

MALATHION DEGRADATION IN TROPICAL SOIL AND AQUATIC ECOSYSTEMS

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ABSTRACT

The degradation of a commonly used pesticide, malathion (a phosphorodithioate insecticide), was investigated in sterile and non-sterile tropical soil and water ecosystems – sewage water, sea water, fresh water and agricultural soil at $100\mu\text{g g}^{-1}$ or ml^{-1} under greenhouse conditions. Residual pesticide in each sample was extracted and assayed colorimetrically at 420nm at different time intervals. After 10 days of incubation no residual malathion could be extracted from any of the sterile and non-sterile water samples while the pesticide was completely degraded in non-sterile and sterile soil samples after 28 and 56 days, respectively. The degradation of malathion was by biological and chemical processes, with chemical processes being of substantial effect, especially in water.

Key words : Malathion, residue, degradation, persistences.

INTRODUCTION

Malathion, (O,O-dimethyl-S-(1,2-dicarboxyethyl) Phosphorodithioate), is an important organophosphorus insecticide widely used in both agricultural and public health contexts. Malathion is used, for the protection of a wide range of crops and stored products (Kayode, 1969; Alloway and Ayres, 1993), to interrupt malaria transmission by mosquitoes in homes (Elliot and Barnes, 1963) and against such mammalian parasites as ticks and mites (Alloway and Ayres, 1993; Sangwan et al., 1995). Malathion is currently used in public health programme for the control of mosquitoes in several states in Nigeria, including Ondo, Imo and River States.

Malathion residues could enter the soil, through direct application as soil contact insecticide or as wash-off from crops, with potential leaching into ground water. A large portion of the pesticide could equally reach rivers and streams directly by its application as a larvicide. Hence the pesticide may cause certain environmental problems if the residues do not degrade at a reasonable rate. However, microbial and chemical degradation of malathion have been observed (Matsumura and Boush, 1966; Konrad et al., 1969) under certain environmental soil conditions. But the effective use of pesticides in soil and water is dependent

upon a thorough knowledge of their behaviour under a range of environmental conditions. Temperature, acidity, soil type and its moisture content alter chemical reactions and microbiological activities which are responsible for the decomposition of organophosphorus insecticides in the environment. There is dearth of information on the persistence of malathion residues in the tropical environment. Moreover, there have been discrepant reports (Walter and Stojanvic, 1973, 1974; Gibson and Burns, 1977) as to the contributions of chemical and biological factors in the degradation of malathion residues in the environment. In this study, we report the contributions of biological and non-biological factors in the degradation of malathion in tropical soil and aquatic ecosystems.

MATERIALS AND METHODS

Collection of Samples.

The soil, sewage water and fresh water used in this study were collected from the Obafemi Awolowo University, Ile-Ife, commercial farm, sewage oxidation pond and Opa water dam, respectively. The sea water was collected from the Lagos Bar Beach portion of the Atlantic Ocean. The soil sample

was collected from the surface 15cm and thoroughly mixed. Malathion (wetttable powder, 50% active ingredient, w/w) was obtained from the Ministry of Health, Ondo State, Nigeria, courtesy of American Cyanamid Co., Princeton. Each water sample was collected with a 10 litre sterile container, stored in the refrigerator and used within 24h of collection. Preparation and incubation of samples with malathion.

The soil sample was air-dried overnight, passed through a 2mm sieve to remove large particles, and analysed by the methods of Black (1965) and Day (1953). Samples (50ml) of each of fresh water, sea water and sewage water were prepared in each of twenty eight (100ml) Erlenmeyer flasks and 50g of the soil sample was prepared in each of another Set of forty flasks. Fourteen sets of the flasks containing fresh water, sea water and sewage water, respectively twenty eight sets of the flasks containing the soil sample were sterilized by autoclaving at 15 psi for 15 min and the others left unsterilized. The soil sample was autoclaved for three consecutive days. Each flask, except the controls, was treated with 10g of the malathion to give a final concentration of 100ppm of water or soil. Special precautions were taken to prevent the contamination of sterilized samples during the incorporation of malathion. The autoclaved samples were assayed for sterility on plate count agar prior to insecticide treatment. The field capacity soil moisture was maintained with deionized water. All the treated and untreated samples were incubated under greenhouse conditions with average daily temperature of 32°C till the complete degradation of the applied malathion.

Chemical assay of malathion residues.

Duplicates of each of the treated and untreated samples were analysed immediately after treatments were set up, for the zero day determination. Subsequent analyses were made for the water samples at intervals of 2 days while for soil, at intervals of 7 days. The analytical periods were predetermined from preliminary studies.

The soil was extracted three times on a mechanical shaker for 30min, each with 30ml benzene-acetone (2:1) mixture. Water sample were shaken three times in separatory funnels for 10min, each with 10ml benzene. The pooled extracts of each sample were decanted

and filtered through anhydrous Na_2SO_4 and then evaporated just to dryness on a water-bath at 50°C. The dried residual extract was taken up in 5ml CCl_4 and 2.5ml transferred to a 250ml separatory funnel. The residue was determined by the colorimetric method based upon the rapid decomposition of malathion by alkali to form dimethyl phosphorodithioate salts, and subsequent determination of the decomposition product (Norris et al., 1954, 1958; Horwitz, 1970). The optical density of the yellow colour formed was measured at 420nm using a spectrophotometer, model spectronic 20. The malathion concentration was then extrapolated from a standard curve prepared by carrying weighed amounts of pure malathion through the same procedure.

Extraction efficiency.

To determine the efficiency of the extraction procedure and percentage recovery of malathion, 50ml of each water sample and 50g of soil were, respectively, amended with 100ppm of the pesticide. Immediately, the amended samples were extracted and analyses as described for the chemical assay of malathion.

Microbiological methods.

The microbial population of each sample was determined, using the dilution plate technique, on the first day of incubation, just before the incorporation of the pesticide, and at the complete degradation of the pesticide. The predominant bacterial and fungal species were from each sample at the end of the degradation periods. The isolates were identified with the outlines of Buchanan and Gibbons (1974) and Skerman (1967). Nutrient agar (Oxoid) and malt extract agar (Oxoid) were used for the bacterial and fungal isolations, respectively.

RESULTS

Soil properties.

The soil sample used has the following properties: sand 81%; silt 7%; clay 12%; organic matter 7%; moisture 20%; pH 5.6. the soil is, therefore, characterized as acid sandy loam type.

Degradation of malathion.

Persistence curves obtained in the determination of the amount of malathion degraded in sterile and non-sterile water and

soil samples are shown in Figs 1 and 2. Each pair of persistence curves in Fig 1 A, B, C shows that non-biological degradative mechanisms were primarily responsible for the breakdown of malathion in water. The initial half-life of malathion in all the sterile and non-sterile water samples was about 3 days.

Malathion was found to have been degraded completely in fresh water and sea water after 10 days (Fig 1 A and B) and in sewage water after 8 days (Fig 1C). The rates of degradation of the insecticide in sterile and non-sterile water samples were not significantly different ($p=0.05$).

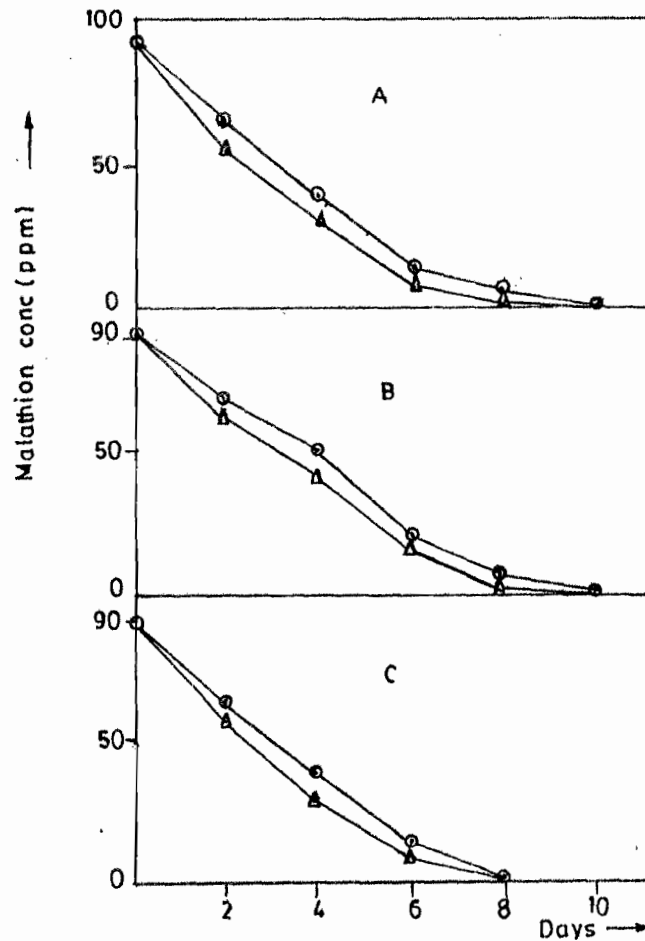


Fig. 1: Malathion degradation rates in sterile (●—●) and non-sterile (▲—▲) fresh water A; sea water B; and sewage water C.

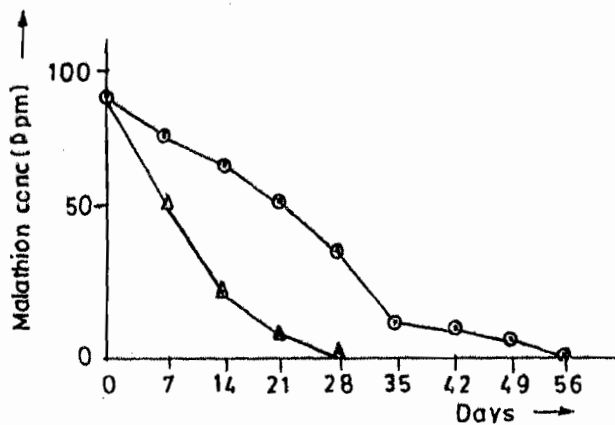


Fig. 2; Malathion degradation in sterile (●—●) and non-sterile (▲—▲) soil.

Malathion degradation was faster in non-sterile than in sterile soil (fig 2). Non biological degradative mechanisms contributed much in the breakdown of the insecticide in the sandy loam soil, but the contributions of biological factors were very well evident as the initial half-life of malathion was 7 days in non-sterile soil and 21 days in the sterile soil. A comparison of the residues remaining in soil after 14 days of incubation shows that 50% of the total insecticide loss was due to biological degradation. Thus the degradation of malathion in the sandy loam soil was significantly ($p = 0.05$) associated with biological factors.

Extraction efficiency.

The percentage recoveries of malathion based on the extraction procedure were fresh water 94%; sea water 92%; sewage water 89%; soil 90%.

Microbiological methods.

The microbial populations of the water and soil samples before the incorporation of malathion and after the complete degradation of the insecticide are given in table 1. There was little difference between total viable counts obtained from the treated and untreated non-sterile water samples during the experimental period. But the treated non-sterile soil sample gave a slightly higher total count than the untreated non-sterile soil after the complete degradation of malathion.

Pure cultures of isolates obtained for the

bacterial species, based on various cultural, morphological and biochemical characterizations, included *Pseudomonas* spp. From all the samples, *Alcaligenes* spp. From fresh water and sea water, *Arthrobacter* spp. And *Bacillus* sp. From soil, *Lactobacillus* spp. And *Proteus* spp. From sewage water, *Serratia* sp. And *Aeromonas* spp. From fresh water and *Actinomyces* sp. From soil and sewage water. The predominant fungal isolates were *Aspergillus* sp. From fresh water, sewage water and soil, *Penicillium* spp. From sea water and soil, *Candida* sp. From sewage water and sea water.

DISCUSSION

The results obtained in this study demonstrate that biological and non-biological factors contributed to the degradation of malathion in all the water and soil samples. In water, malathion was degraded, primarily, through non-biological processes like chemical hydrolysis and volatilization. In contrast, microorganisms degraded 45%-50% of the malathion in soil.

While malathion degradation was observed to be faster in non-sterile than in sterile soil, the rate of degradation of the insecticide was similar in the sterile and non-sterile water samples. Thus the elimination of microorganisms by autoclaving did not prevent the complete degradation of the pesticide. These observations point to the fact that the degradation of malathion in the tropical environment is by a combination of both

Table 1. Microbial population counts (\log_{10} CFU/ml or g) in treated and untreated water and soil samples.

| Microcosm | Preincubation Untreated | Post incubation period (days) | |
|--------------|----------------------------|-------------------------------|-------------------|
| | | Treated | Untreated |
| Fresh water | 6.81 | 7.83 ^a | 7.81 ^a |
| Sea water | 5.68 | 6.30 ^b | 6.04 ^b |
| Sewage water | 7.83 | 8.51 ^c | 8.30 ^c |
| Soil | 8.86 | 8.97 ^d | 8.84 ^d |

Incubation period : a; 10 days
b; 10 days
c; 8 days
d; 56 days.

microbial metabolism and non-biological hydrolysis. The complete disappearance of the insecticide in the autoclaved samples was, therefore, attributable to chemical degradation. But biotic factors contributed substantially to malathion disappearance in soil. Wagnet and Hutson (1990) attributed the general process that determine pesticide leaching to the transformation of the chemical by biological entities that utilize the compound as substrate and the degradation of the chemical through chemical reactions or photolysis.

Matsumura and Boush (1966) and Konrad et al. (1969) had observed the microbial and chemical degradation of malathion, though at varying degrees. The rate of malathion degradation in the water and soil samples is indicative of the non-persistence of the insecticide in both ecosystems as has been shown by eichelberger and Lichtenberg (1971). Malathion displayed a half-life of 7 days in non-sterile soil with complete degradation in 28 days while the half-life in sterile soil was 21 days with complete degradation in 56 days. The complete degradation of malathion in non-sterile soil could be attributed to chemical hydrolysis, adsorption and photolysis. However, Gibson and Burns (1977) showed malathion to display a half-life of $\frac{3}{4}$ day in non-sterile soil while disappearance from autoclaved soil was negligible. But Walter Stojanvic (1973-1974) reported that malathion abatement was more rapid under non-sterile conditions, with biodegradation being of substantial magnitude.

There was little difference between the total viable counts obtained from the treated and untreated non-sterile water samples during the experimental period. The differences in these counts were within the limits of experimental error. The slightly higher total counts obtained in treated non-sterile soil after degradation of malathion may have been due to growth during this period. These data would indicate that large populations of organisms with the capacity to degrade malathion did not build up during the experimental period.

In the present study, malathion showed a relatively greater stability in soil than in the water samples. Such greater stability could both be completely accounted for. But Bowman et al. (1970) reported that in soil, interlammellar adsorption of malathion may prevent its breakdown. The acid pH (5.6) of the soil might have contributed to the greater

stability of the pesticide in soil than in water sample whose pH values are slightly alkaline: fresh water 7.4; sea water 7.6; sewage water 7.8, because malathion has been shown to break down more rapidly under alkaline conditions (Konrad et al., 1969).

The interpretation of data from this study reveals that malathion is not persistent in the tropical environment. The non-persistence of malathion is valuable since if the pesticide is applied on crops and it gets washed into soil and then gets leached into bodies of water, or is applied as larvicide directly onto water, which may be used for domestic and recreational purposes, it would disappear fast.

The non-persistence of malathion is of public health advantage because the ascribed toxic effects of the insecticide as reported for the organophosphorus pesticides (Baron, 1981; Johnson, 1981; Fest and Schmidt, 1982) would be avoided. Malathion could equally be applied as a larvicide with some level of safety, for the control of mosquitoes in streams and ponds since the pesticide would not persist longer than necessary. Agronomically, malathion could be applied for soil treatment of pests since the pesticide would not persist from one cropping season to another thereby reducing the dangers of environmental damage.

Hence more attention should be paid to such pesticide as malathion which would aim at high specific toxicity against the target pest and would not persist longer than necessary to achieve its objective and reduce the rate and danger of environmental pollution. However, the presence of malathion in the ecosystem, should be taken into consideration within the first few days of application before using treated materials.

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