

Aqueous phototransformation of zinc pyrithione Degradation kinetics and byproduct identification by liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry

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Abstract

The photochemical behavior of the antifouling agent zinc pyrithione (ZnPT) was studied in aqueous media of different composition under simulated solar irradiation using a xenon light source. The influence of important constituents of natural water (dissolved organic matter and nitrate) was also examined using a multivariate kinetic model. It was found that photodegradation proceeds via a pseudo first-order reaction. Kinetic experiments were monitored by LC–MS and photolytic half-lives ranging between 9.2 and 15.1 min have been observed. The increasing concentration of dissolved organic matter (DOM) accelerates the photolysis reaction, while the effect of nitrate ions was also positive since it increased the degradation rate, but to a lesser extent. Irradiation of the aqueous ZnPT solutions gave rise to several transformation products that were isolated by means of solid-phase extraction using poly(styrene-divinylbenzene) extraction disks. These byproducts were identified using liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry. Besides 2-pyridinesulfonic-acid, other degradation products formed included pyridine-*N*-oxide, 2-mercaptopyridine, 2,2'-dithiobis(pyridine-*N*-oxide), 2,2-dipyridyl disulfide and the pyridine/pyrithione mixed disulfide, 2,2'-dithiobispyridine mono-*N*-oxide (PPMD).

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1. Introduction

New alternative antifouling paint formulations (based mainly on organic booster biocides) have been developed and introduced in the market as a result of the ban introduced on the organotin compounds due to their negative impact on marine environment. Worldwide around 18 compounds are currently used as booster biocides in antifouling products (the most widely used are: chlorothalonil, dichlofluanid, diuron, Irgarol 1051, Sea-Nine 211, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine (TCMS-pyridine), (thiocyanomethylthio)benzothiazole (TC-MTB), zinc and copper pyrithione, zineb, folpet, mancozeb, thi-

ram, ziram) for amateur and professional use [1]. The continued input of these biocides from the painted hulls of boats directly onto the foreshore has led to reports of elevated concentrations in areas of high yachting activity and low water exchange rates such as marinas [2,3].

Besides used as additive in antifouling paint formulations, the majority of ZnPT (Fig. 1) (*bis*(2-pyridylthio)zinc 1,1'-dioxide) produced has been used as the active ingredient in anti-dandruff shampoo or as an additive in cosmetics and dermatitis treatments. Therefore, two distinct routes into the aquatic environment exist for ZnPT that depend principally upon the mode of usage.

Given the potential human and wildlife health risks associated with toxic pollutants in surface waters, it is important to determine the probability that a certain chemical will persist in the environment by examining the various reactions of the

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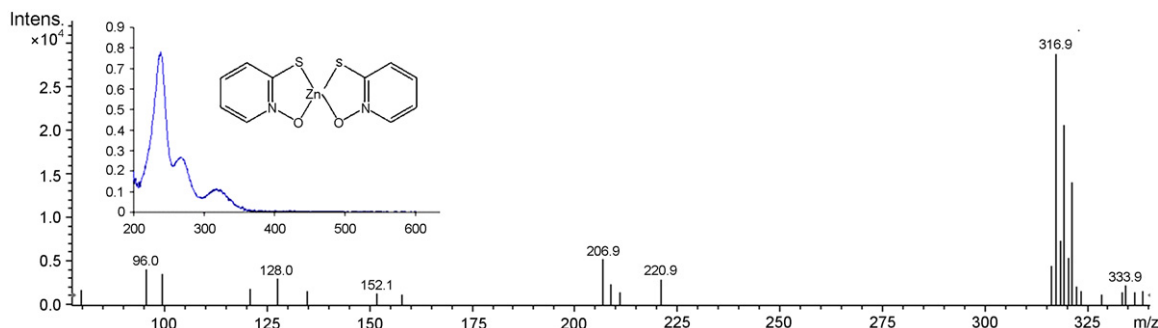


Fig. 1. Structure, UV-vis and APCI-MS spectrum of ZnPT.

molecule. Direct and indirect photochemical reactions are of the most important abiotic processes that may contribute to the degradation of organic micro-pollutants under environmental conditions.

Several studies have dealt with ZnPT photodegradation in distilled and seawater, respectively, mainly in terms of degradation kinetics that have been reviewed before [4]. Zinc pyriothione photodegradation is a rapid procedure with half-lives ranging from minutes to hours depending on the light source and the aqueous matrix [5–7].

Previous research has identified dissolved organic matter (DOM), NO_3^- , and $\text{HCO}_3^-/\text{CO}_3^{2-}$ as significant participants in the photochemical degradation of organic micropollutants in surface waters [8,9]; accordingly, identifying their effect on ZnPT degradation was of interest. The role these constituents play in photochemical degradation is concentration dependent; and can simultaneously respectively decrease and increase photochemical reactions [10,11]. In order to meet these requirements we examined the aquatic photochemical degradation of ZnPT under simulated solar irradiation. A multivariate kinetic model of aqueous ZnPT photodegradation was developed as a function of DOM, and nitrate at concentrations that bracket those commonly observed in natural waters.

Few studies have dealt with the fate of ZnPT in the aqueous environment [12,13]. On the other hand, reports on the development of analytical methods for determining ZnPT residues are still scant due to the lack of sufficient analytical methods for its determination (despite concerns of considerable environmental toxicity at ultra-trace concentrations) and only a few studies have been presented accomplishing their determination [14–16]. Since the study of the photochemical behavior of a contaminant is a key issue in terms of the formation of toxic transformation products; in this context, we now attempt to extend the analytical utility of LC methods towards the investigation of this chemical and the determination of phototransformation intermediates formed.

In a wider context, the aim of the present study is two-fold. First, it strives to decipher the prime mechanisms involved in the fate and environmental behavior of ZnPT and examine the simultaneous effect of natural occurring constituents. Second, isolate and characterize the intermediate products, which are produced during the phototransformation process.

2. Materials and methods

2.1. Chemicals

ZnPT, purity above 90% was purchased from Wako (Tokyo, Japan). 2-Mercaptopyridine-*N*-oxide (POS) and pyridine-*N*-oxide (PO) were obtained from Aldrich (Tokyo, Japan). 2-Mercaptopyridine (PS) and 2,2'-dipyridyl disulfide (PS)₂ were purchased from Tokyo Kasei (Japan). 2-Pyridinesulfonic acid (PSA) was from Synchem and 2,2'-dithiobispyridine-*N*-oxide [(POS)₂] was provided from Chem Service (USA). Sodium hydrogencarbonate (NaHCO_3) and sodium nitrate (NaNO_3) were purchased from Junsei (Tokyo, Japan) while humic acids (HA) were provided by Wako. Pesticide analysis grade solvents were purchased from Pestiscan (Labskan, Dublin, Ireland). HPLC analysis grade solvents were obtained from Merck (Darmstadt, Germany). Poly(styrene-divinylbenzene) (PS-DVB) extraction disks (47 mm) were purchased from 3M Empore (St. Paul, MN, USA), and a conventional filtration apparatus was supplied from Supelco (Bellefonte, PA, USA). NaNO_3 and HA stock solutions were diluted to achieve the respective NO_3^- and DOM concentrations outlined in the experimental section. Natural water samples used in the experiments were collected from the Epirus region of N.W. Greece with the following physicochemical characteristics: seawater (Ionian sea) DOM = 2.1 mg/L, nitrate = 3.3 mg/L, lake water (Pamvotis lake) DOM = 11.0 mg/L, nitrate = 10.3 mg/L.

2.2. Chromatographic conditions

LC-MS was performed under the same conditions optimized in our previous work during the direct analysis of ZnPT by LC-MS [14]. An Agilent 1100 series HPLC system was used, equipped with a quaternary pump, a diode-array detector, an autosampler, and a column compartment. The LC system was coupled to a LC ion trap mass spectrometer complete with an atmospheric pressure chemical ionisation source operated under positive polarity.

The samples were separated on a Unison UK-Phenyl column (50 mm × 3.0 mm) supplied by Imtakt (Kyoto, Japan). For the separation of the degradation products a mobile phase consisted of methanol (A) and water containing 20 mM ammonium acetate

(B) was used. At a flow rate of 0.5 mL/min, a gradient elution was performed starting with 40% (A) held constant up to 3.5 min and then went up linearly to 60% (A) in 20 min before return to initial conditions. The column temperature was set to 20 °C.

The optimisation was performed using a nebuliser pressure of 60.0 psi, a dry gas flow of 4.0 L min⁻¹, a drying temperature of 250 °C, a corona voltage of +2500 V and an APCI temperature of 250 °C. Single ion monitoring (SIM) was performed at *m/z* 316.9 [M + H]⁺ for the quantitation of ZnPT as reported previously [14].

2.3. Photolysis in aqueous solutions under simulated solar irradiation

Experimental solutions were prepared by dissolving ZnPT (30 min sonication) to give a concentration level of 5 mg/L. Then the solutions (150 ml) were put into quartz glass reservoirs and irradiated using a xenon arc lamp light (USHIO, SX-UI500QX) under continuous stirring. The light source was on the top of the reactor and an average irradiation intensity of 3.2 kW/m² was maintained throughout the experiments. The temperature of samples did not exceed 25 °C. A dark control experiment was also conducted in this series of experiments.

2.4. Experimental design

An experimental factorial design of the reaction system was performed for the photolytic transformation of ZnPT to assess the effect of natural water constituents on the degradation rate. Multivariate design was performed according to the methodology of response surface following the methodology described by Fernandez et al. [17]. The initial concentration of DOM and nitrates were considered as the experimental parameters for the generation of the predictive kinetic model (Table 1). The DOM concentration range was considered between 0.05 and 9.95 mg/L while nitrate concentration range varied from 0.1 to 19.9 mg/L. The above concentrations of humic/fulvic acids and nitrate ions were chosen in order to resemble those found in natural waters. The modeled response (*Y*) was the half-life (*t*_{1/2}, min) calculated from the rate constant of ZnPT photolysis.

In addition carbonate radicals were produced from the photolysis of NaHCO₃ (250 mg/L) and NO₃⁻ (20 mg/L) in order to

study their involvement on the degradation kinetics of the target molecule.

2.5. Quantification and extraction procedure

Aliquots of 3.0 mL were taken out from the reactor at predetermined times of irradiation and were injected to the liquid chromatograph in order to follow the reaction kinetics. Quantification was performed with external calibration curves constructed under the same experimental procedure.

Solid-phase extraction (SPE) was employed for the isolation of photoproducts formed during the process. The remaining irradiation solutions (approx. 120 ml) were extracted, by means of SPE [18] as follows: PS-DVB extraction disks were conditioned with 10 ml of acetone for 2 h. In order to allow better extraction, 0.25 ml of methanol modifier was added to the residues. The disks were placed on the filtration apparatus and washed with 5 ml of solvent mixture dichloromethane: ethyl acetate (1:1, v/v) under vacuum followed up with 5 ml of methanol for 3 min, with no vacuum applied. The disks were not allowed to dry and the samples were allowed to percolate through the disks under vacuum. Then the compounds bound to the disks were collected by using 5 ml of the elution mixture, dichloromethane:ethyl acetate (1:1, v/v) twice. The fractions were finally evaporated to 0.1 ml in a gentle stream of nitrogen. Then 3.0 μL were injected into the LC-APCI-MS instrument.

2.6. Calculation of half-life

Pseudo-first order rate constants for ZnPT were observed for all experiments, obtained by linear regression of logarithmic concentration values (ln[C_t]/[C₀]) determined as a function of time. As far as the photodegradation constants (*k*_{phot}) are concerned, they were calculated by subtracting the exponents of different degradation curves representing the apparent degradation (*k*_{app}) and the degradation as a result of hydrolysis, volatilization and biodegradation (dark experiment, *k*_{dark}). In this way the considered rate constants (*k*_{phot} = *k*_{app} - *k*_{dark}) and the half-lives (*t*_{1/2}) refer to the actual photochemical reaction with the exclusion of the contribution of other factors. The half-life was determined using the equation: *t*_{1/2} = ln 2/*k*.

Table 1

Listing of experimental parameters from the factorial design and observed and calculated *t*_{1/2} of the kinetic model

DOM concentration (<i>x</i> ₁) mg L ⁻¹	Nitrate concentration (<i>x</i> ₂) mg L ⁻¹	<i>t</i> _{1/2} (<i>Y</i> _{obs}) min	<i>t</i> _{1/2} (<i>Y</i> _{calc}) min
1.5 (-1)	3.0 (-1)	12.76	12.88
8.5 (+1)	3.0 (-1)	9.98	9.93
1.5 (-1)	17.0 (+1)	11.57	11.62
8.5 (+1)	17.0 (+1)	9.20	9.08
0.05 (-1.4142)	10.0 (0)	13.80	13.69
9.95 (+1.4142)	10.0 (0)	9.70	9.81
5.00 (0)	0.1 (-1.4142)	10.80	10.75
5.00 (0)	19.9 (+1.4142)	9.21	9.26
5.00 (0)	10.0 (0)	9.94	9.95
5.00 (0)	10.0 (0)	9.95	9.95
5.00 (0)	10.0 (0)	9.95	9.95

3. Results and discussion

3.1. Chromatographic separation

Difficulties have been reported concerning the chromatographic analysis of pyrrithione complexes due to problematic unwanted interactions with the silica stationary phase [15]. In a recent work a method was developed and optimized for the direct analysis of ZnPT using LC–APCI–MS by Yamaguchi et al. [14]. In the present study an attempt was made to extend the analytical utility of LC method towards the determination of phototransformation intermediates.

The separation of the analytes in the Unison UK-Phenyl column was optimized by investigating mobile phases of varying composition. Experiments with binary mixtures of various solvents showed that methanol and ammonium acetate 20 mM (in water) produced the best results in terms of both resolution and time of analysis. Ammonium acetate at a concentration of 20 mM in the mobile water phase has been shown to stabilize ZnPT in the LC instrument [14]. Analysis was first conducted under isocratic elution consisted of methanol (A) and water containing 20 mM ammonium acetate (B) (1:1), at a flow rate of 0.5 mL/min. Under these conditions it was not feasible to achieve satisfactory separation of the overlapping peaks. The possibility of obtaining satisfactory resolution in reasonably small time was then exploited using a gradient elution solvent. Different experimental trials were then conducted to investigate the optimum composition and elution program. The composition of the organic solvent in the mobile phase was varied between 20 and 80%. Increasing the content of methanol in the mobile phase abridged the elution time of all species and no satisfactory separation between analytes was achieved. On the other hand, reduction in the organic content of the mobile phase resulted in a gradual separation, although it caused flat peaks and increased the time of analysis (above 20 min). A good separation of the chemicals was achieved when elution was performed starting with 40% (A) held constant up to 3.5 min and then went up linearly to 60% (A) in 20 min before return to initial conditions. As six [(PSA, PO, PS, (POS)₂, ZnPT, (PS)₂] out of seven target species were determined, the exception being the POS, alternative elution programs were tested but it was not feasible to achieve its detection. To ensure the quality of the resolution and maintain a reasonable elution time the above program was finally decided as the optimum.

Since direct analysis of irradiated solutions to LC instrument could not provide any significant information about the formation of degradation products (determination of low concentrations required a preconcentration step) a SPE method using PS-DVB disks was followed according to our previous experience on the isolation of photodegradation intermediates of other micro-pollutants [18]. Although an assessment and validation of the analytical characteristics provided by the SPE method has not been performed (it will be the subject of a future task) the method proved to be sufficient for the preconcentration and isolation of the major degradation products formed during the photolytic process (see Section 3.3).

3.2. Photodegradation kinetics of ZnPT

Dark control experiments showed no loss of ZnPT, as ZnPT does not react with nitrate nor with DOM, and there is no biodegradation. ZnPT photodegradation rates in aqueous media of different composition followed pseudo-first order kinetics allowing for the calculation of the rate constants and the half-lives ($t_{1/2}$), respectively (Table 1). Photolysis in distilled water ($t_{1/2} = 15.0$ min) generally proceeded slower than photolysis in other artificial aqueous solutions ($t_{1/2}$ ranged between 9.2 and 13.8 min). Due to the high direct photolysis rate in distilled water the differences of degradation rates between various matrices were small. What became apparent with our findings is that complex relationships existed between photolysis rates and the varied concentrations of the water components (namely DOM and nitrate).

Table 1 shows the experimental results for the response factor (Y) corresponding to ZnPT $t_{1/2}$ (min), varying the DOM (x_1) and nitrate (x_2) concentration in a defined range of environmental realistic concentrations. The third column in Table 1 presents the observed values obtained for the response factor (Y_{obs}) and the fourth column presents the calculated values by way of the modeling procedure (Y_{calc}).

Solving the matrix of data presented in Table 1, a second grade polynomial was obtained (Eq. (1)) that describes the photolytic degradation of ZnPT under given conditions. The coefficients in the polynomial represent the weight of each variable (x_1 , x_2) corresponding to DOM and nitrate concentration, respectively, as well the interaction between them.

$$Y = 9.947 - 1.368x_1 - 0.527x_2 + 0.901x_1^2 + 0.029x_2^2 + 0.102x_1x_2 \quad (1)$$

Taking into consideration only the first-order effect in Eq. (1), the experimental parameters for the highest photolytic degradation of ZnPT seemed to be when DOM (x_1) and nitrate concentration (x_2) have a high value, since the lowest numerical value of the half-life $t_{1/2}$ (Y) corresponds to such conditions. DOM concentration seems to sensitize to a greater extent the photolytic degradation of ZnPT compared to nitrates, displaying a higher coefficient (2.6-times greater).

The accelerated degradation of the model compound in such conditions could be attributed to oxidation reactions triggered by the reactive species such as singlet oxygen and hydroxyl radicals generated through photo-processes involving excited states of DOM [19,20].

Although the first-order effect shows that increase in both variables x_1 and x_2 favors the photolytic degradation rate, an antagonistic effect was observed between the two parameters. The simultaneous increase of x_1 and x_2 is adverse for the degradation reaction rate ($t_{1/2}$ increased) as shown by the second-order effect of the last term in the polynomial expression. Moreover a very low quadratic effect is associated with the nitrate concentration and a more important quadratic effect can be ascribed to the DOM variable. The values obtained by the model (Y_{calc} , Table 1, last column) are compared with those of experimental data (Y_{obs} , Table 1, 3rd column). These values were in good agreement indi-

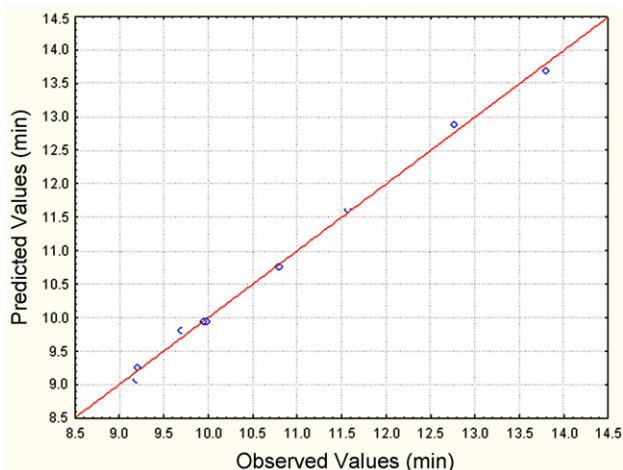


Fig. 2. Predicted half-lives of ZnPT photolysis, were in good agreement with the observed $t_{1/2}$.

cating a correspondence between the mathematical model and experiment (Fig. 2).

Fig. 3 depicts a three dimensional (3D) representation of the polynomial obtained from the matrix. The coordinates of the graph show the DOM and nitrate concentration, respectively. The vertical axis represents the photolytic half-life $t_{1/2}$ (min) of ZnPT.

When the reaction was performed at small to moderate DOM concentration (up to 5 mg L^{-1}), the photolytic reaction was accelerated, irrespectively from the initial nitrate concentration and low half-lives were observed.

However, this positive effect tends to level off for higher DOM concentrations suggesting that light attenuation is important at these conditions. However, the relationship between DOM and $t_{1/2}$ is still positively correlated (although the degree of

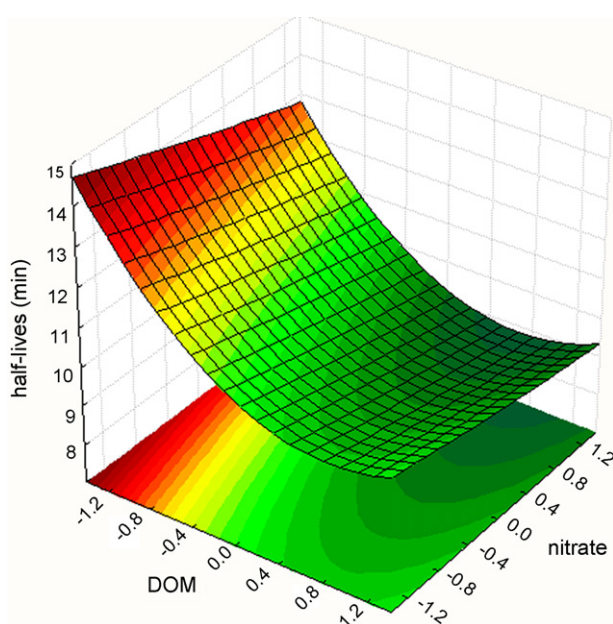


Fig. 3. Response surface showing the effect of DOM and nitrate concentration on the degradation rate expressed as ZnPT photolytic half-lives (min).

correlation and linearity was decreased) showing that photosensitized reactions by the presence of humic matter can still play an important role in the photodegradation of organic pollutants.

While the half-lives decreased with increasing DOM concentrations, how nitrates influenced $t_{1/2}$ appeared to depend on the concentration of DOM in the aqueous matrices. When DOM was present at low concentrations, increases in nitrate concentrations resulted in shorter half-lives, suggesting that $\bullet\text{OH}$ radicals produced from nitrate photolysis [21] aided in ZnPT degradation, although not to a large degree. However, in solutions containing moderate to high amounts of DOM, an increase in nitrate concentrations did not cause half-lives to fluctuate significantly. We assume that under irradiation, nitrate did generate hydroxyl radicals, but they were efficiently scavenged by DOM in artificial or natural water solutions and therefore did not contribute to ZnPT transformation [22].

As predicted by the polynomial, the concentrations of DOM/nitrate for which the highest photolytic degradation rate was observed ($t_{1/2} = 8.84 \text{ min}$) are moderate amounts of DOM (7.4 mg/L) and high nitrate concentration (19.9 mg/L).

Our observations were confirmed by the results of ZnPT photodegradation in natural waters. While the half-life with ZnPT alone (distilled water) was 15.0 min , the presence of DOM (2.1 mg/L) and nitrate (3.3 mg/L) in the natural seawater matrix, decreased the half-life ($t_{1/2} = 12.1 \text{ min}$) which suggests a sensitization effect on the degradation rate at low DOM and nitrate concentration levels. This acceleration effect was more pronounced ($t_{1/2} = 9.3 \text{ min}$) at higher concentrations of these natural occurring components in the water surface (lake water, DOM = 11.0 mg/L and nitrate = 10.3 mg/L) showing the importance of these constituents when considering indirect photodegradation processes and the fate of organic micro-pollutants.

An attempt was also made to assess the contribution of $\bullet\text{CO}_3^-$ in the natural cleansing of ZnPT in natural waters [23]. $\bullet\text{CO}_3^-$ radical was produced from the reaction of hydroxyl radical with bicarbonate ions at realistic environmental concentrations. Photolysis in the solution containing nitrate (20 mg/L)/bicarbonate (250 mg/L) was similar ($t_{1/2} = 15.1 \text{ min}$) to direct photolysis in distilled water ($t_{1/2} = 15.0 \text{ min}$) showing that the role of indirect photolysis via $\bullet\text{CO}_3^-$ would be small.

3.3. Transformation products

In a previous work during a photospectrometric study of zinc and copper pyriothione degradation Yamaguchi et al. [24] have shown that ZnPT was decomposed by visible light irradiation to form 2-pyridinesulfonic acid (PSA) which according to Turley et al. [6] is the main terminal photolysis product. In this study our focus was to extend for the first time the analytical utility of SPE and LC-MS techniques for the isolation and identification of ZnPT photolytic transformation products. An attempt was also made to provide any information regarding the influence of irradiated media on the extent of the production of the byproducts.

Up to six phototransformation products (Fig. 4) [PSA, PO, PS, (PS)₂, (POS)₂ and PPMD] were identified and found to occur in significant amounts during the course of the degradation study.

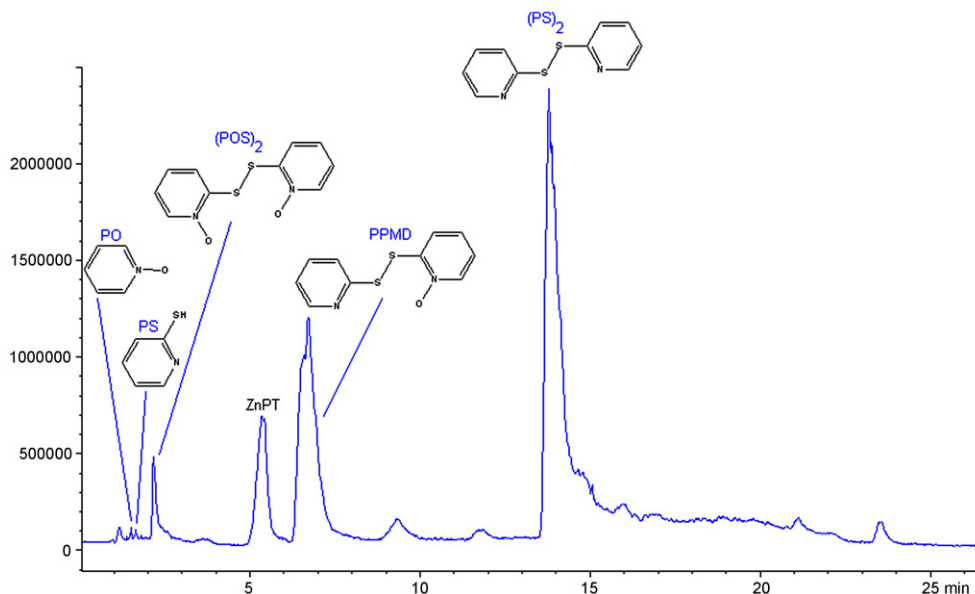


Fig. 4. LC-APCI-MS chromatogram obtained from a SPE extract of ZnPT solution (distilled water) after 10 min of irradiation under simulated solar light.

PSA, PO, PS, (PS)₂, and (POS)₂ were verified by matching retention times and LC-MS mass spectral data (Fig. 5) against those of purchased reference standards.

PSA was only detected ($t_R = 1.1$ min) after direct analysis of aqueous solutions in the LC-MS instrument. It has not been detected in neither aqueous sample that was extracted by SPE since its retention on the PS-DVB matrix was inefficient due to its polar nature. Aquatic toxicity studies with PSA [6] showed no observable effect at concentrations at least three orders of magnitude higher than those for ZnPT. As a result, the worst-case environmental concentration of PSA is expected to be far below the no observable effect concentration.

(PS)₂ ($t_R = 14.4$ min) was found to be the major degradation product after 10 min of irradiation in distilled water. Its presence was also confirmed after analysis of natural seawater sample at the same irradiation time, indicating that it is expected to be one of the major photoproducts in natural waters as well.

The first eluted product after SPE preconcentration procedure was found to be PO ($t_R = 1.3$ min) followed by PS ($t_R = 1.6$ min). Both transformation products seem to be formed to much lower quantities compared to (PS)₂; however, their presence was confirmed both under direct (distilled water) and indirect (artificial and natural waters) photochemical reactions. The formation of these intermediates has been reported previously [5] using spectrophotometric techniques. According to Neihof et al. [5], PS and (PS)₂ could be easily photodegraded; however, this was not the case for PO, that did not appear to be susceptible to photolysis under the same conditions. On the other hand, PS and (PS)₂ seemed to lose their toxicity after photolytic degradation, although PS was found to reduce its toxicity relatively slowly [5].

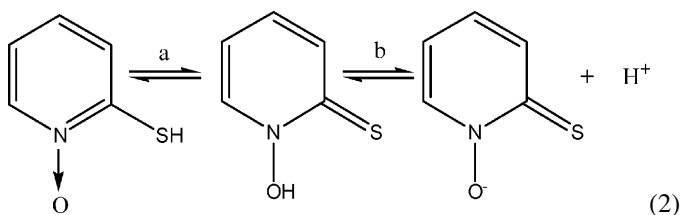
Besides the most abundant product ((PS)₂) an additional high peak of intermediate polarity was observed. This compound was eluted after 6.6 min and gave a molecular ion peak at $m/z = 237.2$ (corresponding to molecular weight of 236).

Another fragment ion at $m/z = 221$ was due to the loss of oxygen atom. The formation of $[M + H - O]^+$ ion is characteristic from *N*-oxides in APCI mass spectra. This intermediate was assigned to the pyridine/pyrithione mixed disulfide 2,2'-dithiobispyridine mono-*N*-oxide (PPMD).

Finally another compound eluted at $t_R = 2.5$ min, was identified as (POS)₂ after confirmation of retention time and mass spectra of authentic standard. Evans et al. [25] presented evidence that (POS)₂ was an early photolysis product of POS, while it exhibited much higher toxicity (against the marine bacterium, *Pseudomonas marina*) compared to POS [5].

These observations clearly demonstrate the concerns of considerable environmental toxicity of photolytic transformation products of ZnPT.

Analyses of irradiated samples of ZnPT in aqueous media of different composition reveal that the main photoproducts are PSA and the various disulfides (PS)₂, PPMD and (POS)₂. PS and PO were also formed, however to much lower quantities. The key transformation product during ZnPT photodegradation seems to be the formation of POS (not determined in the present study). This compound is potentially tautomeric (Eq. (2)) and the thione/thiol equilibrium (a) is solvent-dependent: the thione structure predominates in aqueous media, while less polar thiol tautomer is more likely to exist in non-polar and aprotic solvents.



In addition it also exhibits an acid/base equilibrium (b) and both neutral and ionic forms involved undergo different reactions upon irradiation [26]. A common factor is that irradiation of POS

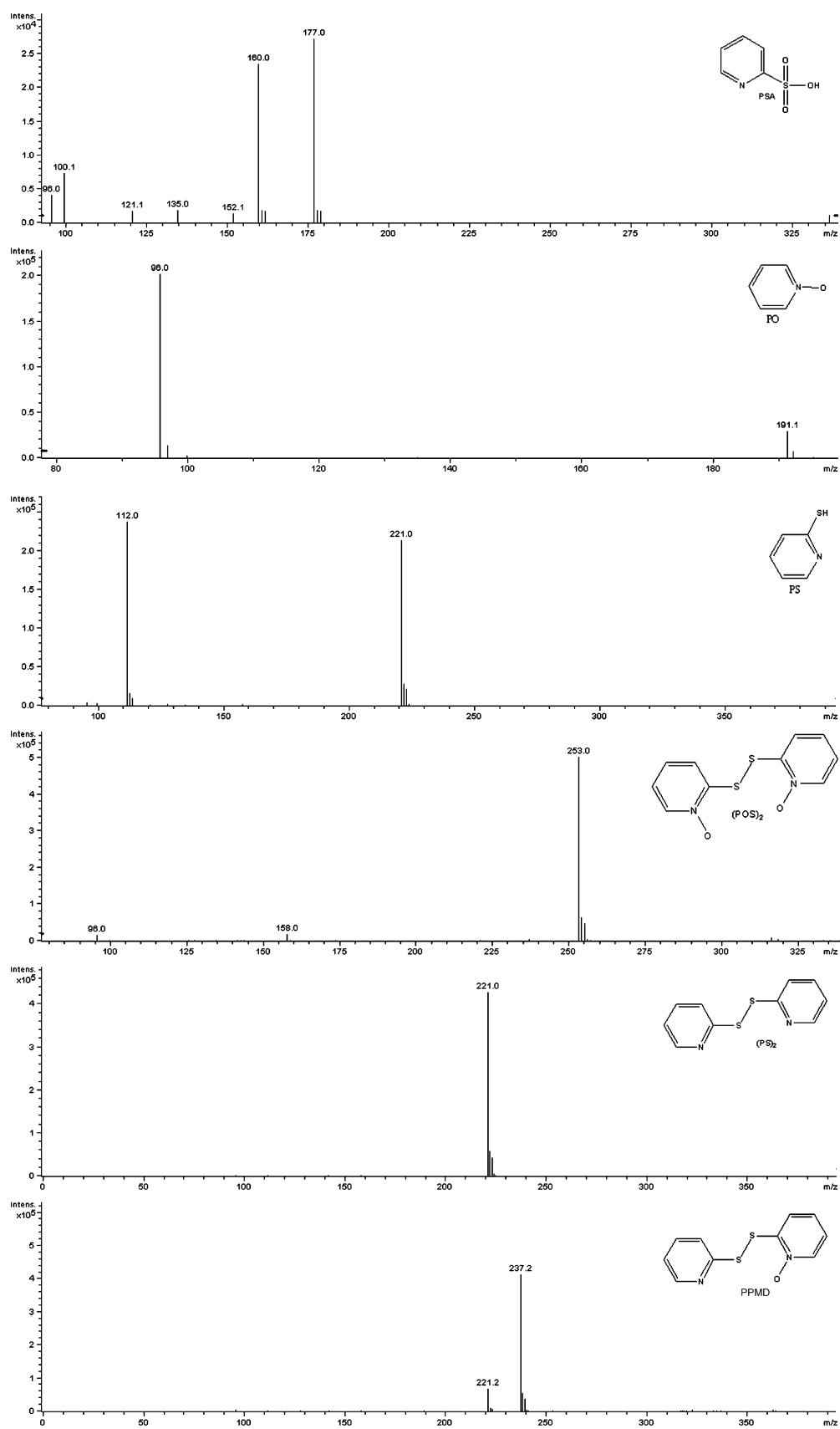


Fig. 5. APCI-MS spectrum of intermediates formed during the photolysis of ZnPT.

in aqueous solution causes homolytic scission of the N–O bond. Besides disulfide (PS)₂, and sulfonic acid (PSA) the mono-*N*-oxide (PPMD) and *N,N'*-dioxide (POS)₂ were found to be the major products of POS irradiation formed by the addition of thiyl radicals PyS• and PyNOS• to the carbon–sulfur double bond of the parent molecule or from radical–radical recombination [26]. Upon exhaustive photolysis (PS)₂ could be converted to PS which with subsequent oxidation of S results in the formation of pyridine sulfinic acid (not detected in this study) and pyridine-2-sulfonic-acid (PSA), respectively, as final product.

The photodegradation of ZnPT in aqueous media and the analysis of data revealed that the photo-processes undergone by this compound on solar irradiation are complex and occur by both parallel and sequential reactions. The primary steps of the transformation processes in regard to ZnPT degradation were the homolytic N–O bond cleavage with subsequent oxidation of S.

The same product profile for direct and indirect photochemical degradation of ZnPT was observed showing that the matrix in which photolysis occurs does not influence the mechanism of the byproducts formed.

One of the main objectives of this research, the identification of transformation products through powerful analytical techniques have been met within the confines of the present study. In a future study the optimization and validation of the proposed analytical methodology for the transformation products will be carried out, considering the large quantities of ZnPT used and the two routes of release in the aquatic environment. Such data have received little attention so far due the lack of sufficient analytical method for ZnPT determination.

4. Conclusions

This study was undertaken primarily to determine the photochemical behavior of ZnPT under simulated solar irradiation. For this purpose the pollutant was irradiated in a variety of aqueous solutions of different composition, as well as natural waters. Overall, photochemical degradation via direct photolysis is expected to be an important degradation pathway. The presence of DOM accelerates the rate of the photolysis while sensitization by NO₃[−] was dependent on the concentration of DOM. On the other hand carbonate radicals did not appear to influence the lifetime of ZnPT. The formation of various transformation products was followed via first-order reactions and six photoproducts could be identified using liquid chromatography-atmospheric pressure chemical ionisation mass spectrometry. Although it is clear that rapid photodegradation of this chemical compound will occur, further environmental monitoring studies should focus on the analysis of transformation products as the parent half-lives will be short.

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References

- [1] K.V. Thomas, J. Chromatogr. A 825 (1998) 29.
- [2] I.K. Konstantinou, T.A. Albanis, Environ. Int. 30 (2004) 235.
- [3] N. Kobayashi, H. Okamura, Mar. Pollut. Bull. 44 (2002) 748.
- [4] V.A. Sakkas, I.K. Konstantinou, T.A. Albanis, in: I.K. Konstantinou (Ed.), Handbook of Environmental Chemistry, Antifouling Paint Biocides, Springer Berlin, Heidelberg, 2006, p. 171.
- [5] R.A. Neihof, C.A. Bailey, C. Patouillet, P.J. Hannan, Arch. Environ. Contam. Toxicol. 8 (1979) 355.
- [6] P. Turley, R.J. Fenn, J.C. Ritter, M.E. Callow, Biofouling 21 (2005) 31.
- [7] K. Maraldo, I. Dahllof, Mar. Pollut. Bull. 48 (2004) 894.
- [8] M.W. Lam, K. Tantuco, S. Mabury, Environ. Sci. Technol. 37 (2003) 899.
- [9] S. Walse, S.L. Morgan, L.L. Kong, J. Ferry, Environ. Sci. Technol. 38 (2004) 3908.
- [10] D. Vialaton, C. Richard, D. Baglio, A. Paya-Perez, J. Photochem. Photobiol. A 119 (1998) 39.
- [11] J. Bachman, H. Patterson, Environ. Sci. Technol. 33 (1999) 874.
- [12] K. Thomas, Biofouling 17 (2001) 73.
- [13] R.M. Galvin, J.M.R. Mellado, R.A. Neihof, Eur. Water Manage. 4 (1998) 61.
- [14] Y. Yamaguchi, A. Kumakura, S. Sugawara, H. Harino, Y. Yamada, K. Shibata, T. Senda, Int. J. Environ. Anal. Chem. 86 (2006) 83.
- [15] J. Bones, K.V. Thomas, B. Paull, J. Chromatogr. A 1132 (2006) 157.
- [16] C.A. Doose, M. Szalaniec, P. Behrend, A. Müller, B. Jastorff, J. Chromatogr. A 1052 (2004) 103.
- [17] J. Fernandez, J. Kiwi, C. Lizama, J. Freer, J. Baeza, H.D. Mansilla, J. Photochem. Photobiol. A: Chem. 151 (2002) 213.
- [18] V.A. Sakkas, I.K. Konstantinou, T.A. Albanis, J. Chromatogr. A 959 (2002) 171.
- [19] R.G. Zepp, G.L. Wolfe, G.L. Baughman, R.C. Hollis, Nature 267 (1977) 421.
- [20] S. Canonica, U. Jans, K. Stemmler, J. Hoigne, Environ. Sci. Technol. 29 (1995) 1822.
- [21] S. Mabury, D. Crosby, Aquatic and Surface Photochemistry, CRC Press, Boca Raton, FL, 1994, p. 149.
- [22] P.L. Brezonik, J. Fulkeron-Brekken, Environ. Sci. Technol. 32 (1998) 3004.
- [23] J. Huang, S.A. Mabury, Chemosphere 41 (2000) 1775.
- [24] Y. Yamaguchi, A. Kumakura, M. Ishigami, K. Shibata, T. Senda, Y. Yamada, in: K. Shibata, T. Senda (Eds.), Proceedings of International Symposium on Antifouling Paint and Marine Environment (InSAFE), Tokyo, 27–30 January 2004, National Maritime Research Institute, Tokyo, 2004, p. 228.
- [25] D.G. Evans, J.K. Sugden, N.J. Van Abbe, Pharm. Acta Helv. 50 (1975) 94.
- [26] B.M. Aveline, I.E. Kochevar, R.W. Redmond, J. Am. Chem. Soc. 118 (1996) 10113.