 (1994).
27. S. Chiron, S. Papilloud, W. Haerdi and D. Barceló, *Anal. Chem.*, **67**, 1637–1643 (1995).
28. A. L. Bard, *Evaluating chemical photodegradation: Instrumental approach* (American Laboratory News Edition. February, 1992).
29. S. Chiron, S. Dupas, P. Scribe and D. Barceló, *J. Chromatogr. A*, **665**, 295–305 (1994).
30. S. Pleasance, J. F. Anacleto, R. Bayle and H. D. North, *J. Am. Soc. Mass Spectrom*, **3**, 378–397 (1992).
31. M. Honing, D. Barceló, B. L. van Baar, R. T. Ghijsen and U. A. Th. Brinkman, *J. Am. Soc. Mass Spectrom*, **5**, 913–927 (1994).
32. W. M. Horfool. *Aspects of organic photochemistry.* (Academic Press 1976), p. 143.
33. M. B. Swanson, W. A. Ivancic, A. M. Saxena, J. D. Allton and G. K. O'Brien, *J. Agric. Food Chem.*, **43**, 513–518 (1995).