The photochemical mineralization of pentachlorophenol in a tropical marine environment

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Abstract

The kinetics of the photochemical mineralization of pentachlorophenol (PCP) in aqueous medium by UV irradiation (254 nm) was studied under laboratory conditions and in an open tropical marine environment. The FTIR analysis and other parameters monitored during the photolysis of PCPNa in soil and water samples indicate a pseudo-first-order kinetics for chloride ion formation; and the presence of octachlorodibenzodioxin (OCDD) as a product of the photochemical reaction. These also suggest a mechanism involving the cleavage of a C–Cl bond adjacent to the C–O bond of an excited pentachlorophenoxide ion via UV irradiation, which simultaneously undergoes electron transfer and photonucleophilic substitution reactions with another similarly excited pentachlorophenoxide ion. The rate of mineralization was found to be strongly dependent on: (i) the initial PCPNa concentration in the sample; (ii) the sample type; (iii) pH of the sample; and (iv) the period of exposure to bright sunlight. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Pentachlorophenol (PCP) finds its use in the tropics primarily as a preservative for timber and lumber. Among the top priority environmental pollutants are chlorinated phenols that find use among other things, as preservatives for wood and in the manufacture of paper [1]. The fate of PCP in tropical soils is not as well understood as that for soils from temperate regions. Tropical soils are typically very old soils characterized by year-round uniformity of a temperature regime and defy easy generalizations. Field investigations of tropical pesticide fate indicate that pesticide dissipation is related to the effect of tropical climates, and that pesticide degradation rates and pathways differ from those encountered in the temperate zones [2]. There is ample evidence that the photochemical degradation of PCP in a temperate environment yields different products under different conditions: for example, carbon dioxide and HCl in the presence of polyoxometalates; tetrachlorophenol (TCP) and octachlorodibenzodioxin (OCDD) in the presence of organic solvents; and pentachloroanisole (PCP-OCH$_3$) in the presence of soil bacteria [3–8].

There has been little impetus for studying the effects of environmental variables on the transport, degradability, and distribution of PCP in the tropics, as evidenced by our search for literature on the subject. An understanding of the dynamics of PCP in tropical soil, particularly in relation to adsorption to soil organic matter, eventually, will enable us to predict the possible mode of transport of PCP and other pesticides into groundwater supplies — a topic of considerable current concern. Moreover, the qualitative and quantitative understanding of the factors which regulate the degradation and transport of PCP and other pesticides in soils and their transfer through aquatic systems is an important prerequisite for providing advice on the safe use of these potentially lethal and persistent compounds in the environment. The overall objectives of this work were to determine the rate and the mode of the photochemical degradation of PCP by tropical sunlight in a typical tropical marine environment, and possibly propose a mechanism for its photochemical mineralization.

2. Experimental details

2.1. Materials

PCPNa was obtained from SADOFOSS s.a., whilst all other chemicals were obtained from BDH Chemicals (UK). The chemicals were purified and dried following standard

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procedures. Soil and water samples were obtained from selected sites in the Western Region of Ghana.

Photolysis was performed using mineralight (Model UVGL-58, Upland, CA, USA) at 254 nm.

2.2. Measurements

A typical photolysis experiment under laboratory conditions was as follows: to a 250 ml flask equipped with a stirrer, 40 ml of 5.2×10^{-2} M PCPNa solution was introduced. Photolysis was carried out with the reaction vessel at a distance of 1.0 m from the UV source, and with constant stirring at 23°C. In the course of the photochemical reaction, 0.5 ml aliquots were drawn from the reaction vessel at 30-min intervals and the chloride ion content analyzed using an automated digital chloride meter (Sherwood Chloride Analyzer Model 926, Cambridge, UK). GC–FID analyses of PCP were carried out on the aliquots using a VARIAN 3700 gas chromatograph interfaced with an IBM computer, whilst the absorption spectra of the degradation products of the photochemical reaction were measured on a SHIMADZU FTIR-8201A spectrophotometer coupled to a SHIMADZU DR-8021 computer.

2.3. Photolysis of PCP in environmental samples

Photolysis experiments were performed on the water and soil samples obtained from the Western Region of Ghana. For the analysis of water samples, 10 ml of the 5.2×10^{-2} M PCPNa solution were added to 30 ml of the water and the pH of the mixture was noted prior to photolysis. With the soil samples, 50 ml of doubly distilled water were added to 20 g of the sample followed by 10 ml of the 5.2×10^{-2} M PCPNa solution. The mixture was subjected to photolysis as described, once the pH was taken. Photochemical reactions were also carried out on the soil and water samples with same substrate concentration in tropical sunlight at the University of Cape Coast (a marine environment). The chloride ion content and other products of the reaction were analyzed as before. Ambient temperature ranged from 36.5 to 46°C.

3. Results and discussion

3.1. Chloride ion formation

Fig. 1 shows the changes in chloride ion content resulting from the photochemical mineralization of PCPNa under laboratory conditions and in the open tropical marine environment. A rapid increase in chloride ion concentration was observed in both cases. Also, a plot of initial degradation rate versus the initial concentration of substrate in each case follows a Langmuir–Hinshewood or Michaelis–Menden kinetics (Fig. 2). Under laboratory conditions, the photolysis of PCPNa afforded an average initial degradation rate of
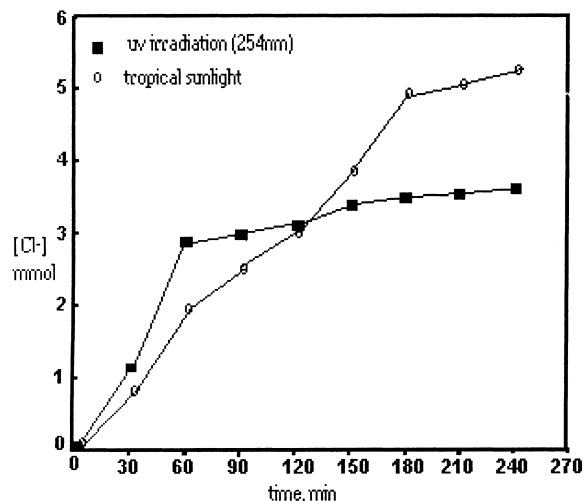

Fig. 1. Formation of chloride ion upon photolysis by UV irradiation (254 nm) and tropical sunlight.

6.26×10^{-7} mol l^{-1} s^{-1} for an initial PCPNa concentration of 5.2×10^{-2} M, whilst the mineralization of the same substrate concentration by tropical sunlight yielded an average chloride concentration at the rate of 4.07×10^{-7} mol l^{-1} s^{-1}. The photolysis of PCPNa by tropical sunlight, though a slow starter compared to direct irradiation by UV light, afforded more chloride ions after 4 h of direct exposure. The rate of formation of chloride ion in the open environment, which was found to depend on the initial PCPNa concentration, also depended on the intensity of sunlight and the period of exposure to sunlight. Consequently, the peak rates were observed during the brightest hours of the day, whilst reductions in the rate of chloride ion formation were recorded
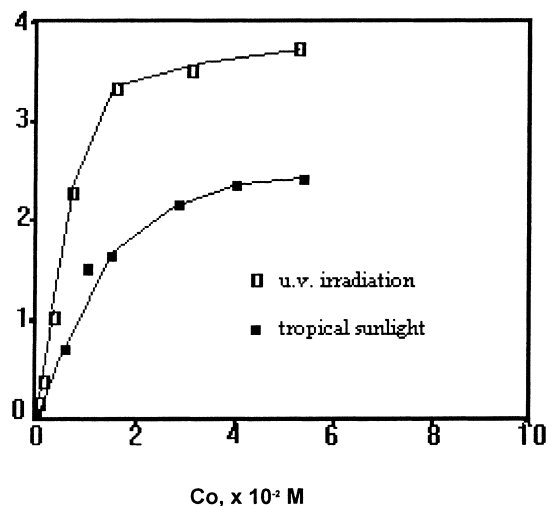

Fig. 2. Variation of the rate of degradation of aqueous PCPNa with initial concentration of substrate upon photolysis by UV irradiation and tropical sunlight.

Table 1
A typical result obtained for the formation of chloride ion from the photochemical mineralization of PCPNa in aqueous medium by tropical sunlight [PCPNa]=5.2×10^{-2} M

Time (min)	0	30	60	90	120	150	180	210	240	270
Cl^- (mg l^{-1})	0	26	66	85	107	133	171	175	185	190

Table 2
pH Dependence of the initial rate of photochemical mineralization of PCPNa in coexisting soil and water samples by tropical sunlight [PCPNa]=5.2×10^{-2} M (t=1800 s)

(a) *Water samples*						
pH	6.2	6.7	7.1	7.3	7.5	7.7
Rate ($\times 10^{-8}$ mol l^{-1} s^{-1})	2.68	5.92	9.01	11.30	17.20	21.10
(b) *Soil samples*						
pH	2.2	4.1	4.3	6.0	8.0	8.5
Rate ($\times 10^{-8}$ mol l^{-1} s^{-1})[a]	−31.50	−17.0	−9.86	−3.10	5.63	9.30

[a] Negative rates signify a decrease in chloride ion concentration.

for dull weather or overnight exposures where there was not much activity (Tables 1 and 2).

3.2. pH Dependence

The pH dependence of the initial rates of the photochemical mineralization of PCPNa in the soil and water samples investigated are shown in Fig. 3. Most of the natural water samples had pH values between 6.2 and 7.7. Although coexisting soil and water samples were analyzed, striking differences in their natural pH values were observed. This resulted in an obvious variation in the rates of mineralization, with the soil samples giving slower rates to negative rates; corresponding to acidic and very acidic soils, respectively. We attributed this trend in the rates of mineralization of PCPNa in the soils to the formation of more of the undissociated pentachlorophenol resulting from the combination of the chloride ions originally present in the reaction vessel with the pentachlorophenoxide ions, and to the adsorption of PCP to acidic soils, consequently, accounting for its persistence in such soils. This observation is in agreement with Crosby and Wong, about the behaviour of PCP in natural systems [9]. Various hypotheses have been suggested to account for the causes of the persistence of organochlorine compounds like PCP in the environment [10–15]. The results of our investigations suggest that chloride ion formation by the photochemical mineralization of PCPNa in tropical soils and natural waters depends strongly on the pH of the sample: reflecting the trend that natural waters with near-neutral pH enhance the mineralization of PCP; whilst very acidic soils discourage the photochemical mineralization of PCPNa; and at the same time enhance the adsorption of PCP to the soils, thereby increasing its persistence in a tropical environment.

3.3. Mechanistic deductions

The ionisation of PCPNa in aqueous medium was found to be a crucial step to its photolability by both UV irradiation (254 nm) and tropical sunlight. It was also observed that the rate of chloride ion formation, which approximated the
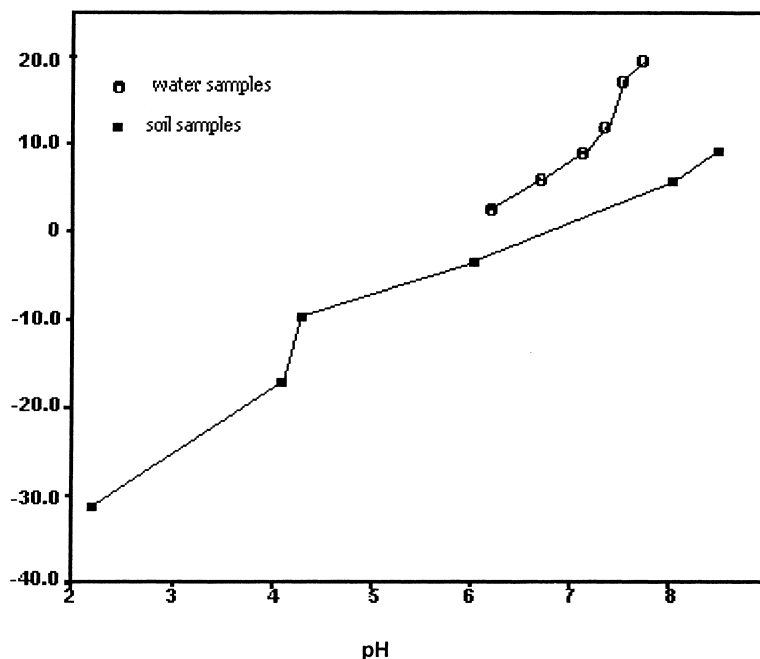

Fig. 3. Dependence of the initial rate of the photochemical mineralization of PCPNa on the pH of the samples.

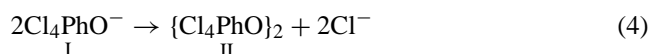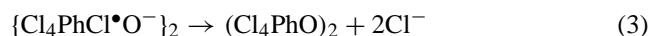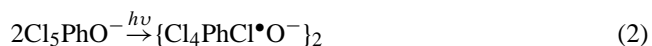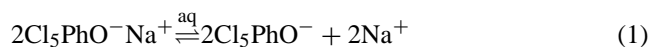degradation rate of PCPNa increased only when photolysis was carried out on PCPNa in its ionized form.

Spectral analyses and identification of the degradation products at the early stages of the photochemical reaction point to the strong presence of the diaryl group of dioxin (which was initially absent), when the change in chloride ion concentration was as little as $3.75 \times 10^{-5} \, \mathrm{mol \, l^{-1}}$.

Moreover, subsequent spectral analyses of the degradation products formed on resumption of photolysis show the retention of the diaryl peak previously observed, as well as a host of other new peaks. Confirmation of the peaks, using standard procedures established the presence of octachlorodibenzo-*p*-dioxin (OCDD) and tetrachlorophenol (TCP). However, no products resulting from C–O bond cleavage were detected.

Practically, for such photochemical reactions involving homogeneous and semi-heterogeneous systems, a plot of initial degradation rate versus the initial concentration of substrate are found to follow a Langmuir–Hinshewood or Michaelis–Menden kinetics [16].

GC–FID analyses of the substrate carried out in that direction show conformity to this hypothesis. The observation and confirmation of OCDD as a photodegradation product at the initial stages of the photochemical reaction coupled with the chloride ion formation suggest a very feasible concerted mechanism in which the aryl radical formed by the UV irradiation of the pentachlorophenoxide ion, cleaves a C–Cl bond adjacent to the C–O bond of the same ion and simultaneously undergoes electron transfer and photonucleophilic substitution reactions with another similarly irradiated pentachlorophenoxide ion, with the concomitant ejection of a chloride ion per pentachlorophenoxide ion.

The general scheme of reactions — the formation of Cl^- ions (Eqs. (1–3)) and the overall reactions (Eq. (4)) — may be presented as shown:

$$2Cl_5PhO^- Na^+ \overset{aq}{\rightleftharpoons} 2Cl_5PhO^- + 2Na^+ \tag{1}$$

$$2Cl_5PhO^- \overset{h\upsilon}{\rightarrow} \{Cl_4PhCl^\bullet O^-\}_2 \tag{2}$$

$$\{Cl_4PhCl^\bullet O^-\}_2 \rightarrow (Cl_4PhO)_2 + 2Cl^- \tag{3}$$

$$\underset{I}{2Cl_4PhO^-} \rightarrow \underset{II}{\{Cl_4PhO\}_2} + 2Cl^- \tag{4}$$

where I and II (in Eq. (4)) represent the pentachlorophenoxide ion and the octachlorodibenzodioxin (OCCD), respectively.

4. Conclusions

The results of this study demonstrate that the photochemical mineralization of PCPNa in aqueous medium by tropical sunlight yields chloride ions at rates comparable to its degradation by direct UV irradiation at 254 nm. The formation of chloride ion is found to be accompanied by the formation of OCDD, TCP and a mixture of other PCP-degradation products. The mechanistic studies conducted suggest a concerted mechanism involving electron transfer and photonucleophilic substitution reactions for the formation of chloride ions from the photodegradation of PCPNa.

Overall, the rates of mineralization of PCPNa suggest that the UV component of sunlight has the necessary energy to decompose PCP. Thus, the photolytic decomposition of PCP by sunlight with the subsequent formation of chloride ions constitutes a very important mode of its degradation in a tropical marine environment.

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