Environmental Aspects of the Photodegradation of Maneb and Propanil in Various Media

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Abstract

Maneb and propanil are two commonly used pesticides that pose many environmental problems. Their rates of photodegradation have been studied by means of spectrophotometric methods using UV-Visible spectrophotometry. The photodegradation kinetics showed that these pesticides were sensitive to light. Second order kinetics was observed in water and therefore pesticides might be very persistent in water. In addition, spectrofluorometry was used to measure their infiltration rates through soil. This was used to assess the level of risks posed by the exposure of pesticides to the environment showing that, Maneb and propanil with respectively infiltration rates of 1.29 cm/h and 26.7 cm/h are potential sources of high risk of contamination for surface and ground waters.

1. Introduction

Pesticides are useful in reducing postharvest losses by farmers. Without the use of pesticides, losses could range from 45 % to 80 % of the cereals, fruits and vegetables (Harvey, 1978; Jolas, 2004; Kacem, 1999; Muhizi, 2008; Nellemann et al., 2009). Considering the world population growth and the current food needs in the world, it is necessary to use pesticides in order to reduce such losses and to meet world nutritional demand. However, it is also necessary to consider the negative impacts that pesticides have on the environment and on human health (European Communities, 2006). Many pesticides are not photochemically stable, and can degrade under sunny conditions (European Communities, 2006). As a result of this, we investigated the effects of UV-visible radiations on two pesticides, maneb and propanil. We also determined their infiltration rate through soils.

Maneb is an ethylene-bis-dithiocarbamate (EBDC), a fungicide used to reduce harvest losses, protect against the deterioration of crops during storage or transport (T and Informa UK Ltd., 2005). Examples of crops used with maneb are potatoes and tomatoes. It is also used on many other vegetables and on commercial products (Rexilius, 2006). Among all fungicides, maneb is by far the most commonly used and is fairly toxic to humans (Lorenz, 2009; Nordby et al., 2005; Occupational Health Services, 1986, 1991). It has been shown that all pesticides belonging to the EBDC family are metabolized in ethylenethiourea (ETU), and are classified as human carcinogens (Holland et al., 1994). Propanil is an herbicide used particularly against latifolia herbs in various cultures like: rice, potatoes and wheat (Krasnova et al., 2000; Sürek, 2001; T and Informa UK Ltd, 2005). This herbicide is toxic when ingested, inhaled or absorbed cutaneously (Kumiai Chemical Industry CO. LTD, 2001). It is also known that patients with heart problems are particularly vulnerable to the toxic effects of propanil-based herbicides (Lorenz, 2009). Health related problems associated with propanil include irritation with drying of the skin (EPA, 2006), irritation of the eyes, conjunctivitis and photophobia (EPA, 2006; Taha &

Gray, 1993). Another toxic property of propanil is that when being decomposed, it releases toxic oxides of nitrogen and carbon or many other products (Epperlein et al., 2006).

2. Experimental

2.1 Reagents

The two pesticides, maneb 69 %w/w and propanil 99 %w/w (Figure 1) were purchased at Cluzeau Info Laboratoire. The following organic solvents were also used: ethanol (Prolabo), methanol (Sigma Aldrich), propanol (Merck), hexane and cyclohexane (Janssen Chimica), chloroform, dichloromethane (Fisher Scientific) and acetonitrile (Prolabo). All the solvents were of spectroscopic grade.

2.2 Apparatus

The UV-visible spectra of the pesticides were recorded using a Helios type spectrophotometer (Gamma Thermospectronic) connected to a PC computer. 1 cm x 1 cm quartz curvette cells with two polished sides, having a path length of 1cm and a volume of 3.5 mL was also used. Photodegradation kinetics was monitored by the absorption spectra. Fluorimetric measurements of the pesticides were carried out at ambient air temperature with a Kontron model SFM-25 spectrophotofluorimeter, connected to a PC computer and driven by Lcwin software. For the samplings; 2 μL, 20 μL and 200 μL Gilson Pipetman micropipettes were used.

Fluorescence measurements were made by using five polished faced quartz cells (trademark Hellma) having 1 cm of optical path. The irradiation of the samples was made by means of a photochemical reactor with an irradiation source Oriel (6137 Model), a 200W OSRAM mercury lamp and a switching box (Oriel, 8500 Model). Irradiated samples were placed on luminous beam trajectory at the distance of 50 cm from the lamp.

Weighing was carried out using a precision balance of accuracy 0.1 mg from Sartorius AG Gottingen (Type BA 110S-OF1). To dissolve the substances, an ultrasound apparatus, the BRANSON 3210 was used.

2.3 Methodology

10^{-3} M stock solutions were prepared in chloroform and in methanol. The substances used were not soluble in water. Freshly prepared solutions were protected against sunlight by covering with aluminium foil and preserved by storing in a refrigerator. All other solutions of different concentrations were prepared by diluting the initial stock solution.

3. Results and Discussion

3.1 Determination of the photodegradation kinetics of the pesticides by UV-vis spectrophotometry

The effects of UV-visible radiations on the pesticides was studied using an OSRAM lamp. The substances were irradiated in different solvents for a particular time interval. Thus, it was possible to monitor the photodegradation kinetics from the peaks of absorption spectra.

3.1.1 Analysis of UV-visible absorption spectra of the pesticides

In this part, it is showed the effects of the irradiation on the UV-visible absorption spectra, of the pesticides in the different solvents. In order to study the effect of light on the two studied compounds, we followed the variation of peak absorbance at the highest wavelength of absorption spectrum as a function of irradiation time.

❖ Example of maneb in water

We recorded the absorption spectrum of a 5×10^{-5} M solution of maneb in water. We note that there is a broadband absorption with a peak at 275 nm and a shoulder at around 230 nm (Figure 2).

The kinetics was monitored for about 3 h. As it is shown in the Figure 2, this molecule is perceptibly photodegradable in water.

❖ Example of propanil in water

UV-visible absorption spectrum of a 2.5×10^{-5} M solution of propanil in water showed a broad and intense absorption band between 200 and 400 nm. This band is characterized by two peaks: one very intense at 208 nm, and the other at 249 nm. Right after each irradiation, we observed a decrease in absorbance at the level of these two peaks. We also noticed the appearance of an absorption band due to an unknown photoproduct between 265 and 400 nm whose optical density increased relatively with irradiation time. The different isosbestic points show the following possibilities: the disappearance of Propanil and the formation of a photoproduct (Figure 3).

It is important to notice that the maximum molar extinction coefficients (ε) of the electronic absorption spectra of the various solutions of non-irradiated maneb are higher than 1000 in the different solvents. The corresponding electronic transitions are therefore of type π-π∗.

3.1.2 Results of the photodegradation kinetics of the pesticides

The following graphs are examples of curves of photodegradation kinetics of the pesticides. These curves are the result of the observation of the absorbance (A) of the characteristic peak of each product in relation to irradiation time in the solvent used.

a) Photodegradation kinetics of maneb

The UV-visible absorption spectra of maneb gave the appearance of a single well-resolved peak at around 275 nm, in all the solvents used (Figure 2). The photodegradation kinetics was followed by observing the absorbance (A) variation from pick of the highest wave length of absorption spectrum versus the time of irradiation (t).

Plotting $(\frac{1}{A} - \frac{1}{A_0})$ in relation to irradiation time (Figure 4), we obtained linear slope with a coefficient of correlation close to unity ($R^2 = 0.996$). This gives second order kinetics (Sarr et al., 2003). This kinetics is characterized by a constant rate $k = 51.81$ mol^{-1}·L·min^{-1} and a relatively high half-life ($t_{1/2}$) of 386 mn (6 ½h) for an initial concentration of 5 x 10^{-5} M. The results (Table 1) show that the photodegradation of maneb follows varied kinetics: second order in water and dichloromethane, first order in acetonitrile and chloroform and zero order in methanol. In all the solvents used, the correlation coefficients exceed 0.99, showing a good correlation of the values obtained for the different kinetics carried out.

Table 1, also shows that maneb is photodegradable in all the solvents used: therefore, it is necessary to protect maneb solutions from light, especially in methanol where photodegradation kinetics is zero order.

With second order kinetics, maneb, under sunlight conditions is without doubt very persistent in water. Therefore, it is important to take a look at the risk of contamination in water ways (by streaming). In addition, with a high rate of infiltration, it could contaminate underground waters. Therefore, since maneb is very slightly soluble in water, we might find it more in surface waters than underground waters.

b) Photodegradation kinetics of propanil

The UV-visible absorption spectra of propanil showed a peak at 252 nm in all the solvents used (Figure 5). Also, the photodegradation kinetics was followed by observing the absorbance (A) variation from pick of the highest wave length of absorption spectrum versus the time of irradiation (t).

Using water as solvent, when we plot $(\frac{1}{A} - \frac{1}{A_0})$ against irradiation times we obtained a linear relationship with a correlation coefficient $R^2 = 0.996$, close to unity (Figure 5). The photodegradation of propanil therefore was found to follow second order kinetics, with a rate constant $k = 30.57$ mol^{-1}·L·min^{-1}; and a half-life, $t_{1/2}$ of 1574 min (26 ½h) for an initial concentration of 2.5 x 10^{-5} M.

The results in table 2 show that the photodegradation of propanil followed second order kinetics in all the solvents used. The correlation coefficients largely exceeding 0.99 are evidence of good linearity observed for the different kinetics (Sarr et al., 2003).

This second order kinetics means that, propanil that under sunlight conditions is persistent in the solvents used, especially in water. As a result of this, it is worth studying it so as to evaluate its risk of contamination in waterways (by streaming) or underground waters (by infiltration).

3.2 Infiltration rate of the pesticides in soils

No matter where a pesticide is applied, only a small quantity of it eventually reaches its target (Pimentel & Levitan, 1986). The remaining diffuses into other parts of the environment (Deveci & Ekmekyapar, 2008). Most of it is swept away by streaming towards surface waters or it percolates into underground waters; at the same time some amount of pesticide still remains in the soil particles (Tiryaki & Temur, 2010).

Therefore, it is important to study the rate of infiltration of pesticides, so as to measure the extent to which they contaminate surface or groundwater.

3.2.1 Plan to study of the infiltration rate of the pesticides

The aim of this work was to determine the permeability of soil for a particular area and to determine the rate of infiltration of the pesticides in the soil used. In order to carry out this study, an experimental apparatus composed

of a PVC tube of diameter 12 cm and length 50 cm was filled with soil; a dropping funnel filled with water was clamped over it.

In order to ensure accuracy of the system and minimize errors, the following precautions were taken.

➤ The bottom opening was blocked with a wire netting so as to retain soil and ensure easy flow of water;

➤ The PVC tube was filled with soil, for example, clay soil, sandy soil or sandy clay;

➤ The PVC tube was clamped in an upright position;

➤ The dropping funnel was filled with water. This allowed the flow of water at a constant rate into the tube;

➤ Water that flowed out the PVC tube was recovered every 30 min for a period of 8 h. The volume of water recovered, (V_{water}) was collected in beakers;

➤ A plot of V_{water} versus time was made in order to determine soil permeability;

➤ The pesticides were sprayed on the soil contained in the tube;

➤ The infiltration rate of the pesticides in the soil was measured by detecting the presence of pesticide in the beakers.

By knowing the time that corresponds to the detection of the pesticide and the distance travelled, it is possible to deduce the infiltration rate of the pesticide.

3.2.2 Study of the permeability of the sand used

Permeability is proportional to the rate at which fluid penetrates through pores of a solid (Abaci & Edwards, 1992; Hoefner & Fogler, 1988). In this part, it was determined the permeability of a column of sand of height 50 cm. The sand used had a diameter of 0.25 mm and was obtained from *M'beubeuss* beach. It was sea sand, containing few pieces of shellfish. Before beginning the work, all the pieces of shellfish were removed with a sieve. The sand was decarbonised and then washed thoroughly with tap water and distilled water before filling the PVC tube with it.

Water flow was fixed at the rate d = 0.5 mL/min with the tap of the dropping funnel after it had been filled with distilled water. Different amounts of water were collected in the beakers for a period of 8 hours. A plot was made of the volume of recovered water versus time of flow. The straight line obtained (Figure 6) shows that the flow of water through the sand was smooth all along the column of sand.

3.2.3 Determination of the infiltration rate of the pesticides through the sand

Concentrated solutions of the two pesticides were prepared in organic solvents; they were slightly soluble in water. Each pesticide was applied to the top in the PVC tube which contained sand, filled up to a height of 40 cm. The sand had been washed previously. Every thirty minutes, portions of water were recovered for analysis after flowing through the sand column.

a) Maneb infiltration rate

The analytical study of the water recovered through the column of sand showed that it contained a fluorescent unknown organic substance. In fact, from the same excitation wavelength of maneb (229 nm), we found an emission coming from a product contained in the sand toward 430 nm, very different from the wavelength of maximum emission of maneb in water (Figure 7).

A 5×10^{-3} M solution of maneb in chloroform was applied to the top of the sand in the PVC tube. A fixed rate of water flow was maintained at 0.5 mL/min. Every 30 minutes the contents of the beaker was analysed. The presence of maneb was detected after 31 hours of water flowing through the sand column. This allowed us to calculate its infiltration rate, taking note of the height of sand, (40 cm). The rate was estimated at 1.29 cm/h on average. The process was repeated many times so as to ensure that it was reproducible.

b) Propanil infiltration rate

Propanil is not fluorescent in water but rather its phototoproduct into cyclohexane. To study its infiltration rate, we proceeded to an extraction. However, the excitation of the unknown product of the sand irradiated at 359 nm (propanil excitation wavelength) gave an emission almost in the same domain as propanil one. We then searched for a solvent that is non-miscible with water and in which propanil is very soluble. Among the different solvents used only cyclohexane (Density = 0.78) was useful: irradiated propanil emits much in this solvent contrary to the unknown sand product that has an inhibited fluorescence.

α) The extraction principle and the distribution coefficient

In order to find out the distribution coefficient of propanil between the immiscible solvents water and cyclohexane, we used a Uv-visible spectrophotometer. With regard to the absorbance, the peak at 250 nm was chosen. Two solutions of propanil in water were prepared, (5×10^{-5} M and 2.5×10^{-5} M). To the solution of propanil 5×10^{-5} M in water, we added an equivalent volume of cyclohexane. And the entire mixture was introduced into a separating funnel. The contents of the funnel were allowed to settle after successively shaking for a few minutes and briefly opening the tap to release pressure. Then, the two phases were separated (Berthod et al., 2004; Christian, 2004; Sangster, 1989; Tingyue, 2000). After separation, we recorded the absorption spectrum of the propanil remaining in the water. This was compared with the solution of propanil 2.5×10^{-5} M in water (Figure 8).

The calculations showed that after extraction the quantity of propanil in water was only 1/4 of the initial amount.

In order to confirm these results, we prepared two solutions of propanil in cyclohexane, with two different concentrations, 5×10^{-5} M and 2.5×10^{-5} M.

To the solution of propanil 5×10^{-5} M in cyclohexane was added an equal volume of water. And then, we followed the same procedure as before. After separation, we recorded the absorption spectrum of propanil remaining in cyclohexane. This was compared with the other 2.5×10^{-5} M solution in cyclohexane (Figure 9). Calculations showed that the propanil remaining in cyclohexane after extraction was 3/4 of the initial amount. This confirmed the results previously obtained.

Therefore, this method makes it possible to determine the presence of propanil in contaminated water by spectrofluorimetery.

β) Calculation of the infiltration rate

Propanil is not fluorescent in water. But in cyclohexane its photoproduct shows fluorescence, and gives a peak of excitation and emission toward 359 and 398 nm, respectively. Even, used sand contains residue which extraction by cyclohexane after irradiation, emits weakly at 380 nm when exciting at 359 nm (Figure 10). This last intensity does not interfere with the emission of propanil extracted into cyclohexane.

After having ensured optimized all previous conditions, we prepared propanil solution of 5×10^{-3} M in methanol. The solution was applied to the PVC tube filled with sand following the same experimental protocol as with maneb. Then, we recovered water fractions every 30 min. After having proceeded to an extraction by cyclohexane, then irradiated around 40 mn, we determined if possible for each fractions, its fluorescent spectrum.

The analysis of different fractions allowed us to detect propanil presence after 1.5 h water flowing into sand column (Figure 11). With this, it was possible to calculate its rate of infiltration with taking into account the height of sand (40 cm). This rate was estimated at about 26.7 cm/h. The procedure was repeated several times in order to ensure reproducibility.

This very high rate shows why propanil is less degradable, for it infiltrates quickly through first centimeters of soil where microbial activities are very important. Groundwater would therefore be more vulnerable to propanil contamination.

4. Conclusion

This research has shown that the two compounds undergo photochemical degradation under conditions of sunlight. The second order kinetics in water shows that maneb and propanil are very persistent under only sunlight conditions. The study of the rate of infiltration has shown that there is a lot of risk associated with the flow of pesticides into surface and ground waters. Maneb with a slower infiltration rate may stay longer in surface waters than propanil. Therefore, propanil has a higher risk of contaminating ground water because of its higher infiltration rate, which would allow it to partially escape microbial biodegradation. In all cases it is important to determine the presence of these chemicals in soils, waterways and groundwater.

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Table 1. Characteristics of maneb photodegradation kinetics in various media

Solvent	Water	Acetonitrile	Methanol	Dichloromethane	Chlorform
Concentrations	5×10^{-5} M	5×10^{-5} M	5×10^{-5} M	5×10^{-5} M	5×10^{-5} M
λ(nm)	274	276.5	273	278.5	281
R^2	0,996	0,998	0,994	0,992	0,986
Order	2	1	0	2	1
a	1.06×10^{-2}	1.01×10^{-2}	0.89×10^{-3}	5.91×10^{-2}	2.67×10^{-2}
k	51.81 $mol^{-1} \cdot L \cdot min^{-1}$	1.01×10^{-2} min^{-1}	18.16×10^{-7} $mol \cdot L^{-1} \cdot min^{-1}$	272.7 $mol^{-1} \cdot L \cdot min^{-1}$	2.67×10^{-2} min^{-1}
$t_{1/2}$(min)	386	58	138	73	26
ε ($mol^{-1} \cdot L \cdot cm^{-1}$)	4.86×10^3	19.5×10^3	4.92×10^3	4.6×10^3	5.18×10^3

Table 2. Characteristics of propanil photodegradation kinetics in various media

Solvent	Water	Acetonitrile	Methanol	Dichloromethane	Chlorform
Concentrations	2.5×10^{-5} M	2.5×10^{-5} M	2.5×10^{-5} M	2.5×10^{-5} M	2.5×10^{-5} M
λ(nm)	252	252	252	252	252
R^2	0,996	0,998	0,998	0,998	0,998
Order	2	2	2	2	2
a	0.33×10^{-2}	1.10×10^{-2}	1.50×10^{-2}	0.29×10^{-2}	1.95×10^{-2}
k	30.57 $mol^{-1} \cdot L \cdot min^{-1}$	25.39 $mol^{-1} \cdot L \cdot min^{-1}$	354.9 $mol^{-1} \cdot L \cdot min^{-1}$	398.61 $mol^{-1} \cdot L \cdot min^{-1}$	233.28 $mol^{-1} \cdot L \cdot min^{-1}$
$t_{1/2}$(min)	1574	1308	113	171	100
ε ($mol^{-1} \cdot L \cdot cm^{-1}$)	20.52×10^3	23.08×10^3	23.6×10^3	71.96×10^3	20.4×10^3

λ: Wavelength of peak characteristic of studied pesticide;
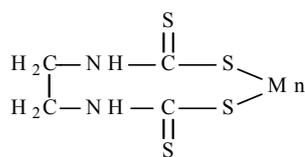
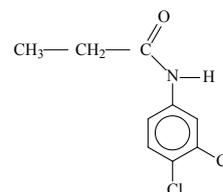a: kinetic straight line slope;

k: constant rate reaction;

$t_{1/2}$: half-life time of reaction;

ε: molar extinction coefficient;

R^2: coefficient of correlation.

(a)   (b)

Figure 1. Structural formulas of maneb (a) and propanil (b)

Maneb (a)

Structural Formula: $C_4H_6MnN_2S_4$

Molecular Weight: 265.29

Density: 1.92

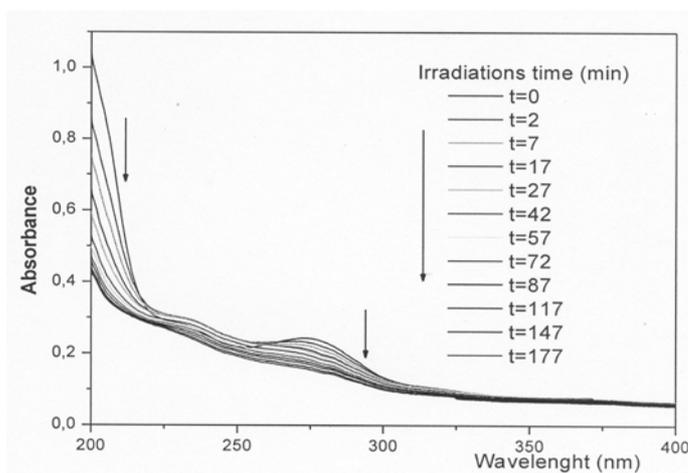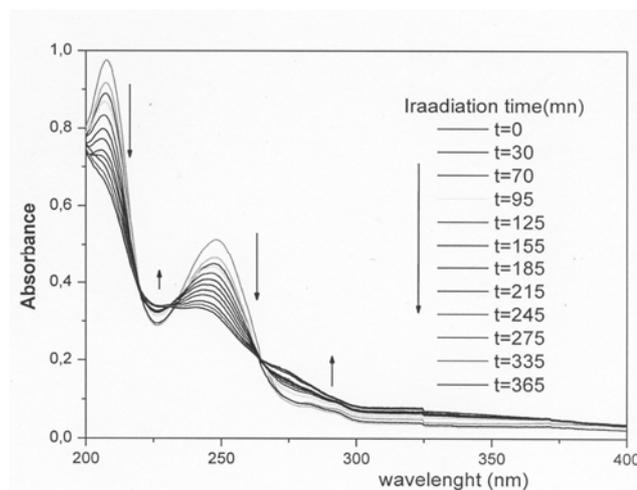Melting point: 131 ℃

Storage temperature: 0-6 ℃

Propanil (b)

Structural Formula: $C_9H_9Cl_2NO$

Molecular weight: 218.07

Density: 1.25

Melting point: 91-93 ℃

Storage temperature: 0-6 ℃

Figure 2. Absorption spectra of 5 x 10^{-5} M solution of maneb in water before and after irradiation

Broad band absorption with a peak at 275 nm and a shoulder at around 230 nm.

Figure 3. Absorption spectra of a 2.5 x 10^{-5} M solution of propanil in water before and after irradiation

Broad band between 200 and 400 nm with two peaks at 208 nm and at 249 nm for propanil. A band for an unknown photoproduct between 265 and 400 nm.
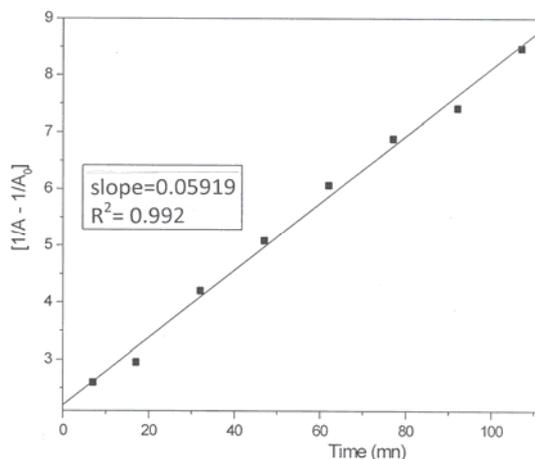
Figure 4. Photodegradation kinetics of maneb 5 x 10^{-5} M in dichloromethane

Constant rate k = 272.7 mol^{-1}·L·min^{-1}. Half-life $t_{1/2}$ = 73 mn. Second order kinetics. Correlation coefficient, R^2 = 0.992.
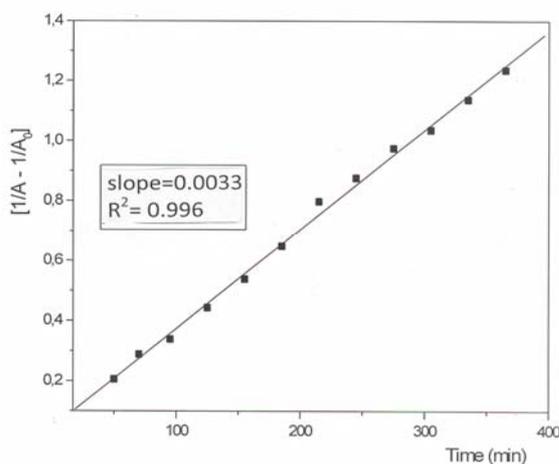
Figure 5. Photodegradation Kinetics of propanil 2.5 x 10^{-5} M in water

Constant rate k = 30.57 mol^{-1}·L·min^{-1}. Half-life $t_{1/2}$ = 1574 mn (26 ½h). Second order kinetics. Correlation coefficient, R^2 = 0.996.
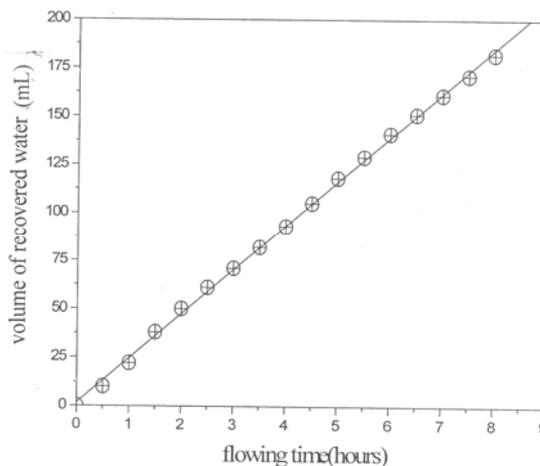
Figure 6. Permeability of sand to distilled water

Height of the column, 50 cm. Diameter of the sand, 0.25 mm. Rate of water flow, 0.5 mL/min. Period of recovery, 8 hours.
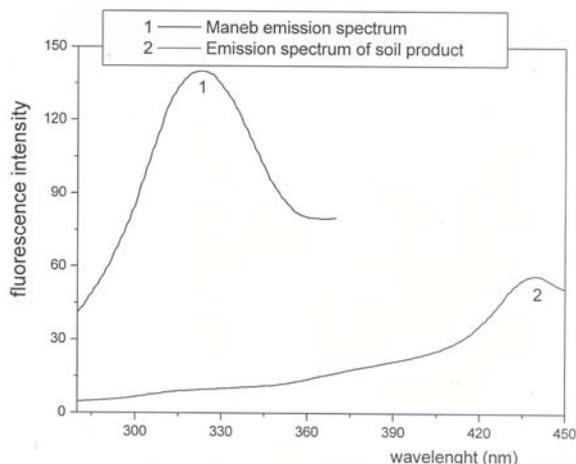
Figure 7. Emission spectra of maneb 5 x 10^{-3} M (1) and unknown product in the sand (2)

Excitation wavelength of maneb (229 nm). Emission from the sand, 430 nm. Solvent used chloroform. Water flow, 0.5 mL/min. Time of recovery and analysis, every 30 minutes. Time of detection of Maneb, after 31 hours. Rate estimated, 1.29 cm/h.
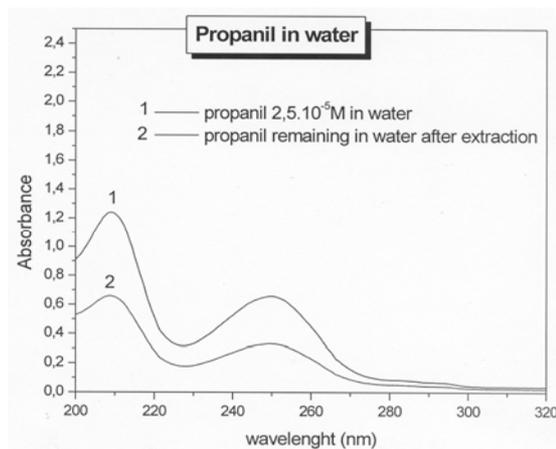

Figure 8. Comparison of propanil absorption spectra before and after extraction

Solutions of propanil in water, 5 x 10^{-5} M and 2.5 x 10^{-5} M. Solvent of extraction, cyclohexane. Quantity of propanil in water after extraction, 1/4 of initial amount.
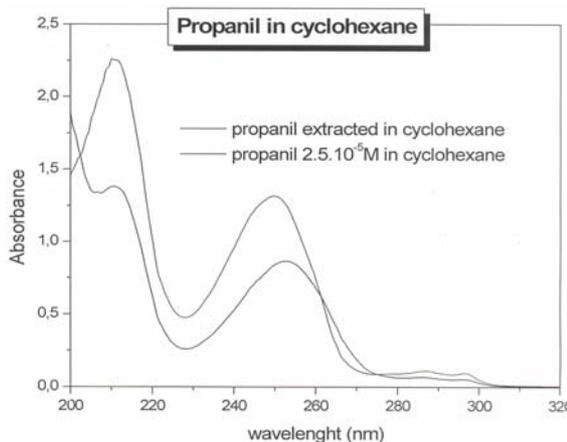

Figure 9. Comparison of propanil absorption spectra in cyclohexane before and after extraction

Solutions of propanil in cyclohexane, 5 x 10^{-5} M and 2.5 x 10^{-5} M. Equal volume of water added. Quantity of propanil in cyclohexane after extraction, 3/4 of the initial amount.
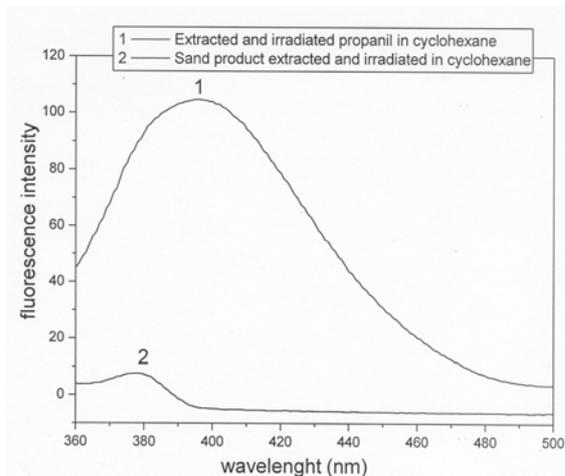
Figure 10. Emission spectra of different products extracted and irradiated in cyclohexane: 1- propanil; 2- unknown sand product

Propanil photoproduct peak of excitation and emission, 359 and 398 nm. Unknown sand product peak of excitation and emission, 359 and 380 nm.
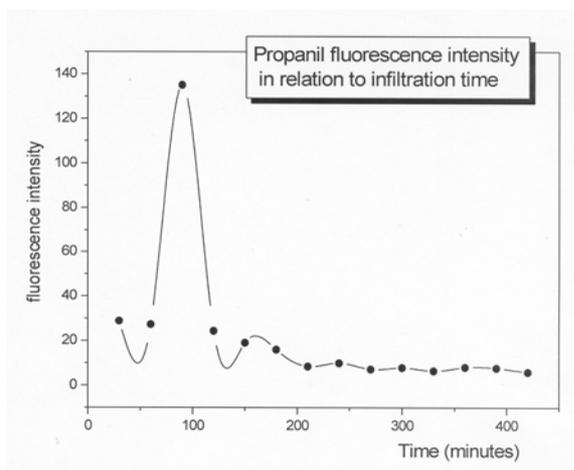

Figure 11. Propanil fluorescence intensity in relation to time of infiltration

Propanil solution of 5 x 10^{-3} M in methanol. Period of recovery of fractions, every 30 min. Time of irradiation, 40mn. Detection of propanil presence, after 1.5 h.