

PHOTOLYSIS OF SELECTED PESTICIDES ALACHLOR, BENTAZONE,
CARBOFURAN AND METHIOCARB IN NATURAL WATERS AND
IDENTIFICATION OF BREAKDOWN PRODUCTS BY AUTOMATED ON-LINE
LIQUID CHROMATOGRAPHY-MASS SPECTROMETRIC TECHNIQUES

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ABSTRACT

The photochemical degradation of the pesticides alachlor, bentazone, carbofuran and methiocarb in distilled water and in river water has been investigated. Photochemistry studies were carried out both under a xenon arc photoreactor and natural sunlight in order to compare their photolysis behaviour and to discuss the environmental relevance of laboratory studies. The analytical determinations were carried out by automated on-line solid phase extraction (SPE) coupled to liquid-chromatography diode-array (LC/DAD) and liquid-chromatography mass-spectrometry (LC/MS) detection systems. The photolysis experiments were performed at low concentration (20-100 µg/L) and analyzing each time 100 mL of sample being an advantage over conventional techniques. For the two carbamate compounds analysis involved also the use of an on-line SPE followed by LC with post column fluorescence detection (EPA method 531.1 for carbamate insecticides).

The photodegradation of alachlor and bentazone are processes that depend on the water type, humic substances and pH. When using a solution of 4 mg/L of humic matter, the estimated alachlor and bentazone half-lives were 90 and 150 min, respectively using a total irradiance of 550 Wm⁻² in the range of 300-800 nm. The degradation of alachlor and bentazone followed pseudo second and first order kinetics, respectively. The photodegradations of carbofuran and methiocarb were fast processes depending on the dissolved organic matter content and compound formulation. Under solar irradiations half-lives of 8 and 15 days were found for carbofuran and methiocarb, respectively. Methiocarb underwent rapidly a chemical hydrolysis and the photochemical degradation in water could be regarded as a minor pathway. Carbofuran is more stable with respect to hydrolysis and photodegradation plays the major role in natural waters.

After photodegradation, a total of 14 photoproducts resulted from alachlor dechlorination with subsequent hydroxylation and cyclisation processes. The two major photoproducts were identified as hydroxyalachlor and 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinone. No significant breakdown products of bentazone could be identified whereas for carbofuran compounds such as 2,3-dihydro-2,2 dimethyl benzofuran-4,7 diol and 2-hydroxy-3-(2-methyl-prop-1-enyl)-phenyl-N-methylcarbamate were unequivocally identified. In the case of methiocarb discrepancies between xenon arc lamp irradiation and natural sunlight were noticed. Methiocarb sulfoxide and 3,5-dimethyl-phenyl-N-methylcarbamate were identified as the major photolysis products of methiocarb when using Xenon arc lamp, whereas under sunlight irradiations the major transformation product was 3,5-dimethyl-4-methylthiophenol.

OBJECTIVES

In view of the different approaches used for carrying out photodegradation studies of pesticides in water, the aims of our work were as follows: (i) the application of novel analytical techniques, involving on line SPE LC/DAD, LC/MS and LC/MS-MS to the aquatic photodegradation studies of pesticides at concentration level of 10-50 µg/l by using a xenon arc lamp. (ii) to study the degradation rate of alachlor and bentazone under various environmentally relevant conditions (using the authentic standards and commercially formulated compounds dissolved in distilled and/or river water containing or not humic substances). This should allow us to measure the enhancement of herbicide photodegradation in the presence of humic substances (HS) and to study the binding of alachlor and bentazone by dissolved HS, (iii) to compare the photolysis behaviour of carbofuran and methiocarb under laboratory studies (using a xenon arc lamp) and under natural sunlight and (iv) to identify the main breakdown products by their synthesis and confirmation by on-line-SPE-LC/MS.

METHOD USED

Irradiations 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&G, Princeton, New Jersey). All of the outdoor tests were performed in Pyrex borosilicate bottles which contained distilled water sample spiked at 100 µg/L of pure methiocarb/carbofuran. Two bottles of methiocarb/carbofuran aqueous solution in distilled water were prepared. One bottle was wrapped with aluminum foil and kept in the dark and served as a blank. The exposures of the solutions encompassed a 8 h a day and experiments were achieved in late September. Solution temperatures were controlled and never exceeded 35 °C. 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 pesticide. River water samples were filtered through a 0.45 µm membrane filter (Millipore, Bedford, MA, USA). Samples were kept in a quartz reaction reservoir and temperature was set at 30°C using a cooling circuit. Additional vessels were wrapped in aluminum foil. These vessels served as the dark control. Studies on the bonding ability of HS were carried out by adding 4 mg/L of HS to distilled water spiked with 20 µg/L of pure alachlor. The dissolved HS and herbicides remained in contact during 24h at room temperature and in the dark in order that the adsorption equilibrium was reached. Solutions were irradiated during 15h and either acidified at pH=1 or not. Difference between pesticide concentrations obtained with or without sample acidification before analysis allowed to estimate the pesticide binding fraction. The synthesis of the tentative transformation products of Alachlor was carried out as described ¹⁾.

At different periods of time, 20 µl of the solution were directly analysed by LC-PCR-FD. In the similar time, or 100 mL of water sample were analyzed on-line in an OSP-2 autosampler from Merck (Darmstadt, Germany) was successively connected on-line to a LC-UV, LC/TSP-MS and/or LC/high flow pneumatically assisted electrospray (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 conditioning 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 were 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 in an analytical column, as described elsewhere ²⁾.

RESULTS AND DISCUSSION

Degradation rates of alachlor and bentazone under a xenon arc lamp.

Alachlor absorbs radiations weakly between 290 nm, which is the lower wavelength limit for sunlight radiation, and 320 nm. The direct photolysis of alachlor is therefore slow and when irradiation of analytical grade alachlor in distilled water was carried out, all of the alachlor was depleted within 10 h. Alachlor is fairly stable in river water and none losses via chemical hydrolysis processes were found after at least one month with solutions kept in the dark at pH 6.8 (ammonium acetate buffer). The reaction did not appear to be first order. However, first order kinetics were previously reported when using a medium pressure mercury lamp³). From plots of $1/C-1/C_0$ versus time, the reaction apparently fits a second order kinetic and the half life ($T_{1/2}$) was estimated around 140 min. The appearance of hydroxyalachlor followed a first order kinetic suggesting that a stable radical intermediate reacting with water is formed. The intermediate formation can be explained by the loss of chlorine, following the absorption of photons. Such a radical is likely at the origin of complicate photolysis mechanisms. In addition it has to be pointed out that alachlor undergoes conformational equilibrium in solution around amide bound which has not effect on the alachlor loss rates in water.

The binding of alachlor to HS was demonstrated by irradiating alachlor solutions during 15h in order to ensure that the whole photodegradation of dissolved alachlor was achieved. However, changing the pH from 7 to 1 leads to the release of the pesticide. This alachlor fraction was bound to HS and it was never available to photolysis action. The binding fraction was estimated around 5% of the initial alachlor concentration. Binding by physical sorption is reversible and Van der Waals forces are involved in these interactions rather than covalent binding to form stable aggregates. The masking behavior of humic matter was optimum within a contact time of 24h before irradiation. The contact time required in the case of alachlor implies direct reaction with functional groups. At constant pH 6.8 an increase in ionic strength (0.05 M to 0.1M of NaCl) induced a decrease in binding rate. K_{OC} of alachlor depends therefore on its solubility in different waters. Furthermore, different HS were extracted from Rhône river delta water samples with a water salinity rate of 0, 4.5, 6.2 and 33 ‰, respectively and their binding behavior was investigated. The binding fraction of alachlor increases when the water salinity rate increases reaching 10% for HS extracted from water with 33 ‰ of salinity. The binding of pesticides by HS may not only depend on the chemical characteristics of the water but also on the structural characteristics of the HS. More studies are required to understand whether this fraction is irreversibly bound to HS in real condition or whether it is steadily released in water becoming a constant source of contamination.

In order to study the influence of HS on photolysis rates, the alachlor binding fraction was omitted from kinetic experiments by subtracting this constant amount from alachlor concentration values obtained during the kinetic. In these conditions, a decrease of 55 min in half life was observed. Besides, chemical changes of aquatic humic material took place under xenon lamp irradiation.

Complete photolysis of bentazone in its dissociated form (pKa = 3.4 and water pH was set at 6.8 with a 0.1M ammonium acetate buffer) took place within 16 h in distilled water. Bentazone is rather more stable than alachlor as regards to hydrolysis (dark control) and photolysis in aqueous environment. Reaction appeared pseudo first order with a $T_{1/2}$ around 2 h 30 min. The $t_{1/2}$ for formulated bentazone was 2h 45 min. No quenching or photosensitizing effects can be attributed to the wetting agents in this case.

Bentazone was not observed to bind to any of the studied HS. These finding followed expectations since both bentazone and humics are dominant anionic nature substances. However, when experiments were carried out with distilled water spiked with 4 mg/L of HS and bentazone in its dissociated form photochemical degradation increased and the reaction was depleted within 8h. If the reaction medium pH is set at 2 with sulfuric acid and bentazone was in its non dissociated form degradation rate was slower, 11h. As alachlor,

bentazone degradation kinetic is strongly influenced by the HS. HS acted as photosensitizer and produced under Xenon arc lamp reactive intermediate. These findings suggest that oxidation or hydroxylation may be the main routes of photodegradation of alachlor and bentazone in water.

Carbofuran and methiocarb degradation

Carbofuran and methiocarb strongly absorb radiation in the solar region and as a result undergo photodissociation. However photodegradation processes compete with chemical hydrolysis in aqueous medium. 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 ($T_{0.5}$) in river waters were estimated around 23 and 102 min, for methiocarb and carbofuran, respectively. Besides, after 2h of irradiation reactive medium pH dropped down to 5.8 and 6.4 for carbofuran and methiocarb respectively. Phenol release may be responsible of the acidification of the medium and hydrolysis pathway may slow down when acidification of the irradiated solutions occurs. Adding wetting agents resulted in a decrease in the degradation rate of methiocarb. When experiments were carried out in river water, dissolved organic matter (DOM) had a quenching effect on carbofuran photodegradation and as a consequence, an increase of 24 min in half life was observed. No effect of DOM was observed in case of methiocarb. This discrepancy in the photolysis behaviour between the two carbamate insecticides is likely linked to a difference in photolysis mechanism.

Wavelength distribution and incident light intensity are the most important factors affecting the photodegradation rate of a compound ⁴). A comparison between the xenon arc lamp and Almeria sunlight spectral outputs between 286 and 400 nm showed that UV emission contribution is more significant for laboratory experiments and the irradiance is between 5 to 10 times higher according to the wavelength with xenon arc lamp as regards to sunlight. In addition, xenon arc lamp does not account for the daily and seasonal variation in sunlight. In these conditions, carbofuran and methiocarb degraded more slowly in outdoor conditions, their half lives being 8 and 15 days, respectively. Carbofuran degradation rates remained first order reaction while methiocarb reaction appeared no longer to be first order. In the later case hydrolysis and photolysis may strongly compete while in the former case, one of the two degradation pathways may predominate ⁵).

Identification of alachlor photoproducts.

Fourteenth photodegradation products have been detected using either UV or MS detection. Among them, 4 are isomers with a Mw 251: Two are isomers with a Mw 269: ones are isomers with a Mw 233: . At the end of the irradiation period, 10h, the sum of their concentration has been estimated at 40 % of the alachlor originally present. Identical photoproducts have been found using distilled water and Ebro river water. The different compounds identified in full scan traces, when using distilled water samples were confirmed in Ebro river water experiments using the selected ion monitoring mode. Each compound has been characterized by two diagnostic ions. The CH_3OCH_2 moiety was preserved under xenon arc lamp irradiation. Losses of 31 or 32 and 45 mass units corresponding to losses of OCH_3 , HOCH_3 and CH_3OCH_2 , respectively is a common fragmentation pattern of all the compounds . After a dechlorination step a first pathway involved an hydroxylation process. Hydroxyalachlor is the second most important compound. Its identification was obtained by matching its GC/EI-MS and the LC/TSP-MS spectra with those of an available standard from synthetic origin. For unequivocal characterization tandem MS could be applied by using the $[\text{M}+\text{H}]^+$ ion as the precursor ion . The MS-MS spectrum of hydroxyalachlor show losses of 32 mass units due to losses of CH_3OH from the methoxymethyl lateral chain. A second photodegradation pathway

involved the cyclisation of the compound after losing chlorine atom. One of the compounds was identified as 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetrahydroquinone. The unequivocal identification of this compound was provided by matching its LC/TSP-MS and GC/EI-MS spectra with those of a synthetic standard. In order to understand the origin of these further photodegradation products and to better clarify the photodegradation pathway of alachlor, hydroxyalachlor and this compound were irradiated under identical conditions with those used for alachlor. Both products are stable in distilled water and no breakdown product could be identified after 5h of irradiation.

Identification of bentazone photoproducts

No significant photodegradation products have been detected in UV after 12 hours of irradiation in distilled water sample spiked at 20 µg/L with analytical grade bentazone, although aromatic ring breakdown is not an easy photochemical process (results not shown). An exhaustive investigation on the photochemistry of bentazone at concentration ranging from 5 mg/l to 500 mg/L in pure water has been already published and postulated that bentazone underwent, as a main pathway, an oxidative photodimerization involving the N-1 nitrogen of one bentazone moiety and the benzene of another one⁶⁾. Dimerization did not occur at low concentration and none of the two dimers previously described have been detected either in UV or in MS detection. Photodimerization process can be regarded in this case as an artifact of the experimental conditions. pH of the reaction mixture had fallen down to 2 after 5 hours of irradiation and only one photoproduct was detected in LC/TSP-MS using NI mode corresponding to a deprotonated molecular $[M - H]^-$ ion at $m/z = 135$ tentatively identified as amino-2 benzoic acid. Concentration level estimation was difficult because these compounds have so low breakthrough volume on C-18 sorbent that it could not be quantitatively recovered.

Identification of methiocarb TPs

The whole compounds contained the carbamate group necessary for postcolumn fluorescence detection and CONHCH₃ moiety was preserved under xenon arc lamp irradiations. These findings agree with previous literature involving related carbamate compounds⁷⁾. LC-UV detection mentioned also two TPs. The on-line SPE-LC/TSP-MS methodology using negative and positive chemical ionization afforded the unequivocal characterization of two photoproducts in distilled water, methiocarb sulfoxide and 3,5-dimethyl-phenyl-N-methylcarbamate (compound 2). 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 has been 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 irradiations 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 aromatic ring breakdown is not an easy photochemical process and by the presence of carbamate group (confirmed by LC-PCR-FD). Upon sunlight irradiations the major TPs was 3,5-dimethyl-4-methylthiophenol which has never been detected under artificial irradiation source. Methiocarb sulfoxide has only been detected after 4 days of irradiation. Compound 3 with a Mw 168 was fully identified by matching its NI TSP-MS spectrum with that of a synthetic standard (see experimental part). Hydrolysis pathway is strengthened upon sunlight irradiation and accounted for at least 90% of the methiocarb detoxification processes. Using the lamp implied shorter exposure times which mitigated the influence of hydrolysis on the whole degradation processes.

Identification of carbofuran TPs

Electrospray (ESP)-MS provides in addition to the molecular weight information abundant fragment ions at extraction voltage values higher than 40 V very useful for structure identification. 2,3-dihydro-2,2 dimethyl benzofuran-4, 7-diol was identified.. Besides, this compound has already been identified by EI-GC-MS during the sunlight photodegradation of carbofuran in distilled water⁸). The two other photoproducts contained the carbamate group, since they were detected under LC-PCR-FD. 2-hydroxy-3-(2-methyl-prop-1-enyl)-phenyl-N-methylcarbamate was the major TPs and may be formed by ether rearrangement under UV irradiations. . When experiments were carried out upon sunlight irradiation, the same TPs have been detected showing that unlike methiocarb degradation pathway, hydrolysis pathway does not predominate and photolysis pathway accounted for at least 90% of carbofuran detoxification processes.

CONCLUSION.

This study pointed out, in line with earlier literature, the role of dissolved organic matter (DOM) in photodegradation kinetic experiments. DOM retarded by a factor 1.5 the carbofuran degradation. Humic substances affect the photodegradation of pesticides showing the importance to carry out photolysis experiments in natural waters. It was confirmed also that alachlor and bentazone are moderately persistent as regards to photolysis and the same TPs have been found in distilled water as in natural water. The bentazone photodegradation pathway is not still well elucidated because of the likely formation of highly polar breakdown products and their extraction from water remains a difficult topic. The carbamate insecticides, carbofuran and methiocarb are not persistent with regards to hydrolysis and sunlight photolysis in surface waters, being their half lives 15 and 8 days, respectively. Methiocarb detoxification process occurs mainly through an hydrolysis, while carbofuran degradation involves a chemical rearrangement leading to the release of a carbofuran isomer. Since discrepancies still arise from laboratory and outdoor experiments, it is recommended the laboratory results should be validated by field experiments.

The present work has expanded the list of pesticide photolysis products available up till now. This is due, mainly, to the use of aqueous solutions and the use of on-line SPE-LC/MS for detection purposes. Hyphenated LC/MS techniques appeared to be a powerful tool in order to detect and identify the more polar photodegradation products and exceeded the possibilities of GC/EI-MS in this area.

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