

BIODEGRADATION OF CHLORPYRIFOS AND LANNATE INSECTICIDES IN AQUATIC ENVIRONMENT.

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ABSTRACT

Biodegradation of chlorpyrifos and lannate insecticides in fresh water ecosystem was found to proceed after a lag period of 15 and days, respectively. Degradation was enhanced in presence of sewage microflora. Biodegradation was found to follow a first order reaction kinetics.

The K values revealed that degradation of chlorpyrifos proceeds at a higher rate compared to lannate . Consequently, the half - life time of the former compound ranged between 8 and 30 days whereas in case of lannate the half - life time ranged between 10 and 50 days . Such variations are dependant on the concentration of pesticide and presence of acclimatized microflora in the aquatic medium .

INRODUTION

Organic pesticides enter surface water bodies either by direct application or indirectly through the discharge of wastewater and runoff from agricultural lands (Livingston 1977) Being toxic chemi-

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cals, pesticides adversely affect water quality and non-target organisms leading to changes in the aquatic ecosystem structure (Koemen, 1979). It has been estimated that only 5% of the pesticide applied reaches the target pests, Hence about 95% of the pesticides used end up in other parts of the environment. This is the case particularly with aerial application techniques and uses of pesticides in the aquatic environment (Pimental and Goodman 1974).

Toxic hazards of pesticides will persist as far as the chemicals maintain their chemical stability in water. Hence biological degradation of such compounds by aquatic microflora presents an important environmental factor in the decay of such pollutants.

The present study aimed to evaluate the role of natural aquatic microflora of River Nile Water and sewage in the degradation of chlorpyrifos (organophosphorous) and lannate (carbamate) insecticides

MATERIAL AND METHODS

Insecticides used

a- Chlorpyrifos : [(O,O-dimethyl-O (3,5,6 trichloro-2-Pyridyl) phosphorothioate)]

b- Lannate (S-Methyl-N-(methyl carbamoyl) - oxythioacetimidate) The insecticides used were of 99.9% purity.

Extraction of pesticide

Residues of chlorpyrifos were recovered from the water sam-

ples by liquidliquid extraction using 15 % methylene chloride in 85 % hexane .

Aknown volume of water samples (100 ml) was extracted 3 times with 50 ml of the mixed solvents and the combined extracts were dehydrated with anhydrous sodium. sulphate and finally concentrated to about 2ml by evapouration under vaccum In case of lannate,water samples were extracted 3times with 50ml portions of methylene chloride.The combined extracts were treaed as previously given for chlorpyrifos .

Analytical Procedures

Chlorpyifos was identified and measured using a GC unit fitted with an electron capture detector (Ni 63), data base and a conventional stainless steel column .

The column was packed with 4 % ov + 101 + 6 % ov - 210 on chromosorb W 80 / 100 mesh . The column, injector and detector temperatures were 180 °C, 220 °C and 270 °C, respectively, Nitrogen was the carrier gas at a flow rate of 30 ml / min .

Lannate was measured by a UV - spectrophotometer at 210 nm as described by APHA (1985).

Standard Solutions

Stock standard solutions of the compounds studied were prepared by dissolving 0.1g of either compounds in 100 ml of hexane . Serial working standard solutions were prepared in hexane to rep-

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represent the specific concentrations needed . Stock Standards were kept in refrigerator until used .

Biological Degradation .

For each of the compounds studied a set of 3 pyrex flasks, each of 10L capacity , was used. One flask contained 5 liters of River Nile water, another flask contained 5 liters of the River Nile water and 10 ml /L of settled sewage. The third flask of each set contained 5 liters of the River Nile water and was sterilized by autoclaving at 120 °C for 15 minutes . The standard solutions of compounds studied were added to each set to the corresponding flasks to attain the required concentrations . A fine stream of air bubbles was passed through the water samples in the flasks retained for biological degradation to ensure aerobic conditions . Finally 1 ml / L of the phosphate buffer used for the BOD test (APHA 1985) was added to the flasks to adjust the pH at 7-8 and to enhance biological growth . The flasks were kept at room temperature (25±2 °C) . At various time intervals, water samples were withdrawn and analyzed for the residual concentration of each pesticide tested. Where chemical analysis revealed that the added dose of pesticide was almost utilized by microflora, a second dose was added together with 2 - litres of the river water .

RESULTS AND DISCUSSION

Biological degradation of both chlorpyrifos and lannate was followed for more than 60 days . Available results are given in Fig (1) for chlorpyrifos and Fig (2) for lannate.

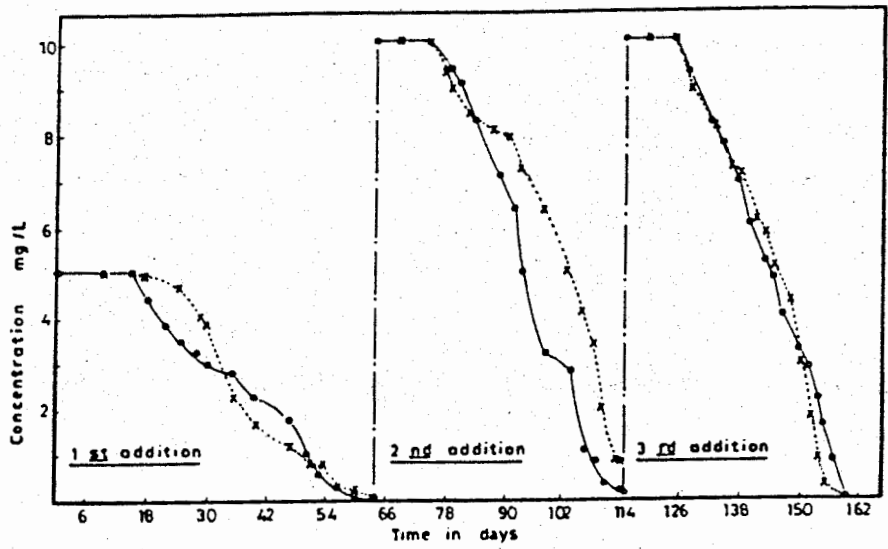


Fig. 1 Biological Degradation of Chlorpyrifos .

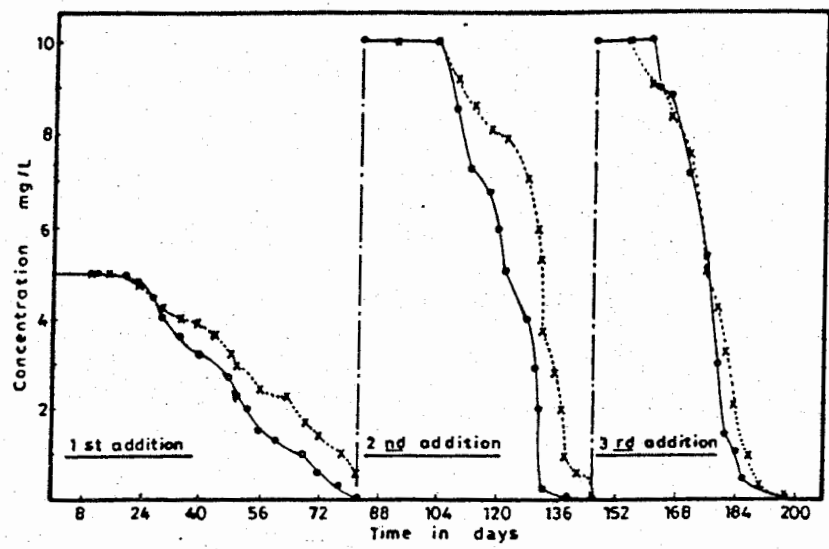


Fig. 2 Biological Degradation of Lannate .

Fig (1) for chlorpyrifos and Fig (2) for lannate.

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A lag period characterized the degradation of the studied compounds which extended to 15 and 20 days in case of chlorpyrifos and lannate, respectively. After the lag period, however, biological degradation proceeded at an accelerated rate especially where sewage microflora were added. Increasing the concentration of chlorpyrifos and lannate to 10 mg / L (second addition) resulted in another lag period before active degradation was recorded to proceed at a higher rate.

Asimilar trend was observed after the third addition of the both studied compounds with a general tendency for biological degradation to proceed within a short period .

The studied compounds maintained their concentration in the sterilized river water almost constant . By expressing the results of biodegradation according to the first order reaction kinetics as given by Glasston (1951) and Meites (1981) (Fig 3) , rate constants (K) was determined and Presented in Table (1) for chlorpyrifos and lannate .

The (K) values clearly show that the rate of degradation progressively increased as the microflora get adapted to the utilization of these studied insecticides . The increase in (K) values in presence of sewage microflora, also indicates that biodegradation is a function of the type and number of microorganisms present in the aquatic medium .

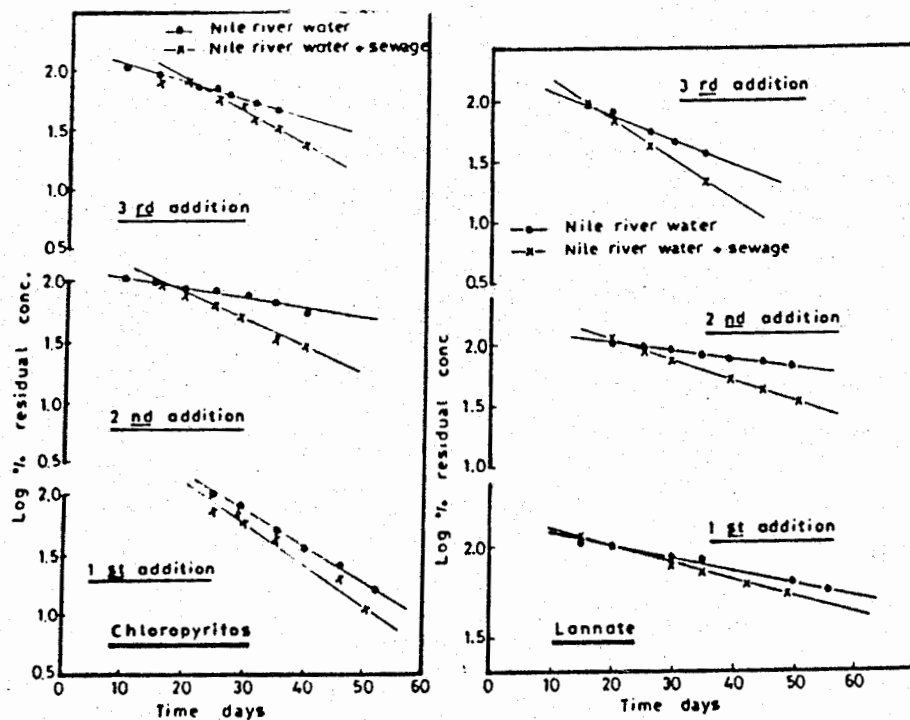


Fig. 3 Biological Degradation Rate of Chloropyrifos and Lannate .

The rate of biodegradation of chlorpyrifos and lannate in presence of sewage microflora is much less than the rate of sewage mineralization which amounts to be about 0.17 / day (Sawyer and MC carty, 1978). Such variations in (K) values reflect the differences in the nature of organics present in sewage compared to the complex chemical structure of synthetic pesticides.

Considering the values of the half life time (0.5.day) reveals that chlorpyrifos is more amenable to microorganisms than lannate,

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(Table 1) Rate constants of biodegradation of chlorpyrifos approach that previously reported for the degradation of triazine herbicides (Gardoprim and Igran) in aquatic ecosystem (Abou Waly, 1987). However, biodegradation of patoran and dicuran (phenylureas) in similar conditions, succeeded at relatively lower rates, 3.8×10^{-2} and 4×10^{-2} , respectively.

Table 1. Kinetic data for biological degradation of chlorpyrifos and lannate in River Nile water

Insecticide	Lag period(days)		K day ⁻¹		T _{0.5} (days)	
	R.W.	R.W.+ Sewage	R.W.	R.W.+ Sewage	R.W.	R.W.+ Sewage
First Addition 5 mg / L						
Chloropyrifos	15	15	0.0086	0.007	8.06	10.04
Lannate	20	20	0.0014	0.0021	49.5	33.0
Second Addition 01 mg/L						
Chloropyrifos	10	10	0.0025	0.0062	23.27	11.17
Lannate	21	20	0.0019	0.0038	36.47	18.23
Third Addition 10 mg/L						
Chloropyrifos	10	10	0.0023	0.0059	30.13	13.95
Lannate	17	15	0.0055	0.0071	12.6	9.76

* R.W = River water

According to Hassel (1990) the half life time of chlorpyrifos in soil ranged between 3 and 50 days . Such variation was attributed to the type of soil , pesticide formulation and mode of application .

The present study revealed that aquatic organisms will be exposed to the toxic effects of chlorpyrifos and lannate as far as these compounds maintain their stability in water during the lag period .

However aquatic microflora have the ability to utilize these insecticides and the rate of biodegradation will depend on the type and number of such microorganisms .

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ملخص العربي

كثيرا ما تتعرض المسطحات المائية للتلوث بالمبيدات العضوية والتي لها تأثيرا ضار على الأحياء المائية مما يسبب خلافا في التوازن البيئي بين الكائنات .

لذا يعتمد هذا البحث بدراسة الآثار الناجمة على استخدام أحد المبيدات العشبية وهو مبيد الجليفوسيد علي نوعين من أنواع الطحالب التي تمثل ركنا هاما في مجتمعات العوالق النباتية المائية هما طحلب الأنايينا وطحلب السيلينيسترم وكذلك على عينة طبيعية من طحالب مياه النيل مجتمعة بعد تركيزها .

وأضيفت لهذه المسزراع جرعات مختلفة من المبيد أظهرت الدراسة أن تركيز ١ مليجرام في اللتر لا يؤثر على زى من هذه النوعيات موضع الدراسة . وبتزايد التركيزات وجد أن مقاومة الطحالب لهذه التركيزات كما يلي :

طحلب الأنايينا < طحلب السيلينيسترم < طحالب مياه النيل .

كما وجد أن مبيد الجليفوسيد يؤثر تأثيرا كبيرا على التوازن البيئي بين طحالب مياه نهر النيل وأن مجموعة الدياتومات هي أكثر المجموعات الطحلبية مقاومة .