Dissipation Studies of Metalaxyl M Pesticide on Potatoes In Nyandarua County, Kenya

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ABSTRACT

Vegetables are widely consumed because of the vital role they play to provide vitamins and minerals in the diet, besides supplying proteins and energy. However they are prone of attacks by various pests and diseases leading to high loses and poor quality products. The overall objective of this study was to assess whether dissipation of Metalaxyl M on potatoes in Nyandarua County was contributing to ineffective management of the crops evidenced by high loses of the crop produce irrespective of continuous application of the pesticide. We collected samples from the farms and markets analysed resides of Metalaxyl M using GC-MS. The half-life of Metalaxyl M dissipation was calculated using the Langmuir-Hinshelwood kinetic model. The results revealed Metalaxyl M dissipation half-life of 3.13 days and 3.61 days on potatoes and soil respectively. The residues of Metalaxyl M were below the limit of detection after the 7th day of application suggesting that the pesticide was no longer effective early and late bright. All the Potatoes samples collected from the three markets open air of Njabini, Kiburu and Tulaga had no residues of Metalaxyl M. Lack of integrating data on dissipation of Metalaxyl M pesticide in developing application intervals of the pesticide is contributing to ineffective control of crop pests and diseases in production of potatoes in the region.
Keywords: Metalaxyl M dissipation, pesticides half-lives, crop pests and disease protection.

I. INTRODUCTION

Horticulture sector has grown in the last few decades to become one of the major foreign exchange earner in many developing countries. In Kenya the major crops include fruits, vegetables and cut flowers production.[1] Inaddition, agricultural sector, mainly livestock husbandry and crop production, accounts for about 25% of Kenya's GDP with an estimated 75% of the population depending on the sector either directly or indirectly.[2] Among the crops, Irish potato (Solanumtuberosum) is one of the most common vegetables grown by farmers in Kenya.[3] They have a wide variety of uses, for instance they can be consumed when fried, boiled, roasted or mashed.[3] They are a good source of nutrition in that they are rich in carbohydrates, potassium, fiber and Vitamin C.[4] In 2012, yield was 2.9 million tonnes which had a value of 50 billion Kenya shillings.[2] The main potato growing areas in Kenya are Nyandarua, Nakuru, Meru and Bungoma counties.[2]

Chemicals contamination in food has been described as a potential risk to human health, including the development of chronic diseases.[5] Food is the main exposure route and exposure to pesticide residues through the diet is assumed to be five orders of magnitude higher compared to other routes such as air and drinking water.[6] Because fruits and vegetables are mainly consumed raw or semi-processed, it is expected that they contain higher residue levels compared to other food groups of plant origin, such as bread and other processed foods. Given the potential risk of pesticides for public health, the use of pesticides in fruits and vegetable production is subjected to constant monitoring.[7] Pesticides maximum residues levels were established to ensure food safety. The MRLs are always set far below levels considered to be safe for humans.[8,9] In 2005, Kenyan passion fruit and French beans were intercepted in Sweden and Belgium during routine

monitoring. The passion fruits were found to have dithiocarbamates and Chlorothalonil residues, while the French beans were found to have Chlorothalonil, Dimethoate, Tebuconazole and Omethoate residues.10

A study on dissipation and degradation of Malathion and Dimethoate from soil and garden pea plant was carried out by Getanga11 revealed foliar dissipation rate of Dimethoate from garden pea of 29 days (t1/2 =29) while the foliar dissipation rate of Malathion from the pea plant was fast during the initial stages and slowed afterwards.

Metalaxyl-M is a systemic fungicide for foliar, soil and seed treatment. It is widely used for the treatment of potato bright (photophthora) and penospora in vines. It is used on vegetables, peas, hops, citrus, other fruits and tobacco. It is often sold in combination with protectant fungicides such as mancozeb and copper fungicides. Metalaxyl is a recemic mixture of two isomers, one of which, the R-enantiomer is the active form. This enantiomer is the basis of the fungicide, Metalaxyl-M (Mefenoxam), which is effective at half the application rate of Metalaxyl. The toxicological profile of Metalaxyl and Metalaxyl-M was evaluated in the framework of Directive 91/414/EEC, which resulted in an acceptable daily intake (ADI) and an acute reference dose (ARfD) being established at 0.08 mg/kg bw per d and 0.5 mg/kg bw, respectively. The MRL proposals were derived from the use of Metalaxyl-M but it cannot be excluded that the use of Metalaxyl leads to higher residue levels than those observed for Metalaxyl-M.12

Indiscriminate use of systematic fungicides especially Metalaxyl (Ridomil) provides chance to develop resistance strain of the fungus. Metalaxyl resistant strain of P infectans has been reported in Bangladesh.13 Phenyl amide fungicides are a class of systematic compounds including Metalaxyl (ridomil oxadxyl benalaxyl and ofurace) that show excellent protective, curative and eradicative antifungal activity and exclusively control diseases caused by peronospoles.14 An increase of Metalaxyl – resistant isolates of phytophtora infestans was observed between 1981 and 1984, the period during which phenyl amide fungicides were suspended in Ireland and the Netherlands. The active ingredient of Ridomil Gold is Metalaxyl M which is shown in Figure 1.
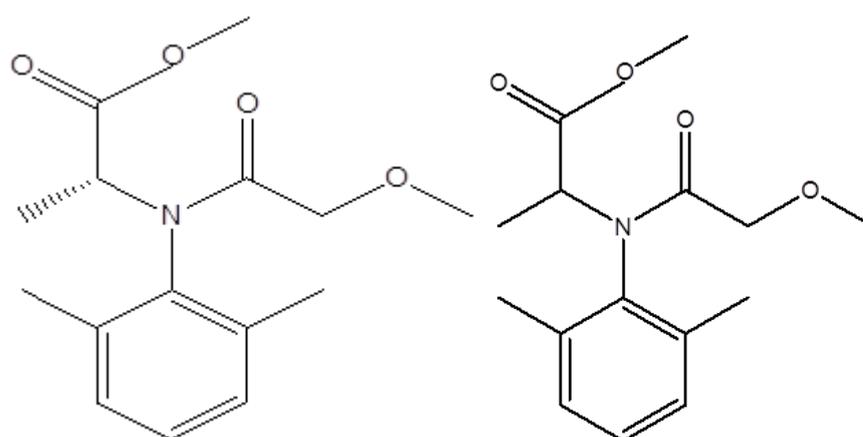
(a) Metalaxyl M Methyl N-(Methoxyacetyl)-N-(2,6-xylyl)-D-alaninate

(b) Metalaxyl Methyl N-(Methoxyacetyl)-N-(2,6-xylyl)-S-alaninate

Figure 1. Chemical structures of Metalaxyl M and Metalaxyl

A study carried out in Estonia for 3 consecutive years 2003, 2004 and 2005 showed that the increase of frequency of Metalaxyl- resistant isolates was detected. Metalaxyl – resistant isolate were less frequent among isolates collected in 2003 than in 2004 and 2005. Metalaxyl –resistant isolates was found to fluctuate from year to year due to the fact that the quality of Metalaxyl resistant isolates had increased compared with previous results.15 The reason for the increase could be the more consistent with the regular use of fungicides containing

Metalaxyl. As long as Metalaxyl is used according to the recommendations it is unlikely that Metalaxyl –resistant isolates will completely displace sensitive isolates.15 They noted that inspite of the occurrence of resistance strains the use of fungicides consisting of Metalaxyl could be used effectively for control of potato late bright at maximum of two times at the beginning of the fungicide treatment. By following the application rules for Metalaxyl fungicides it is possible to restrict development of Metalaxyl – resistant strains thus avoid the reduction of efficacy of the fungicide. 15

The overall objective of this study was to conduct dissipation studies of Metalaxyl M on potatoes and to investigate the levels of Ridomil Gold pesticide residues in market products of potatoes in Nyandarua County.

II. MATERIALS AND METHODS

A. Study area:

In Nyandarua County, potato farming is a venture that is helping the small scale farmers to boost their income. However, the yields are profoundly affected by fungi and pest such as insects. Pesticides are of great benefit to agriculture in Kenya due to decreasing quality and quantity of crop production due to insects, weeds, plant diseases, rodents and other pests. Furthermore, in the recent past farmers complained of ineffecetiveness of Ridomil Gold against fungi on potatoes.

B. Materials:

Anhydrous sodium sulphate, Na_2SO_4 for use was prepared by backing it for 16 hours at 200 ^{0}C in the oven to remove all the impurities. SiO_2 (1.8g per sample) was dried overnight at 200 ^{0}C to make it 100% active (remove all water). Deactivation of SiO_2 with water: SiO_2 (1.5%, w/w) was carried out by adding 1.5 ml of HPLC grade water to 98.5 g of activated SiO_2 in a 250 ml Erlenmeyer flask and shaken by hand until all lumps were eliminated. The Erlenmeyer flask was placed on a shaking platform for half an hour. After deactivation, these chemicals were left overnight to condition. The performance of SiO_2 was tested before use with real samples.

Copper powder was activated by shaking with 9 ml of dilute hydrochloric acid solution (3:1 ration for H_2O: HCl). The mixture was centrifuged for 1 minute at 300 rpm and acid solution discarded. The powder was rinsed three times with methanol to eliminate all the hydrochloric acid, and the supernatant discarded. The remaining powder was dried under a gentle stream of white spot nitrogen before use.

C. Sample Preparation:

The laboratory samples of potato leaves, stems, roots and tuber were homogenized using Hobart food processor. The homogenized wet analytical sample (10 g) was placed in a motor. For every gram of wet sample, 3g of baked out anhydrous Na_2SO_4 was added. This mixture was ground using a pestle to a homogeneous powder. This was then covered with aluminium foil and left overnight to dry further. This was done in triplicate.

The dry sample for extraction was put in a thimble made of filter paper and placed in a Soxhlet. Solvents hexane and acetone in the ratio of 1:1 were placed in a 250 ml round bottomed flask and the Soxhlet extraction was set in triplicate for each sample and was allowed to extract the sample for 16 hours. Three replicate samples of (5 g each) of the homogenized wet sample were weighed in a weighing glass and were kept in an oven to dry for moisture content determination. After drying the dry mass was re-weighed and the moisture content was determined from the two masses. This was repeated for all the samples extracted.

For soil extraction, 20 g was weighed into a beaker and ground with Na_2SO_4 added in the ratio of 1 g of sample to 2 g of $Na_2SO_4.$ The ground sample was covered with aluminium foil and left overnight to dry further. Soxhlet extraction was set as described above and allowed to extract for 16 hours. In all cases anti-bumping chips were added to allow smooth boiling. The extract was rotary evaporated (concentrated) to 1ml using rotary evaporator and then taken for clean-up process.

Sample clean-up was done using silica. A chromatographic clean-up column 20 cm length and 2 cm internal diameter (with frit) was packed with anhydrous Na_2SO_4 to 1 cm height (equivalent to 2 g) and 1.8 g of SiO_2 followed by 0.5g of activated charcoal and another 1 cm of Na_2SO_4. After every addition, the column was tapped to allow the particles to settle uniformly. The column was then conditioned by eluting with 15 ml of hexane: acetone mixture (ratio 1:1) and discarded.

The Soxhlet extract of the sample was transferred quantitatively to the column. The tube was further rinsed with five 1 ml portions of hexane: acetone mixture and

the rinsing transferred to the column as soon as the sample extract had eluted without leaving the column to dry completely. The column was then eluted with 165 ml of hexane: acetone mixture (ratio 1:1). The eluant was collected in a 250 ml round bottomed flask. Eluant was rotary-evaporated to 1.0 ml. The extract was transferred to a GC sample vial (auto vial) and further concentrated to 0.5 ml using a gentle stream of nitrogen. The extract was now ready for analysis by GC- MS for Metalaxyl M.

To remove sulphur from the cleaned soil extracts, approximately 1g of freshly activated copper powder was added to the sample in a vial. A black coloring appeared to all extracts containing sulphur which indicated a formation of copper sulphide compound. The extracts were then filtered through glass funnel which was packed with glass wool and activated 2g anhydrous sodium sulphate. 5 ml of HPLC hexane: acetone mixture (ratio 1:1) was used to condition the anhydrous sodium sulphate and the sample was introduced and eluted with 20 ml of HPLC grade hexane: acetone mixture (1:1) into round bottom flask and concentrated to 3 ml using rotary evaporator. The concentrated samples were transferred to clean auto vials and then concentrated to 0.5 ml under a gentle stream of white spot nitrogen gas and taken for GC-MS analysis for Metalaxyl M.

Analysis of the pesticide residues was carried out using Agilent 6890 GC equipped with 5972-2 MSD avavailable at the University of Nairobi, Department of Chemistry pesticide laboratory. DB-5 fused silica capillary column of 30 m x 0.25mm i.d. x 0.25μm film thickness was used for separation. The carrier gas was helium N6 with 99.99% purity, at a flow rate of 1.0 ml/min. Oven temperature was maintained initially at 70 ^{0}C for 1 min, increased at 15 ^{0}C/min to 175 ^{0}C, then at 2 ^{0}C/min to 215 ^{0}C, at 10 ^{0}C/min to 265 ^{0}C and finally at 20 ^{0}C/min to 290 ^{0}C and held for 8 minutes. Injection volume was 1μL, in splitless mode at injection temperature of 250 ^{0}C.

D. Quality Assurance and Quality Control:

Control pots for dissipation of Metalaxyl M in potatoes and in soil were set alongside the experimental pots. The control pots were separated to exclude any contamination from the treated pots. Analysis of controls was carried out alongside the samples to ascertain that no artifact in the crop derived from local conditions gave rise to interference in the analysis and to establish the transport and storage stability of any residue. Field blanks consisting of distilled anhydrous Na2SO4 were carried along at every field trip to track field contamination and were then subjected to the entire analytical procedure as the samples. Extraction was carried out in triplicate.

E. Moisture Content Determination:

Moisture content in plant and soil samples was determined by heating 5 g of the sample in pre-cleaned and pre-weighed watch glass in an oven (model E 28# 04-71528) at 105oC for 24 hours. The difference in weight between wet and cool dry sample was taken as the moisture content. Percentage moisture was calculated as:

% moisture = $\dfrac{\text{Moisture content}}{\text{Weight of wet sample}}$ x 100

F. Statistical Data Analysis:

The data obtained was analyzed using Statistical Programme for Social Scientists (SPSS) and Microsoft Excel programme. Calculation of half-life was done using Langmuir rate equations. Results are presented as mean of triplicate analysis with standard deviation.

III. RESULTS AND DISCUSSION

A. Method accuracy and Recovery Tests:

Recovery data for pesticide residue analysis method were generated by fortifying blank samples with 50 μl of 1 mg/kg Metalaxyl M. These were then analysed to establish the recovery of the analyte. The cleanup stage was optimised and gave recovery of 105.30 % for Metalaxyl M with elution of 165 mls hexane:acetone (ratio 1:1), 95 % for Metalaxyl M with elution of 165 ml of hexane. 165 ml of hexane:acetone mixture (ratio 1:1) was therefore used as eluting solvent for clean up. Potatoes, soil and blank (unhydrous Na2SO4) samples were spiked with 50 μl of 1 mg/kg Metalaxyl M and the percentage recoveries calculated. The recoveries of Metalaxyl M ranged between 75.15 % and 92.95 %. The recovery of Metalaxyl M was found to be 86.50 % in soil, 75.15 % in potatoes and 92.95 % in blank samples respectively (Table 1). The recoveries were within the acceptable range of 70 % - 120 %.

Table 1: Method Recovery, data in % for Metalaxyl M

Sample type	Metalaxyl M
Potatoes	75.15±2.3
Soil	86.50±2.8
Control	92.95±5.4

B. Quantification Tests:

Quantification was based on calculations from calibration curve for Metalaxyl M. The calibration curve of the standard was linear with R2 of 0.99. Figure1 below shows calibration curve for Metalaxyl M. Concentrations of analytes were obtained using the equation: Y= mx+c. Where Y = Peak area (Instrument response); x = Analyte concentration ; m = gradient ; and c = Constant.
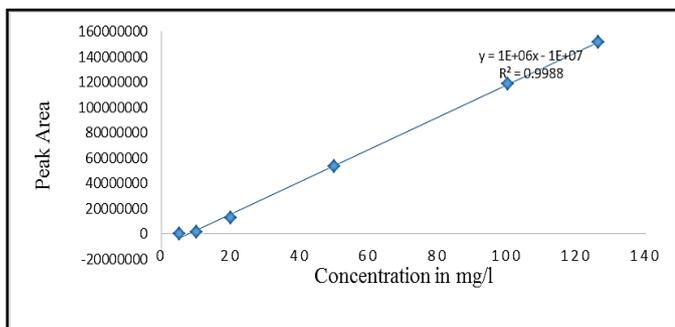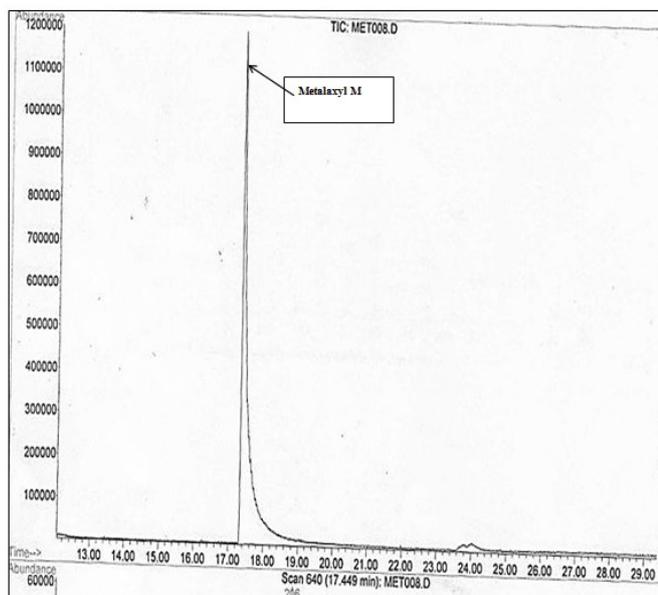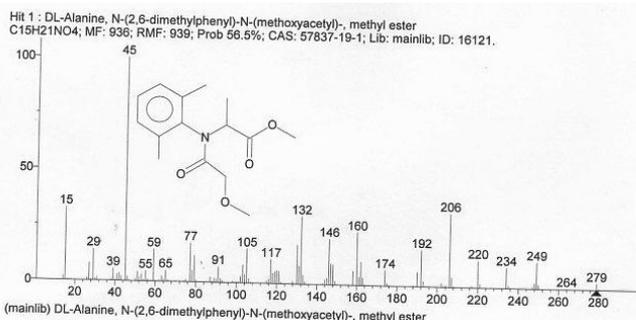

Figure 2: Calibration curve of Metalaxyl-M standard

The ion chromatogram of metalaxyl M is shown in Figure 2 below. The average retion time was 14.45 minutes.

(a)

(b)

Figure 3 : Ion chromatogram and mass spectrum of Metalaxyl M standard. (a) Ion chromatogram (b) mass spectrum

C. Dissipation of Metalaxyl M in potatoes:

The spray mixture applied to the potatoes contained guarantee Metalaxyl M 40 g/kg of Ridomil Gold. The potatoes (matures in 90 days) were treated once with Metalaxyl M to determine the effectiveness of a single application. Samples were collected on day 0, 2, 4, 7, 14, 21 and 28 and for residues of Metalaxyl M. The results obtained are presented in Table 2.

Table 2 : Results of Metalaxyl M Dissipation in Potatoes in mg/Kg (Dry weight).

Day	Treated Potatoes	Untreated Potatoes
0	9.01±0.52	<0.05
2	4.05±0.24	<0.05
4	3.45±0.02	<0.05
7	1.72±0.06	<0.05
14	<0.05	<0.05
21	<0.05	<0.05
28	<0.05	<0.05

The residues of Metalaxyl M were below the limit of detection after the 7th day of application suggesting that after that period, the crops were nolonger protected agaianst early and late bright.

The dissipation behavior of Metalaxyl M is shown in Figure 5 obtained by plotting determined concentration of Metalaxyl M against time in days. The concentration of Metalaxyl M in potatoes decreased over time. The average initial deposition of Metalaxyl M was 9.01±0.52 mg Kg−1 (day 0) and the final residue was 1.72±0.06 mg Kg−1 on day 7. After 2 days 44.95 % of Metalaxyl M remained in the potatoes while after 4 days 38.29 % of the initial deposited pesticide remained in the potatoes and 19.09 % of the initial deposited Metalaxyl M remained in the plant by day 7. No residue was detected after day 7. The results showed that there was rapid dissipation of Metalaxyl M in the potatoes for the first 2 days and that the characteristic two-phase dissipation pattern showing the initial faster dissipation rate followed by slower rate starting after 2 days was seen.
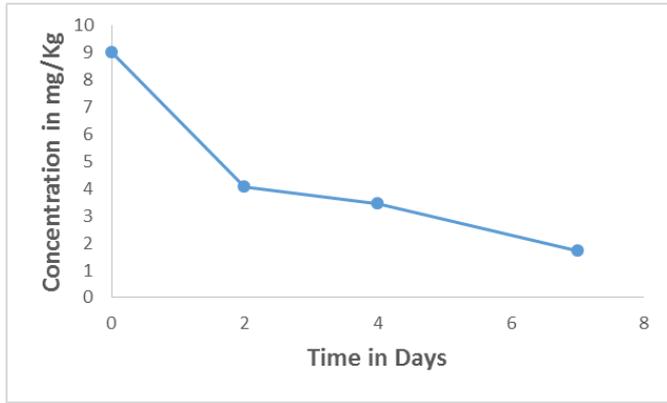
Figure 3: Trends of Metalaxyl M Dissipation in Potatoes

The data was fitted into Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial reactant concentration.[16]

$$R = dC/dt = kKC/(1+KC) \text{---------------(1)}$$

Where R is the rate of reaction (mol/L.min), C is the equilibrium concentration of reagent (mol/ L), t is the time (min), k is the rate constant (1/min), and K is the Langmuir constant (L/mol). When the initial concentration Co is $<<<1$, the denominator in equation 1 above can be ignored as 1, and the equation can be simplified to an apparent first-order equation:

$$dC/dt=kKC \text{------------------------ ---(2)}$$
$$dC/C=kKdt \text{--------------------------------(3)}$$
$$dC/dt = -Kt \text{- - - - - - - - - - - - - - - - - - -(4)}$$

Integrating equation 3 and taking boundary conditions of C = Co at t = 0, gives
$$Ln(Co/Ct) = kKt = k_{abs} \text{---------------------(5)}$$
Or
$$Ct= Coe^{-kt} \text{---------------------------- --- -----(6)}$$

This is the first order rate equation, also written as:
$$\ln C_t = \ln(C_0) - K_{obs} Xt \text{- - - - - - - - - - - -(7)}$$
Where; C_t= pesticide concentration at time, t; K_{obs} = first order rate constant; t= time in days; and C_o = the original Metalaxyl M concentration.

Consider the half-life of the reaction where the remaining concentration of the pesticide is half the original amount; C_t= C_o/2 and substituting in equation 7 above gives:

$$Ln(C_o/2C_o=-Kt_{1/2} \text{--------------------------- (8)}$$
$$Ln\ 0.5=-Kt_{1/2} \text{--------------------------- -- (9)}$$

$$-0.693/K =t_{1/2} \text{----------------------------- (10)}$$

The regression curve for the disappearance of Metalaxyl M is shown in Figure 6 which was obtained by plotting a graph of negative logarithm of the concentration of residues against time and it had correlation of R^2 =0.9483.
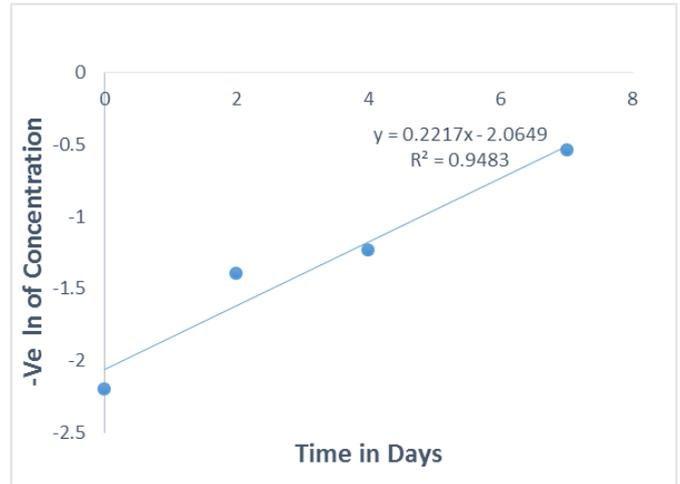

Figure 4 : Regression curve for disappearance of Metalaxyl M from Potatoes

Equation 7 is in the form of y = mX + C. A plot of ln (C_t) verses time (t) gives a straight line, the slope of which upon linear regression equals the apparent first-order rate constant K_{obs}. In this case, the K_{obs} are the observed degradation rate constant. The values obtained by this analysis were the same as that of the exponential regression analysis. Based on first order kinetic, a plot of negative ln concentration of residues versus time t (days) Figure 6, gave a regression equation, y = 0.2217x-2.0649. A gradient of 0.2217 was obtained (which is equivalent to the constant K_{obs}). In this study the degradation of Metalaxyl m follows Langmuir-Hinshelwood kinetic equation and using equation 10, the half-life of Metalaxyl M in Potatoes was 3.13 days by the Langmuir-Hinshelwood kinetic model.

D. Dissipation of Metalaxyl M in soil:

This study was conducted to establish whether application of Metalaxyl M on crops growing on treated soil resulted in elevated residue. The results are presented in Table 3.

Table 3: Results of Metalaxyl M Dissipation in Soil (mg/Kg, dw)

Day	Treated Soil	Untreated Soil
0	5.03±0.25	<0.05
2	2.52±0.01	<0.05
4	1.91±0.09	<0.05

7	1.23±0.02	<0.05
14	<0.05	<0.05
21	<0.05	<0.05
28	<0.05	<0.05

Figure 7 below shows Metalaxyl M dissipation in soil, with fastest rate experienced during the first two days but later declines over time. The average initial deposition of Metalaxyl M was 5.03±0.25 mg Kg^{-1} (day 0) and the final residue was 1.23±0.02 on day 7. The rapid dissipation of Metalaxyl M in soil during the first 2 days followed by lower rate revealed a two-phase dissipation pattern.
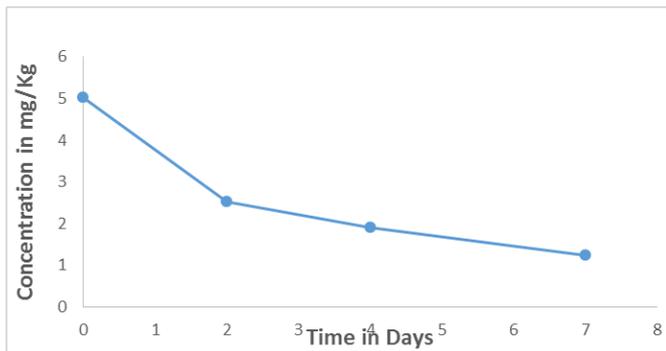

Figure 5: Trends of Metalaxyl M Dissipation in Soil

The data fitted well into Langmuir-Hinshelwood kinetic model for reaction rate dependence on initial reactant concentration.[16] The regression curve for the disappearance of Metalaxyl M in soil is shown in Figure 8 below obtained by plotting a graph of negative logarithm of the concentration of the residues against time. A correlation of $R^2 = 0.9456$ was obtained.
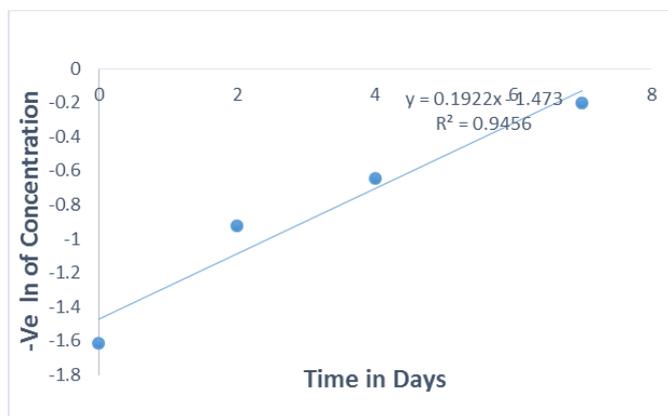

Figure 6 : Regression curve for disappearance of Metalaxyl M from Soil

The half-life of Metalaxyl M in soil was calculated using equation 10 and data obtain (Table 3). The half-life (t1/2) of Metalaxyl M was calculated through regression analysis assuming the loss of Metalaxyl M follows Langmuir-Hinshelwood kinetic model, after k was determined (gradient = 0.1922) and was found to be 3.61 days.

E. Assessment of Metalaxyl M Residues in Potatoes:

Potato samples from three open air markets of Njabini, Kiburu and Tulaga were analysed for Metalaxyl M residues. The results presented in Table 4 below show that Metalaxyl M residues were not detected in all potatoes from the three markets surveyed. Potatoes sold in the three markets had residue levels below the European Union limit of 0.05 mg/Kg.

Table 4 : Assessment of Metalaxyl M Residues in Potatoes

Season	Njabini	Kiburu	Tulaga
Wet (October-November)	<0.05	<0.05	<0.05
Dry (January-March)	<0.05	<0.05	<0.05

F. Discussion of results:

The average initial concentration of Metalaxyl M was 5.03±0.25 mg/kg on day 0 and decreased to 1.23±0.02 mg/Kg by the 7th day. The dissipation curve for the pesticide showed that the dissipation of the residues has initial fast rate for the first two days followed by a slower rate. The half-life was found to be t1/2 = 3.61 days. The amount of residues at harvest depends upon factors such as the rate of application, time interval between last application and harvesting, and the type of crop. Other factors include environmental factors such as temperature, precipitation and humidity and air movement (wind) which influence the persistence of pesticides in plants. The total quantity and form of pesticide reaching plants and soil depends on the site and method of application, type of equipment together with the formulation type. These consequently influence pesticide persistence on both the plants and soil.17, 18,19 Plant factors that affect persistence include plant species, nature of harvested crop, structure of cuticle and metabolic activities like rate of uptake, growth, translocation storage and excretion.17 In this study the observed trend may be attributed to environmental factors due to high precipitation and low temperatures experienced in Kinangop Sub-County.

IV. CONCLUSION AND RECOMMENDATION

There are major pests' problems in Kinangop Sub-County and therefore an active pest management programme is necessary to secure the harvest in the region. Metalaxyl M pesticide did not exhibit persistence in both soil and potatoes. The half-life was 3.13 days and 3.61 days in Potatoes and soil respectively. Metalaxyl M residues after day 7 were below the limit of detection, clearly indicating that after day 7 the pesticide is not effective protection of the crops against early and late bright in potatoes. The concentration of Metalaxyl M residues in all potato samples collected from the three open air markets of Njabini, Kiburu and Tulaga was below detection limit. Since Metalaxyl M residues were below detection limit within 7 days of applicationson potatoes, farmers should be advised to incorporate data on dissipation of the pesticide for effective control against early and late bright. Metalaxyl M pesticide was not detected in all market samples analysed indicating that the potatoes are safe for consumption if they are sprayed at recommended dosage and harvested at normal post harvesting interval of 14 days. More sampling times is suggested for study of dissipation rate on single and multiple application of Metalaxyl M to investigate residual effects under different seasons and application modes. National Pesticide Residues Monitoring and Surveillance is recommended on produce sold in the Kenyan markets and those destined for export to protect consumers and control misuse of pesticides to support safe trade.

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