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Stability studies of propoxur herbicide in environmental water samples by liquid chromatography–atmospheric pressure chemical ionization ion-trap mass spectrometry

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Abstract

Liquid chromatography–atmospheric pressure ionization ion-trap mass spectrometry has been investigated for the analysis of polar pesticides in water. The degradation behavior of propoxur, selected as a model pesticide belonging to the *N*-methylcarbamate group, in various aqueous matrices (Milli-Q water, drinking water, rain water, seawater and river water) was investigated. Two interfaces of atmospheric pressure ionization, atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI), were compared during the study. Propoxur and its transformation product (*N*-methylformamide) were best ionized as positive ions with both APCI and ESI, while another transformation product (2-isopropoxyphenol) yielded stronger signals as negative ions only with APCI. In addition, the effects of various pH, matrix type and irradiation sources (sunlight, darkness, indoor lighting and artificial UV lamp) on the chemical degradation (hydrolysis) were also assessed. From the kinetic studies of degradation, it was found that the half-life of propoxur was reduced from 327 to 161 h in Milli-Q water with variation of irradiation conditions from dark to sunlight exposure. Degradation rates largely increased with increasing pH. The half-life of the target compound dissolved in Milli-Q water under darkness decreased from 407 to 3 h when the pH of Milli-Q water was increased from 5 to 8.5. These suggest that hydrolysis of propoxur is light-intensity and pH-dependent. In order to mimic contaminated natural environmental waters, propoxur was spiked into real water samples at 30 μg/l. The degradation of propoxur in such water samples under various conditions were studied in detail and compared. With the ion trap run in a time-scheduled single ion monitoring mode, typical limits of detection of the instrument were in the range of 1–10 μg/l.

Keywords: Stability studies; Water analysis; Environmental analysis; Pesticides; Methylcarbamates; Carbamates; Propoxur

1. Introduction

N-Methylcarbamate pesticides as alternatives to organochlorine insecticides have become increasingly popular in recent years due to their short-term environmental persistence and low mammalian toxicity [1]. The *N*-methylcarbamates are a family of compounds whose general structures (R–OCONH–CH_3) are derived from carbamic acid by the introduction of different substituents. Their great success in agricultural applications has led to a continued increase in the use of these pesticides. Unfortunately, their acute toxicity is now threatening the long-term survival of major ecosystems by disruption of predator–prey relationships and loss of biodiversity. Because of the high water solubility of *N*-methylcarba-

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mates, they are usually distributed in aqueous environments. Through net loss of soil by poor agricultural practices and through water logging of irrigated land, these pesticides are discharged into surface and/or ground water. The sea, rivers, or lakes have become the immediate environmental reservoir for all possible carbamate pesticides. Furthermore, carbamates transformation products (TPs), which are formed by corresponding hydrolysis, photolysis [2], or microbial degradation [3], generally are more toxic than the parent compounds (e.g., 1-maphthol is more toxic to aquatic organisms than carbaryl, its parent compound [4]). Hence, evaluation and monitoring of trace levels of *N*-methylcarbamates and their TPs from different environmental water are imperative.

Propoxur [2-(1-methylethoxy)phenylmethylcarbamate, Baygon], an important *N*-methylcarbamate, was selected as a model compound for this study since it is widely used in controlling numerous species of household and public health pests. Due to its high solubility and instability in water, propoxur and its TPs are potential contaminants of aquatic environment and food resources. Accurate, sensitive, analytical methods are required for the monitoring of trace levels of propoxur and its TPs from pesticide-contaminated water.

Besides spectrophotometric methods [5–12], chromatographic techniques are commonly used to determine propoxur and its TPs both qualitatively and quantitatively, such as thin-layer chromatography [13–15], gas chromatography (GC) after derivatization [16], and liquid chromatography (LC) [17–20]. LC has occupied a prominent place for the analysis of *N*-methylcarbamates and their TPs because of their low volatility and thermal instability, which prevents direct analysis by GC. However, the lack of detection sensitivity and selectivity limits the use of LC for the determination of analytes in complex matrix at trace level. With the commercialization of mass spectrometry (MS) instruments using soft ionization techniques such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), LC–MS has become one of the most powerful techniques for the analysis of *N*-methylcarbamates residues.

Many LC–MS methods, particularly thermospray (TSP) MS, for the determination of *N*-methylcarbamate pesticides have been widely studied in recent years [21–25]. However, the instability of the TSP interface, which is well documented, results in the need for a high proportion of calibration to sample injections and has inhibited routine use [26]. The atmospheric pressure ionization (API) techniques (APCI and ESI) are highly sensitive, show greater ionization stability and are more universally applicable than other LC–MS techniques. Pleasance et al. evaluated APCI and ESI for the analysis of *N*-methylcarbamate pesticides (including aldicarb, carbofuran and 3-hydroxy-carbofuran) and compared these techniques with TSP-MS and with particle beam MS [27]. Doerge and Bajic reported the application of LC–APCI-MS for the determination of *N*-methylcarbamates: carbofuran and 3-hydroxy-carbofuran, and the analysis of triazine herbicides in water [28]. LC–ESI-MS has been also successfully applied for the simultaneous determination of carbamate pesticides [27,29–32]. In addition, with the introduction of ion-trap mass spectrometry (IT-MS), higher sensitivity and accuracy of the structural information on analytes can be obtained, that achieve the requirements of the European Union for water analyses [33].

In our previous work, the thermal degradation behavior of some carbamate (propoxur thiuram, propham, methiocarb, chlorpropham) in soil was investigated by using microwave-assisted extraction coupled to HPLC–ultraviolet (UV) detection [34]. As part of our continuing interest in degradation of such pesticides in aqueous matrices, analyses for propoxur and its metabolites in aqueous samples were carried out. Our aims in this work were as follows: (1) to identify the major TPs of propoxur by means of LC–API-IT-MS. The performance of two MS ionization techniques (ESI and APCI) for such identification purposes are compared; (2) to investigate the degradation of propoxur, selected as a model *N*-methylcarbamates, in Milli-Q water under different pH and irradiation sources (sunlight, darkness, indoor lighting and artificial UV lamp) by using LC–APCI-IT-MS with single ion monitoring (SIM) of quasi-molecular ions; and (3) to investigate the degradation of propoxur in environmental water at concentration level of 30 μg/l (close to natural

environmental contamination levels) under various irradiation condition (as above) by LC–APCI-IT-MS.

2. Experimental

2.1. Reagents and sample preparation

All solvents used in this study were either pesticide-grade or HPLC-grade and obtained from Fischer Scientific (Fair Lawn, NJ, USA). The water used was purified using a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Propoxur (purity 99%) was purchased from ChemService (West Chester, PA, USA). The stock solution containing propoxur (1000 μg/ml) was prepared in methanol and diluted with different solvents to obtain working solutions at various concentrations. Two sets of standards of propoxur dissolved individually in methanol and Milli-Q water were prepared with the concentrations of 0.025, 0.05, 0.10, 0.25,0.50 and 1.0 ng/μl, respectively. A set of solvent-based (methanol–water, 50:50) standards was also prepared at the same concentrations. All the above standards were prepared from the same stock solutions. All the solutions were stored at 4 °C in the dark.

Four natural water samples were collected from local sites (sea water, river water, rain water and drinking water). They were filtered through a 0.45-mm membrane (Millipore) to eliminate particulate matter before analysis.

Freshly spiked water samples were prepared by adding an appropriate volume of spiked solutions into the Milli-Q water and the natural water samples prepared as described above.

Hydrolysis products of carbamates were obtained by hydrolyzing the corresponding carbamate esters in alkaline solutions. Propoxur dissolved in methanol (1 mg/ml; 1 ml) was mixed with 0.5 *M* NaOH solution (1 ml). The mixture was heated at 70 °C for 5 h and then neutralized with 1 *M* HCl solution, was analyzed by HPLC–UV (detection wavelength was 225 nm) and LC–APCI-IT-MS.

2.2. Preconcentration by liquid–liquid extraction (LLE)

Liquid–liquid extraction with dichloromethane was used for concentrating propoxur and its TPs from the water samples because of the efficiency and simplicity of this extraction method. A 100-ml sample was firstly adjusted to pH 3, and then transferred to a 250-ml separating funnel and shaken with 20 ml dichloromethane. The lower organic layer was decanted into a 100-ml round-bottom flask. The aqueous layer was further extracted with two successive 20-ml portions of dichloromethane. After each successive extraction the organic layer was decanted. All the organic fractions were combined, and evaporated to dryness in a rotary evaporator. A 1-ml volume of methanol was added to dissolve the residue, which was directly analyzed by LC–MS.

2.3. LC–MS measurement

The LC–API-MS analyses were performed with a Thermo Separation gradient HPLC system (SCM 1000) coupled to a Finnigan MAT LCQ ion-trap mass spectrometer (ThermoQuest, San Jose, CA, USA). The instrument was initially tuned based on a mixture of caffeine, L-methionyl-arginyl-phenyl-ananyl-alanine acetate·H_2O and a mixture of perfluoroalkoxycyclotriphosphazenes in both positive and negative ionization modes as suggested by the manufacturer. Scanned acquisitions of all tested compounds were obtained using APCI and ESI in both ionization polarities. In order to obtain the respective optimum tuning conditions, the standard of each compound was delivered into the API source through an electronically controlled syringe pump.

Typical tuning conditions were: positive APCI: vaporizer temperature 450 °C, sheath gas flow-rate 80 arb (arbitrary units), auxiliary gas flow-rate 20 arb, discharge current 5 μA, capillary temperature 150 °C, capillary voltage 35 V, tube lens offset 5 V, corona voltage 4.5 kV. Negative APCI: the same as positive APCI except corona voltage was −4.5 kV. Positive ESI: spray voltage 4.5 kV, capillary temperature 250 °C; other conditions as for positive APCI. Negative ESI: the same as positive ESI except that the spray voltage was −4.5 kV.

For the LC separation of propoxur and its TPs, a mixture of Milli-Q water–methanol (50:50) was used as mobile phase at a constant flow rate of 0.6 ml/min. A Phenomenex (Torrance, CA, USA) ODS 150×3.2 mm, 5-μm particle size column was used. The HPLC system was interfaced to the ion trap through the API source. Mass spectra collected in full scan mode were obtained by scanning over the m/z range from 50 to 250. Maximum inject time was set at 150 ms. Time scheduled mass conditions were as follows: LC time 0.00–2.00 min, full scan from 50 to 250 m/z; LC time 2.00–7.00 min, SIM mode (m/z 60); LC time 7:00–15.00 min, full scan as above; LC time 15.00–22.00 min, SIM mode (m/z 151 and m/z 210), LC time 22.00–30.00 min full scan as above, total data acquisition time was 30 min. The HPLC system also included a UV6000LP UV detector (ThermoQuest), which was used to help identify the TPs of propoxur.

3. Results and discussion

3.1. Identification of TPs of propoxur and comparison of ESI and APCI

The results showed that under alkaline condition (0.5 *M* NaOH), propoxur was hydrolyzed to two TPs (**1**, and **2**) completely (see Fig. 1a). When propoxur (B) was added to the above hydrolysis product mixture, the two TPs can be effectively separated from propoxur under HPLC (Fig. 1b). Based on the hydrolysis mechanism of carbamates, the most likely pathway of propoxur hydrolysis is outlined and also displayed in Fig. 1.

In order to confirm the TPs of propoxur hydrolysis, two LC–MS ionization techniques (ESI and APCI) were used and compared in this study. The results show that propoxur can be monitored at m/z 210 ($[M+H]^+$) by both APCI and ESI techniques. But for its TPs **1** and **2** (in Fig. 1), the techniques have different responses. Evidence is presented in Fig. 2, which shows some typical full scanning chromatograms of both TPs by using APCI and ESI. From the figure, it is clear that TP **1** can be detected under positive-ion modes $[M+H]^-$ by using both techniques (Fig. 2a and b; LC time ~3.3 min), whereas TP **2**, the most intense peak $[M-H]^-$ was

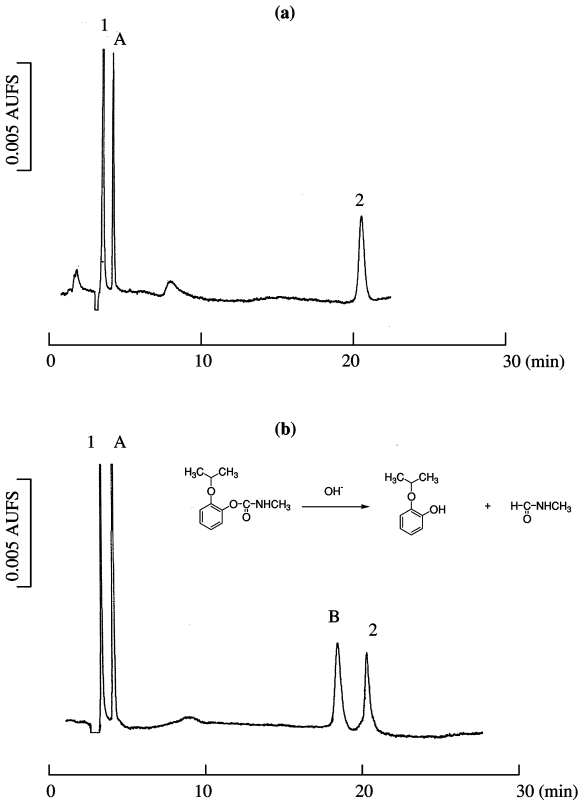

Fig. 1. HPLC–UV chromatogram obtained after hydrolysis reaction under alkaline conditions (NaOH). (a) Hydrolysis products; (b) hydrolysis products with added propoxur. Peak identities: (**1** and **2**) transformation products; (A) methanol; (B) propoxur.

obtained only by using APCI under negative-ion conditions (Fig. 2c, LC time ~20.4 min). There was no obvious response by ESI in either negative or positive ion conditions. This may be due to the lower polarity of TP **2**, so that it is difficult to be ionized under the applied ESI conditions. Furthermore, TP **1** can be confirmed to be *N*-methylformamide as the base peak $[M+H]^+$ was obtained at m/z 60 by both mass techniques. The other TP was 2-isopropoxyphenol, for which the most intense $[M-H]^-$ ion was at m/z 151 obtained by APCI.

Approximate limits of detection (LODs) were estimated from direct injections using positive APCI and ESI for propoxur and *N*-methyl formamide. Both MS techniques were comparable for *N*-methylformamide, while for propoxur APCI was the more sensitive technique than ESI. Based on the above

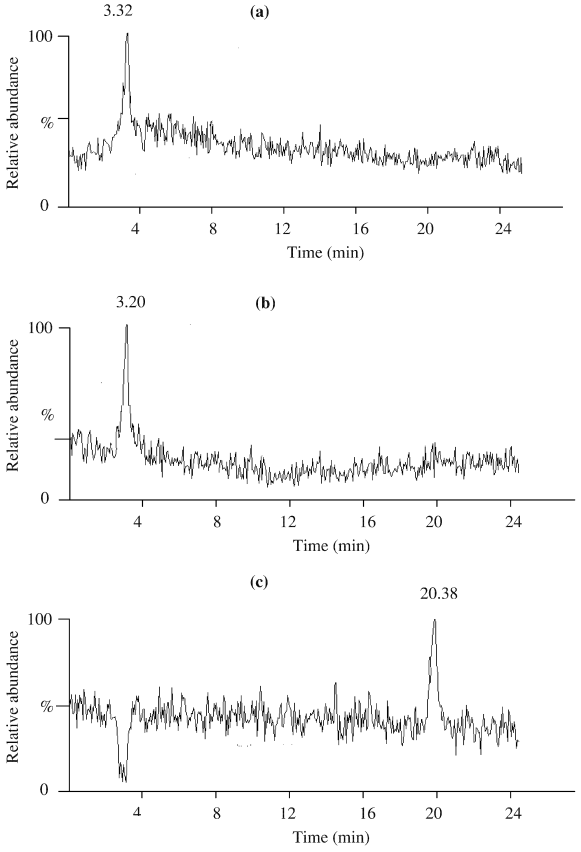

Fig. 2. Full scan chromatograms of TPs of propoxur using LC–APCI-IT-MS and LC–ESI-IT-MS. (a) Transformation products by positive ESI. (b) Transformation products by positive APCI. (c) Transformation products by negative APCI.

considerations and the greater flexibility regarding LC flow-rates associated with APCI, APCI was selected as the technique by which to study the hydrolysis behavior of propoxur in water samples at various pH and irradiation conditions.

3.2. Degradation of Propoxur in Milli-Q water

3.2.1. Calibration curves

In order to investigate instrument sensitivity and calibration, matrix-matched and solvent-based standards at the same concentration of propoxur were kept paired but analyzed in random concentration order. Fig. 3 shows the calibration curves for propoxur in a range of solvent-based standards (methanol–

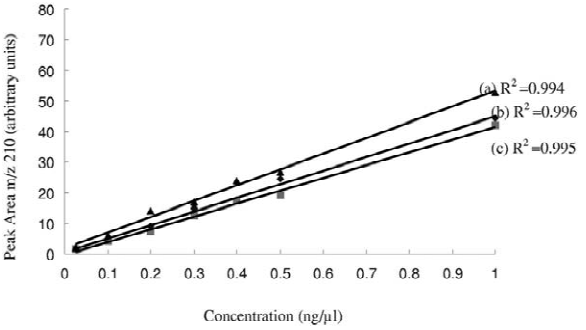

Fig. 3. Calibration curves based on peak areas (m/z 210) over the concentration range 0.025–1.0 ng/μl. (a) Solvent-based propoxur standards. (b) Milli-Q water based propoxur standards. (c) Methanol-based propoxur standards.

water, 1:1) and two matrix-matched standards (Milli-Q water, methanol). It can be seen that the linear range was similar for these three sets of standards (0.025–1.0 ng/μl). Correlation coefficients were 0.994, 0.996 and 0.995 for methanol–water-based standards, Milli-Q-water-based standards and methanol-based standards, respectively. In addition, the use of solvent-based or matrix-based standards was found to influence precision. Thus the relative standard deviation (RSD) at the 0.1 ng/μl level for standards prepared in solvent was 5.5% ($n = 8$) but that for the same concentration in matrix-based standards was lower than 3.2% ($n = 8$). Therefore, matrix-based standards were used throughout to quantitate the extracts in this study.

It can also be observed from Fig. 3 that an enhancement or suppression effect was noticed for these three different propoxur standards. Close agreement is observed between the two sets of matrix standards (Milli-Q water, methanol) indicating only a slight matrix enhancement effect on the ion signal, whereas the calibration curve for the propoxur obtained from the solvent based standard (methanol–water, 1:1) demonstrated a large enhancement effect. Therefore, during the following investigation of propoxur degradation in real water samples, methanol was used to dissolve the final target compounds after preconcentration instead of water due to its similar effect with water on the ion signal and the higher solubility of targets dissolved in it than in water.

3.2.2. Effect of light irradiation and pH on degradation

Carbamate pesticide can undergo three general types of degradation processes in the aquatic environment, namely, chemical (hydrolysis), biological and photochemical. Although there is a wealth of literature on *N*-methylcarbamate degradation, most of it deals with the biochemical transformation rather than with environmental metabolism, however [35] the present study was aimed at monitoring the degradation kinetics of propoxur in water in order to obtain its chemical degradation curves and half lives. For this purpose, Milli-Q water samples containing 1.0 ng/μl propoxur at various pH values (adjusted with dilute HCl or NaOH), under three different conditions: natural sunlight, no light (darkness) and ordinary indoor lighting, respectively, were studied. At different periods of time, aliquots of 10 μl were taken from the samples and analyzed directly by LC–APCI-IT-MS.

The degradation curves obtained over a 4-week period for propoxur in Milli-Q water at pH 5 (a), pH 6 (natural pH) (b), pH 7 (c), pH 8.6 (d), pH 10.5 (e), are shown in Fig. 4. Water samples were periodically sampled each minute, each hour, each day, and finally two times a week according to experimental requirements; duplicate measurements were made in all cases. From Fig. 4, it can be seen that the signals for propoxur were decreased with increasing time under all applied conditions as a result of hydrolysis. Moreover, propoxur degraded more significantly under natural sunlight exposure than under indoor lighting and dark conditions, indicating that its hydrolysis is very much light-intensity dependent. It also can be seen from Fig. 4a–c, that propoxur remained stable for a longer time under darkness and indoor lighting than under sunlight exposure. At pH 5 (Fig. 4a), it remained stable for 24 h under darkness and at least 20 h under indoor light, compared to only 8 h under sunlight. At the natural pH of Milli-Q water (Fig. 4b), propoxur remained stable for more than 16 h under indoor lighting and darkness, compared to only 4 h stability when it was exposed to sunlight. However, a very interesting observation was obtained when the pH was above 8. Faster degradation occurred under alkaline conditions. It appeared that in comparison to an alkaline environment, all other conditions that affected degradation, such as light intensity, became insignificant. Evidence is presented in Fig. 4d and e, which show that when pH is adjusted up to 8.5, propoxur was virtually completely hydrolyzed within 24 h (pH 8.5) and 10 min (pH 10.5), respectively, no matter what type of irradiation was involved.

Based on the above results, it is obvious that the effect of pH on the hydrolysis of *N*-methylcarbamates is significant. Generally, mild alkaline conditions at room temperature are sufficient to cause hydrolysis. Published literature about carbofuran indicates that its degradation in water is very much pH dependent, with values of 10 or 0.58 days when the pH is raised from 7 to 8.7 [36]. The influence of pH on the hydrolysis of propoxur in Milli-Q water was investigated and results are shown in Fig. 5. (Special care must be taken here, to avoid continuous degradation of targets during the detection period.) Aqueous samples containing propoxur at variable pH were adjusted to pH 3 after being allowed to stand for 30 min, and then direct analyzed by LC–APCI-MS. From Fig. 5, it is clear that the signals for propoxur decreased with increasing the pH value above 4. Above pH 8, propoxur was significantly hydrolyzed in water. Less than 5% of the propoxur was detected after 30 min in water at pH 10 and almost 100% loss occurred at pH above 10.5. In addition, the applied irradiation (sunlight, indoor lighting and darkness) appeared to affect degradation at a range from pH 5 to 9, which demonstrated again light intensity affected hydrolysis only under mild alkaline conditions. Above pH 9, degradation was so fast that pH seemed predominant. Like carbofuran, propoxur hydrolysis is also very much pH-dependent.

3.2.3. Degradation kinetics

The chemical degradation of *N*-methylcarbamate fits a first-order degradation curve, $C_t = C_0\ e^{-kt}$, where C_0 and C_t are the initial concentration and concentration at time t, respectively. K is the first-order rate constant, which is calculated as the negative slope of the regression line where the natural logarithm of the percentage of the compound remaining is plotted against time (h^{-1}). The half-life ($t_{1/2}$) designates the time at which the pollutant concentration is equal to one-half the initial concentration ($t_{1/2} = \ln 2/k$). The half-lives of propoxur

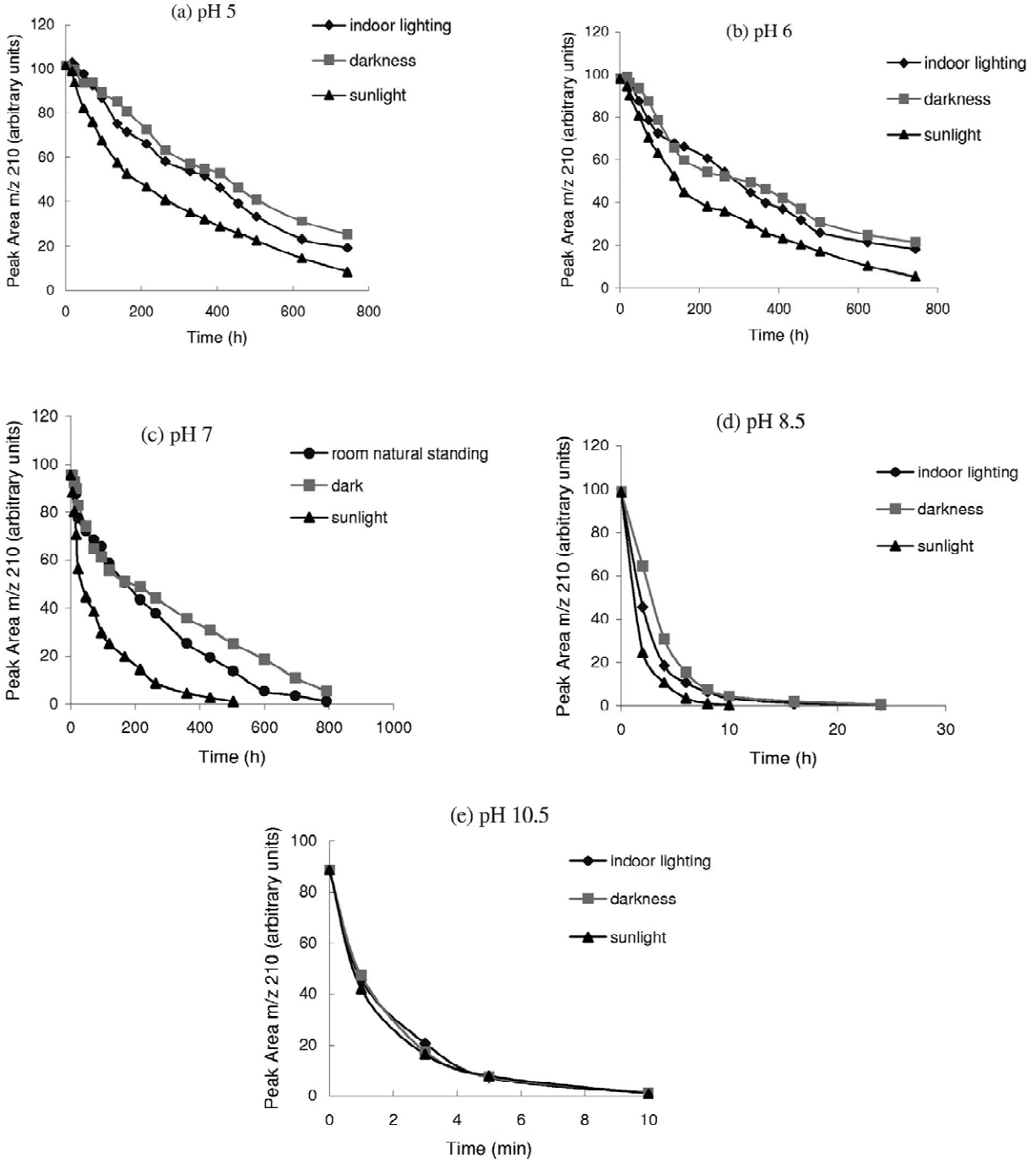

Fig. 4. Degradation curves for propoxur spiked in Milli-Q water under various irradiation and pH conditions. (a) pH 5; (b) pH 6; (c) pH 7; (d) pH 8.5; (e) pH 10.5.

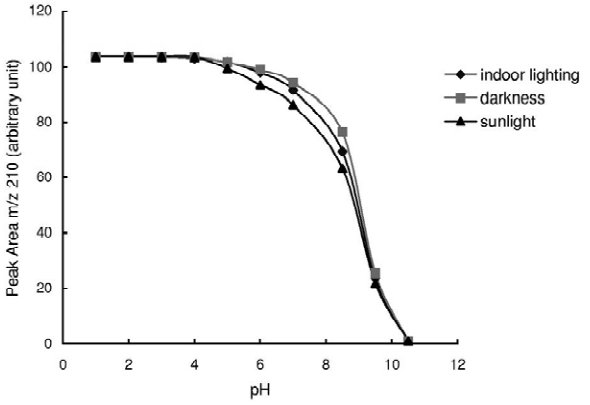

Fig. 5. Influence of pH on the hydrolysis of propoxur in Milli-Q water under various irradiation conditions.

in Milli-Q water under various conditions (pHs and irradiation) are shown in Table 1. The degradation of propoxur increased with increasing K. As a result, the half-lives decreased accordingly. For example, at pH 5, K increased from 1.70×10^{-3} under darkness to 3.96×10^{-3} under sunlight; correspondingly, the half-lives were reduced from 407 to 175 h. Based on the results of Table 1, a conclusion can be drawn that the half-lives decrease in the order of increase of light intensity (darkness > indoor lighting > sunlight), although at high pH (pH > 8.5), this decrease is slight.

Table 1
Rate constants (K) and half-lives ($t_{1/2}$), for propoxur in Milli-Q water under different conditions

pH	Irradiation	K (h^{-1})	$t_{1/2}$ (h)
5.0	Darkness	1.70×10^{-3}	407
	Indoor lighting	2.15×10^{-3}	322
	Sunlight	3.96×10^{-3}	175
6.0	Darkness	2.12×10^{-3}	326.8
	Indoor lighting	2.65×10^{-3}	261.5
	Sunlight	4.31×10^{-3}	160.9
7.0	Darkness	2.18×10^{-3}	318.2
	Indoor lighting	2.77×10^{-3}	250.6
	Sunlight	1.30×10^{-2}	53.3
8.5	Darkness	2.26×10^{-1}	3.07
	Indoor lighting	3.30×10^{-1}	2.1
	Sunlight	4.85×10^{-1}	1.43
10.5*	Darkness	1.15×10^{-2}	60
	Indoor lighting	1.33×10^{-2}	52
	Sunlight	1.54×10^{-2}	45

*At pH 10.5, units of K and $t_{1/2}$ are S^{-1} and S, respectively.

3.3. Degradation of propoxur in natural water

In order to provide a better comparison with real environmental data, degradation studies in natural water were conducted for propoxur at a concentration of 30 μg/l, within normal environmental levels (20–100 μg/l) of the herbicide. Different types of water samples, namely: river water, seawater, rain water and drinking water were selected as matrices. Because propoxur is not present in natural water (in Singapore), all the water samples were spiked with 30 μg/l of propoxur. Liquid–liquid extraction was used here to concentrate propoxur and its TPs after hydrolysis. The degradation curves obtained over a 1-month period for propoxur at various irradiation conditions in seawater as an example are shown in Fig. 6. It can be observed from Fig. 6 that propoxur in seawater hydrolyzed quickly, especially under sunlight and indoor lighting. Under the above conditions, the half-lives of the target were 11.5 and 12 h, respectively. More than 50% degradation occurred within 40 h even under darkness, probably aided by the pH (7.8) of the seawater used, which causes rapid hydrolysis (see above). Degradation curves, describing hydrolysis under sunlight

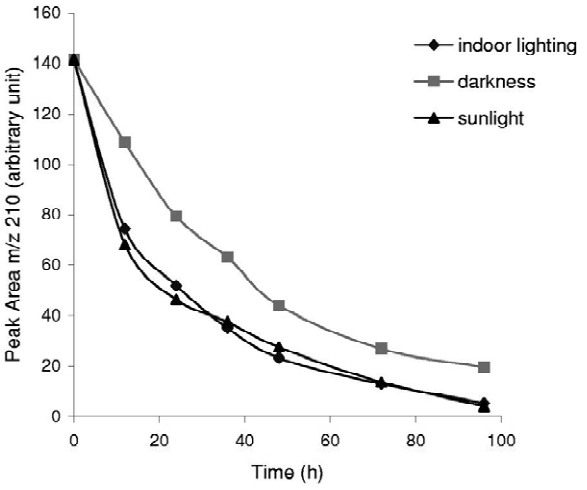

Fig. 6. Degradation curves for propoxur in seawater under various irradiation conditions.

and indoor lighting (Fig. 6), are quite similar. However, these were different from that for degradation under darkness. In addition, the hydrolysis behavior of propoxur under irradiation (either natural sunlight exposure or indoor lighting) was much faster. For example, more than 95% of propoxur under irradiation was degraded after 72 h (3 days), whereas less than 80% of the target disappeared under darkness over that time. Furthermore, half-lives were estimated to be around 12 h under both types of irradiation, whereas under darkness, the half-life was about 35 h.

The effects of matrix on degradation behavior of target were also studied. Results are presented in Fig. 7, which shows the effect of irradiation time on the degradation behavior of propoxur when four water samples (drinking water, rain water, seawater and river water) respectively, were exposed to sunlight at the same time. It is clear that degradation rates increase in the order of increasing pH (seawater [pH 7.8]/river water [pH 7.6]>drinking water [pH 7.03]>rain water [pH 4.2]). For example, the percentage of degradation in seawater and river water were almost 100% after 100 h sunlight irradiation, but over that time only 33% of the target degraded in drinking water. When experiments were carried out on rain water, very slight degradation was observed during the first 100 h. Therefore, it is obvious that the effect of pH is a crucial factor on the degradation of propoxur in water samples. We also noticed that degradation was much faster in both seawater and river water than in drinking and rain water. This is

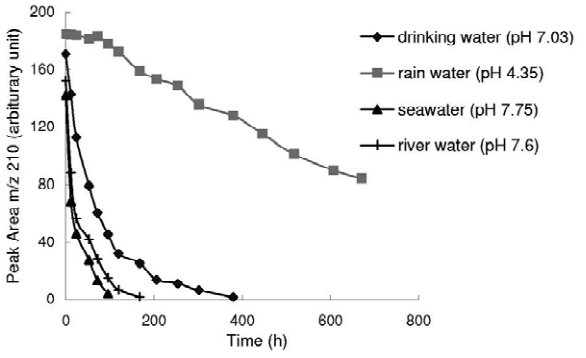

Fig. 7. Degradation curves for propoxur in various matrices (drinking water, rain water, seawater and river water) under sunlight exposure.

because dissolved salts and organic matter possibly enhance degradation of propoxur in sea and river water, Seiber et al. reported a remarkable decrease in the half-life of carbofuran in paddy water instead of distilled water [37]. In addition, microbial degradation in both waters can be of importance, which affects the degradation positively, as reported for carbaryl [38]. Furthermore, degradation behavior in drinking water was quite similar to that in Milli-Q water at pH 7. This is probably due to their similar pH (pH of collected drinking water was 7.03). Although it could still be observed that degradation rate was a little faster in drinking water, this slight difference is not considered to be significant. What is surprising is that although pH of rain water was only 4.2, propoxur degradation occurred. Nevertheless, in contrast to the result shown previously in Fig. 5 in which degradation in Milli-Q (~pH 4) is depicted to be slight, this is probably due to the dissolved particles in rain water, which had a positive effect on degradation [37]. The comparison of degradation rate and half-life of propoxur in different matrix under various light exposures were investigated and the results are shown in Table 2. It can be seen that light intensity affects the K and $t_{\frac{1}{2}}$ in each natural water sample. K increases and $t_{\frac{1}{2}}$ decreases accordingly when the light intensity increases in the order of darkness, indoor lighting and sunlight. This indicates that light exposure can prompt hydrolysis in various types of natural water. Thus the effect of light intensity in natural water is similar to that in Milli-Q water, that is, light intensity could affect hydrolysis positively at mild alkali conditions. Furthermore, the degradation is very much pH dependent as K and $t_{\frac{1}{2}}$ are significantly altered with increase in pH. For example, when the pH of the matrix increased from 4.2 (rain water) to 7.8 (sea water), $t_{\frac{1}{2}}$ was reduced greatly from 660 to 18 h.

3.4. Effect of UV irradiation

We also tested propoxur degradation in Milli-Q water, rain water and seawater under artificial light (UV lamp 220–340 nm). The results are shown in Fig. 8. Rapid degradation was observed under UV irradiation, especially in seawater where complete degradation occurred within 60 min. In the other two matrices (Milli-Q water and rain water), the degra-

Table 2
Rate constants (K) and half-lives ($t_{1/2}$), for propoxur studied under applied light irradiations in four different water samples, respectively

Matrix	Irradiation	K (h^{-1})	$t_{1/2}$ (h)
Rain water (pH 4.2)	Darkness	9.12×10^{-4}	760
	Indoor lighting	1.07×10^{-3}	650
	Sunlight	1.20×10^{-3}	580
Drinking water (pH 7.03)	Darkness	2.19×10^{-3}	316.3
	Indoor lighting	2.75×10^{-3}	252
	Sunlight	1.37×10^{-2}	50.5
River water (pH 7.6)	Darkness	2.17×10^{-2}	32
	Indoor lighting	3.59×10^{-2}	19.3
	Sunlight	4.20×10^{-2}	16.5
Seawater (pH 7.8)	Darkness	2.41×10^{-2}	28.7
	Indoor lighting	4.95×10^{-2}	14
	Sunlight	6.08×10^{-2}	11.4

dation of propoxur was also much more serious than that in the same matrix under any of the other light conditions applied previously. For example, about 90% of propoxur was degraded within 40 h under UV irradiation in Milli-Q water, whereas over that time, more than 80% of the compound was intact under sunlight irradiation in the same matrix.

4. Conclusion

In summary, this study confirms and extends earlier findings that *N*-methylcarbamate pesticides are not persistent in water. Propoxur was selected as a model compound to study the degradation behavior in Milli-Q water, drinking water, rain water, river water and seawater under various pH and irradiation sources (sunlight, darkness, indoor lighting and artificial UV lamp). Hydrolysis is very much pH dependent irrespective of the type of water matrix. Light intensity can prompt degradation significantly under mild alkaline conditions, while its influence is minor at higher pH (pH$>$9). Furthermore, half-lives and degradation rates were obtained in various matrix and irradiation sources. Based on kinetic studies, propoxur was found to degrade more rapidly at higher light exposure and pH.

For the first time, LC–APCI-IT-MS was used to investigate the chemical degradation behavior of propoxur. Our experience indicated that this technique was a powerful tool to analyze polar and thermal-labile pesticides and their TPs in terms of sensitivity, accuracy and precision.

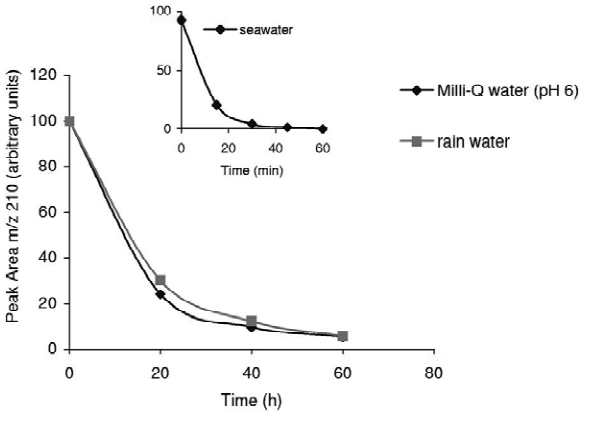

Fig. 8. Degradation curves for propoxur in Milli-Q water, rain water and seawater under UV irradiation.

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