Optimal Instar and Method of Meta-tolyl-N-Methyl-carbamate Application for Killing *Aphrophora costalis* Matsumura

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For determining the effects of meta-tolyl-N-methylcarbamate (MTMC, metolcarb) on *Aphrophora costalis* Matsumura (ACM) and the migration and leaching law of MTMC in soil, the thin-layer chromatography method was used. The characteristics of migration and leaching of MTMC in the dark brown soils, and the most critical influences such as soil type, pH, and amount of water were considered to evaluate the impact of leaching rate. The results showed that 25% MTMC diluted 1,000 times was most effective in controlling ACM, with a mortality reaching 87.8% by root irrigation, and a mortality of up to 94.4% by root burial. For dark brown soil, clay minerals are primarily quartz, as well as small amounts of agalmatolite, mica, and kaolinite. Adsorption of MTMC by dark brown soil begins within 2 h, which increases rapidly in capacity before 16 h, and tends to balance with a decrease in the gradient concentration after 16 h. The desorption capacity of MTMC exhibits a gradual increase within 2 h, showing a maximum around 12 $\mu g \cdot g^{-1}$, which tends to stabilize after 12 h. MTMC has moderate mobility in dark brown soil. This research has important practical significance for controlling tree diseases and insect pests and protecting the environment.

Keywords: MTMC; Aphrophora costalis Matsumura; Nymphal stage; Adsorption; Desorption; Mobility

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INTRODUCTION

Pesticides are widely used for controlling plant diseases and insect pests that cause devastating crop losses (Oerke 2006). However, if it is not used properly, they will have an adverse impact on groundwater and the ecological environment. For example, the residues of highly toxic organochlorine pesticides such as DDT (dichloro-diphenyl-trichloroethane) and BHC (benzene hexachloride) not only can migrate for a long distance in the atmospheric environment, but they can also easily penetrate underground, causing adverse effects on ground-water and ecological environment (Ibrahim and Adebote 2012). Although the degradation cycle of organophosphorus pesticides is short, some are highly toxic organic pollutants and remain in the environment for a long time; they also enter the water environment through surface runoff and leaching, resulting in pollution (Lacorte *et al*. 1995). Carbamate pesticides have the characteristics of remarkable insecticidal effect, rapid decomposition, rapid metabolism, and short residue period. They are high-efficiency and broad-spectrum insecticides that were developed rapidly after organochlorine and organophosphorus pesticides (Wu *et al*. 2011). However, with the expansion of the use and scope of carbamate insecticides, its residual part and its toxicity to human health and the environment have also attracted more and more attention.

For *Aphrophora costalis* Matsumura (ACM), one major pest of willows, pesticide application is an effective way to kill them. As a member of the superfamily Cercopoidea in the order Homoptera, ACM adults and nymphs suck the sap of 1 to 2 years old twigs of willows, which endangers the landscaping outcomes and the willow twig production severely (Liang *et al*. 2007). There is interest in a more effective pesticide against ACM. The syntypes of four Uhler species found in London's Natural History Museum are also documented, one of which is ACM (Liang *et al*. 2000). Thompson (1999) discovered that the actinorhizal plants are major hosts for ACM, and the world host records indicate primary associations of ACM with at least 17 actinorhizal hosts in such genera as Alnus, Casuarina, Ceanothus, Comptonia, Elaeagnus, and Myrica (Thompson *et al*. 1999). The pesticidal efficacy of meta-tolyl-N-methylcarbamate (MTMC) against host pests has been explored extensively (Lin *et al*. 1979). Zhang *et al.* (2019) inspected 47 commercial wine samples in China by disposable pipette extraction (DPX); the study found 0.02 to 0.09 mg/L residues of pesticides including sulfacarb. Babić *et al.* (1998) investigated the factors affecting the fate and behavior of pesticides in the soil system. Their study revealed the direct or indirect effects of adsorption–desorption phenomena, claiming that adsorption was one of the chief factors affecting the interaction between pesticides and soil colloids. Bollen (1961) extracted pesticides from soil by the ultrasonic solvent ex-traction and determined the pesticide recovery through RP-18 TLC.

MTMC is a carbamate pesticide that is often used for the control of ACM. If it is widely used for a long time, while ensuring the control of diseases and pests, a large number of residual pesticides may not only cause direct toxicity to human body, but also pollute the ecological environment. However, there are no reports on the migration and leaching of MTMC in soil. Therefore, it is of great practical significance to study the migration and leaching behavior of MTMC in soil environment for environmental protection. This study systematically observed the life habits of ACM and conducted small-scale control experiments, which were based on the ACM observations between 2016 and 2019. The research objectives were to find the best amount of MTMC to kill insects and to consider the migration and leaching behavior of MTMC in soil environment, which has important practical significance for controlling tree diseases and insect pests while protecting the environment.

EXPERIMENTAL

Materials

ACM eggs, plant, and soil

Aphrophora costalis Matsumura (ACM) eggs were collected from the landscaping siuz willows on the campuses of Heilongjiang Forestry Vocational & Technical College and Mudanjiang Normal University in Mudanjiang of Heilongjiang, as well as from the roadside trees with high occurrences around the campuses.

Salix gracilior (Siuzew) willow was collected from the Qingmei Experimental Forest Farm of Heilongjiang Forestry Vocation–Technical College. Dark brown soil was also collected from the Qingmei Experimental Forest Farm of Heilongjiang Forestry Vocation–Technical College. All soil samples were from 0 to 20 cm layers, which were air-dried, ground, and passed through a 40-mesh sieve for subsequent experimentation. The particle size of powder is greater than 40 mesh.

Agents

25% MTMC, 3% phorate granules, 3% carbofuran granules, 3% isofenphos-methyl granules, 80% dichlorvos, 50% chlordane emulsion, and 40% omethoate were all purchased from the Hlj.Pingshan Pharmaceutical Factory of Forestry (Harbin, China). Distilled water, methanol (HPLC grade), nylon yarn (40-mesh), quartz sand, medium speed filter paper (pore size 30 to 50 microns), siphoning device, and 5 mL centrifuge tube were also purchased from the above pharmaceutical factory.

Methods

ACM rearing observation

Egg stage: In April, the collected ACM eggs were placed into a triangular flask, petri dish, and index tube containing several wet cotton balls. Development of the eggs was observed on a daily basis, which was supplemented by field surveys. Egg development was observed daily while combined with a field survey to verify whether there was diapause in their development.

Nymphal stage: On April 10, the rooted siuz willow seedlings of the year were cut to 20 to 50 cm, and then planted in flasks indoors. Meanwhile, an ACM nymph hatched on the same day was placed on each live tree, and a total of 34 groups (multiple nymphs per plant in the case of joint rearing) were reared in succession. Every day, observation was carried out, which was supplemented by field surveys. Around June 20, the tree groups were covered with wooden frame plastic cages (1 m× 1 m× 1.1 m) for joint rearing of nymphs, in order to proceed to the adult stage observation.

Adult stage: The willow branches were arranged with two types of cylindrical plastic cages (length 70 cm, diameter 30 or 18 cm, length 40 cm), which contained male and female ACM adults. A total of 15 groups (multiple adults per cage for joint rearing) were reared in succession. Observation was performed every day, and the spawning branches were cut out timely for fecundity surveys. In the field, three piles of *Salix saposhnikovii* were selected to test the fecundity and other factors once every ten days.

ACM control with varying concentrations of 25% MTMC diluents

The experimental site was the Qingmei Experimental Forest Farm of Heilongjiang Forestry Vocation–Technical College, whose geographical coordinates are 129°39'10"–129°54'37" east longitude and 44°36'44"–44°40'24" north latitude.

For severely damaged trees, the rhizosphere application was implemented. After peeling off the soil to expose the root bark, MTMC was applied, followed by covering with soil. As shown in Fig. 1, a favorable effect was attained 7 d later.

XRD analysis

The experimental procedure conformed to ASTM D8064 (2016). The 300-mesh sieved, air-dried dark brown soil was prepared into oriented films and then characterized with a Rigaku X-ray diffractometer (Ultima IV, Tokyo, Japan), thereby analyzing the principal components of the soil. Prior to experimentation, the samples were placed flat on the stage for compaction. XRD was performed at a tube voltage of 40 kV and a tube current of 40 mA over a scanning range of 5 to 40° (2θ) at a 5°/min rate (Ismail *et al.* 2018; Zheng *et al.* 2019).

Fig. 1. MTMC buried in the willow roots

Micromorphology analysis

During experimentation, the samples were prepared into small blocks with a cutter. After flattening, the cut surfaces facing upwards were placed on the sample holder, and they were glued tightly with conductive carbon glue on both sides, followed by evaporation in the vacuum evaporator (FEI Company, Eindhoven, The Netherlands) and gold film formation. Conforming to ASTM E1588 (2017) standard, the sample morphologies were observed at an accelerating voltage of 30 kV with a QUANTA 200 electron microscope (FEI Company, Eindhoven, The Netherlands) (Laflèche *et al.* 2018).

Adsorption Kinetics Experiment

Adsorption and desorption of various 25% MTMC diluents in soil

Specimens of 10.00 g of various soil samples were weighed accurately into an Erlenmeyer flask, and added with an appropriate amount of 0.01 mol·L^{-1} Ca Cl_2 aqueous solution to stabilize the pH at 8.0. Subsequently, 1.0 mL of MTMC standard solution (1,000 μg·mL^{-1}) was pipetted accurately into each of the aforementioned Erlenmeyer flasks, which were then stoppered to prevent the solution loss. Afterwards, the solutions were shaken in a thermostatic oscillator (Agilent Technologies, Palo Alto, USA) under 150 r·min^{-1} and (25±1) °C conditions. Samples were collected at 0, 10, 20, 30 min, as well as 1, 2, 4, 8, 10, 12 and 24 h, respectively, followed by centrifugation at 3,500 r·min^{-1} for 10 min at room temperature. Finally, appropriate amounts of supernatants were aspirated and then subjected to measurement on Agilent 1100 HPLC system (Agilent Technologies, Palo Alto, USA). The procedure was repeated twice (Aharoni *et al.* 1991; Wang *et al.* 2009).

Desorption Kinetics Experiment

Each 10.00 g of various air-dried soil samples was weighed accurately into an Erlenmeyer flask, added with 48.5 mL of 0.01 mol·L^{-1} $CaCl_2$ solution and then with 1.50 mL of 1,000 μg·mL^{-1} MTMC standard solution to make the final volume 50 mL. Next, the solutions were shaken in a thermostatic oscillator (Agilent Technologies, Palo Alto, USA) under 150 r·min^{-1} and (25±1) °C conditions for 24 h, and then centrifuged at 3,500 r·min^{-1} for 10 min to separate the supernatants. Afterwards, the residues were added with 0.01mol·L^{-1} Ca Cl_2 solution until the volume was 50.0 mL, and then they were further shaken under the above conditions for 0, 10, 20, 30 min, as well as 1, 2, 4, 8, 10, 12, and 24 h, respectively, followed by centrifugation at 3,500 r·min^{-1} for 10 min. Finally, appropriate amounts of supernatants were aspirated, and then subjected to measurement on Agilent 1100 HPLC system (Agilent Technologies, Palo Alto, USA). The fore-described procedure was done twice (McLaren *et al.* 1998; Lewis *et al.* 2001; Major *et al.* 2010; Long *et al.* 2015).

Soil mobility experiment

For mobility comparison of MTMC in soil, thin layer chromatography (TLC) analysis was employed. Each 25 g of soil samples was placed in a 250 mL Erlenmeyer flask, added with distilled water as per a certain ratio, and shaken for 10 min into a slurry, which was then applied onto a glass plate and dried at room temperature while keeping the soil layer 0.50 to 0.70 mm in thickness. Meanwhile, each 0.3 mL of MTMC standard solution was smeared onto a thin plate and then placed into a developing tank (20 cm×30 cm× 30 cm) after evaporation of organic solvent while keeping the inclination at around 30°. The thin plate was taken out when the developing solvent (water) reached the front, and then it was dried at room temperature in a horizontal position. Each section (2.0 cm in length) of soil samples was transferred into a 5 mL centrifuge tube, added with 2 mL of methanol, ultrasonicated for 10 min, and subjected to centrifugal separation. Afterwards, the supernatant was transferred into a test tube, added with 2 mL of methanol, and extracted once again. The two resulting supernatants were combined and brought to a constant volume, followed by the HPLC determination of MTMC content. The R_f value of the pesticide on the thin plate was calculated according to Eq. 1, while its migration rate in the thin plate was calculated by Eq. 2 (Lewis *et al.* 2001),

$$R_f = \frac{Z_c}{Z_w} \tag{1}$$

$$Z_c = mt^{\frac{1}{2}} \tag{2}$$

where Z_c is the distance from the center of zone with highest pesticide content to the origin, Z_w is the distance from the origin to the solvent front, t is the migration time (h), and m is the migration rate (cm·h$^{-1/2}$).

MTMC determination

MTMC contents were determined by utilizing an Agilent 1100 HPLC system (Agilent Technologies, Palo Alto, USA), where the chromatographic conditions were set as follows: TC-C18 (4.6 mm×250 mm×5 µm) column, gradient elution of mobile phases methanol (A) and water (B) for 0 to 20 min from 100% B to 100% A, a determination wavelength of 258 nm, a column temperature of 25 ℃, an injection volume of 100 µL, and a retention time of 16.84 min (Ding *et al.* 2010; Major *et al.* 2010; Yao *et al.* 2012).

Leaching experiment in soil column

To investigate the downward movement of MTMC with infiltration water in the vertical soil sections, the column leaching procedure was employed. At the bottom of a plexiglass column 1.0 cm in inner diameter, a layer of filter paper and a layer of 40-mesh nylon gauze were placed, followed by slight placement of fine sand. Then, the column was filled with 50 g of test soil evenly and compactly. After filling, 2 mL of MTMC standard solution was added at the top, which was then covered with a layer of quartz sand and further padded with a layer of filter paper, onto which a small amount of coarse sand was placed. Utilizing a siphoning device, the water flow rate was controlled via a regulator valve. Initially, the soil column was presaturated with a certain amount of water, and it was let stand for a period of time to balance the adsorption adequately. Next, the soil column was leached with a certain amount of water. After completion of leaching, soil samples were collected in 10 sections, each of which was extracted by shaking with 25 mL of methanol, centrifuged, and then determined by HPLC. In the meantime, leachates were sampled from the lower end of the soil column at 50 mL per time for HPLC determination. On these bases, the pesticide mobility in different soils was investigated at varying leachate pH and volumes.

RESULTS AND DISCUSSION

Life Habits of ACM

ACM has one generation a year, which overwinters on the current-year shoots in egg form. By late April of the following year, where the average temperature reaches 12.8 ℃ and the relative humidity is above 40% on average, the overwintered eggs begin to hatch. Early to mid-May is the peak hatching period. Newly-hatched nymphs like sucking the juices from new shoots by gathering at the shoot base. In the meantime, they cover their bodies with bubbles secreted from abdomens, while the tails are raised at times to be exposed outside of the bubbles, as shown in Fig. 2.

Fig. 2. Habitual behaviors of ACM

Nymphal stage spans from mid-May to mid-to-late June. The newly-hatched nymphs crawl slowly and tend to cluster. They have white crystals at the end of their abdomens. After the third instar, the nymphs show increased mobility. Most of them damage the 1 to 2 years old twigs, with significantly enhanced food intake and increased bubbles that cover their whole bodies. The nymphs shed their skins in the bubbles four times in total. As detailed in Table 1, the average duration of nymphal stage is 975.4 h or 40.6 d.

Table 1. Instar Durations and Morphological Characteristics of ACM Nymphs

Instar	Duration	Number of ACM surveyed	Longest (h)	Shortest (h)	Average (h)
1	May 13–May 24	30	217.4	121.9	174.8
2	May 1–May 27	30	130.2	122.5	129.2
3	May 9–June 9	30	289.6	123.8	194.7
4	May 16–June 12	30	218.3	143.2	173.3
5	May 21–June 24	30	409.8	265.7	289.6
Nymphal stage	May 13–June 24	30	1058.1	914.3	975.4

From late-June to the end of August, ACM reaches its adult stage. The newly-emerging adults have their wings curled into a tube, which then unfold slowly. Except for brown compound eyes and scutella, light gray abdomen and dark red ventral area, the rest parts are all light yellow. Feeding begins 2 to 4 d later. Adults like damaging the middle and upper shoots, which are often fixed in one place to suck juices continuously. The affected branches have brown scar streaks on their xylem surface, a site prone to breakage. When frightened, the ACM adults bounce immediately or fly short distances. Gradually, they transfer from tall siuz willows to the saplings or nursery seedlings. After adequate nutrition supplementation, the adults begin to mate and lay eggs in mid-July. Most of the eggs are laid on new shoots 1 to 2 years of age, which begin to wilt and wither a few days later. August is the peak spawning season, and the spawning ends in early October. The newly-laid eggs overwinter in the tender shoots of the branches. As shown in Table 2, the eggs are laid once a year, and the egg stage spans as long as 8 to 9 months.

Table 2. Life Cycle of ACM

Year	Month							
	April	May	June	July	August	Septem-ber	Octo-ber	Novem-ber to March
One gener-ation a year	Hatch-ing	Hatch-ing						
		Nymph	Nymph	Nymph				
			Adult	Adult	Adult	Adult	Adult	
				Mating & spawning	Mating & spawning	Mating & spawning	Mating & spawning	
				Egg over-wintering	Egg over-wintering	Egg over-wintering	Egg over-wintering	Egg over-wintering
Pest stage	√	√	√	√	√	√		

Root Burial and Irrigation Techniques

Pesticide burial

Long-acting, broad-spectrum systemic pesticides were used, such as aldicarb and carbofuran, which were applied at the sites with highest number of siuz willow absorbing roots. The pesticide solutions were absorbed, transferred, and transmitted to various tissues on the ground via the root system. After eating such siuz willows, ACM would be poisoned to death, thereby attaining pest control. With a mortality of 94.4%, the root burial of 25% MTMC granules exhibited the optimal control effect. Table 3 details the control outcomes.

Pesticide irrigation

Through a combination of pesticide irrigation and watering, the systemic pesticide solutions, such as 80% omethoate and 25% MTMC diluents (500X), were irrigated onto the willow root bases. This approach also enabled the control of ACM. With a mortality of 87.8%, the root irrigation of 25% MTMC diluent yielded the optimal control effect. Table 3 details the control outcomes.

Chemical control approaches have the following advantages and drawbacks: 1) Advantages: Ultralong efficacy period (up to approximately 60 d) owing to the slow-release technology, good control effect, control of both nymphs and adults, little harm to natural enemies, non-pollution of urban air, low pesticide consumption, and low control cost. Meanwhile, through rational utilization toxic chemical pesticides, the low-toxic application of highly toxic pesticides can be achieved. 2) Drawbacks: Easy pollution of water sources and soil.

Table 3. ACM Outcomes with the Pesticide Burial and Irrigation Techniques with Various Pesticides

Pesticide type	Application method	Number of twigs surveyed	Number of dead ACM	Number of live ACM	Mortality (%)
3% phorate granules	Root burial	30	44	9	83.0
25% MTMC granules	Root burial	30	51	3	94.4
3% carbofuran granules	Root burial	30	52	8	86.6
3% isofenphos-methyl granules	Root burial	30	42	10	80.7
80% dichlorvos diluent (1000X)	Root irrigation	30	43	9	82.6
25% MTMC diluent (1000X)	Root irrigation	30	58	7	87.8
50% chlordane diluent (1000X)	Root irrigation	30	41	14	74.5
40% omethoate diluent (1000X)	Root irrigation	30	45	13	77.5

Control Efficacies of Different Concentrations of 25% MTMC Diluents

In Table 4, the survey results after 24 h of application are listed. The efficacies of 80 to 100% could be achieved during early and mid-May by spraying different concentrations of 25% MTMC diluents at various instar stages. The best efficacy was observed for killing nymphs of instars 1-2, with substantial ACM being dead 2 h after application.

According to observations, the bubbles on the treated twigs decreased or disappeared after rearing ACM nymphs for a period of time. The mortalities were quite high for all treatment groups, all of which reached 80 to 100%. Meanwhile, the average adjusted mortalities were all above 90% after treatment with 500X or 1000X diluents of various pesticide extracts. It is also clear from Table 10 that during instars 1 to 2, the 1000X diluent of 25% MTMC exhibited the highest insecticidal rate, with an average mortality reaching 100%, which was remarkably potent. With the prolongation of instar, the insecticidal effect tended to weaken, which was attributed to the enhanced immunity of ACM. Nevertheless, the mortality by poisoning remained above 97%.

The test results indicated that the 25% MTMC diluents were partially transmitted into the tree branches through root burial and irrigation, thereby affecting the vitality of some insects with piercing and sucking mouthparts that fed on these branches. The most evident manifestation was the marked reduction in ACM bubbles following the pesticide treatment. ACM has a large food intake, which needs to secrete bubbles during feeding. The mortality was rather high since this spittlebug species sucked the 25% MTMC that was mixed into the bubbles. The degree of ACM susceptibility against 25% MTMC varied by the dilution level of the pesticide. Hence, the 1000X diluent of 25% MTMC had a stronger insecticidal efficacy against ACM.

Table 4. ACM Insecticidal Experiment Tests with 25% MTMC Diluent and Clear Water

Pesticide type	Conc.	Test date	Exam. date	Number of plants tested	Number of twigs examined	Number of ACM surveyed	Number of live ACM	Number of dead ACM	Mortality (%)	Instar of ACM tested
25% MTMC diluent	500X 1000X 1500X 2000X	6.3	6.4	2 2 2 2	10	100	0	100	100 100 100 100	1-2
Control	Clear water	6.3	6.4	2	10	100	98	2	2	1-2
25% MTMC diluent	500X 1000X 1500X 2000X	6.20	6.21	2 2 2 2	10	100	4 2 8 13	96 98 92 87	96 98 92 87	3-4
Control	Clear water	6.20	6.21	2	10	100	100	0	0	3-4
25% MTMC diluent	500X 1000X 1500X 2000X	7.5	7.6	2 2 2 2	10	100	5 3 10 15	95 97 90 85	95 97 90 85	5
Control	Clear water	7.5	7.6	2	10	100	100	0	0	5

Table 5. Selected Physical and Chemical Properties of Dark Brown Soils

Statistical Index	Soil horizon			(g•kg^{-1})	(g•kg^{-1})	(g•kg^{-1})	pH
		Bulk Density (g•cm^{-3})	Organic Matter (g•kg^{-1})	Total-N (g•kg^{-1})	Total-P (g•kg^{-1})	Total-K (g•kg^{-1})	
Mean	A	1.33	33.85	1.47	1.28	19.61	5.92
	AC	1.41	16.42	0.82	0.99	19.14	6.38
	C	1.46	8.21	0.53	0.66	20.61	6.78

Adsorption and Desorption of Various 25% MTMC Diluents in Soil

Physical and chemical properties of dark brown soil

Dark brown soil was collected from the Qingmei Experimental Forest Farm of Heilongjiang Forestry Vocation–Technical College. During sampling, surface debris was removed initially, and then soil samples were collected at 5 to 20 cm depths of surface layers by five-point method, which were mixed uniformly and air-dried, followed by removal of organic matters by KBrO oxidation, removal of free iron by sodium hydrosulfite–sodium citrate–sodium bicarbonate method, and removal of calcium carbonate by dilute HCl leaching. All of the processed soil samples were ground, passed through a 300-mesh sieve, and dried. The specimens were then sealed inside double-sealed plastic bags plus kraft paper and placed in the drier for subsequent experimentation. Table 5 details the physical and chemical properties of dark brown soil.

The experimental region, Mudanjiang, is located in the southeast of Heilongjiang Province, on the east side of Zhangguangcai Mountain. Since the Mesozoic Era, low mountains, hills and plains have been formed in the region due to the tectonic movements such as ridging, subsidence and faulting. From southwest to northeast, mountains, hills, valleys, and depressions are intersected. Regarding vegetation, mixed broadleaf-conifer forests, secondary broadleaf forests, sparse forest meadows and swamp communities are distributed from high to low areas. These soil-forming factors constitute the dark brown soil in the present experimental forest farm. According to the XRD pattern, the peaks at 3.38, 2.28, and 1.83 indicate that the dark brown soil contained quartz components, whereas the peaks at 3.19 and 2.45 indicate mica components. Additionally, the peak at 4.45 indicates that the soil contained agalmatolite, and the peaks at 2.45 and 1.62 represent kaolinite and montmorillonite, respectively. As shown in Fig. 3, the clay minerals of dark brown soil were dominated by quartz, which were accompanied by small amounts of agalmatolite, mica, and kaolinite.

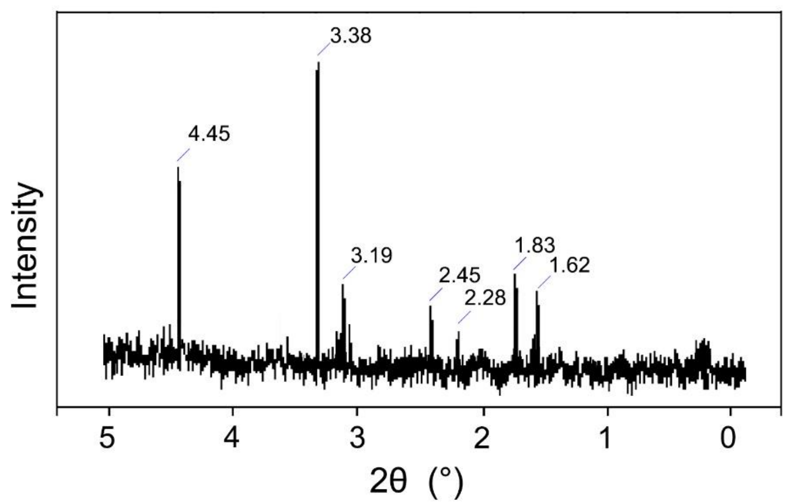

Fig. 3. XRD pattern of dark brown soils

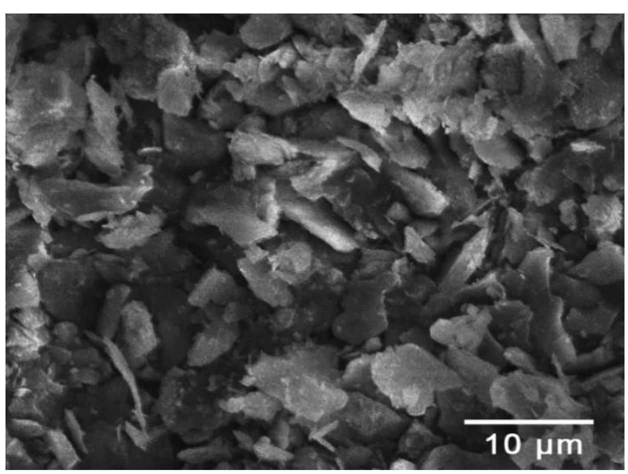

Fig. 4. SEM image of the clay mineral particles of dark brown soils

Scanning electron microscopy (SEM) found that the clay mineral particles of the surveyed soil were in a layered structure, with a distinct heterogeneity on the surfaces. The clay minerals had smooth surfaces, as shown in Fig. 4.

Adsorption–desorption kinetics of 25% MTMC in soil

The main determinant of the migration and fate of pesticides in the soil environment is their adsorption and desorption behavior in the soil. The environmental behaviors such as migration, transformation, and degradation of pesticides in the soil depend on their adsorption capacity. Therefore, it is of great significance to study the adsorption and desorption behavior of MTMC on soil for rational application of insecticides and reducing soil environmental pollution. As shown in Fig. 5, the MTMC adsorption capacity by the tested soil increased rapidly within 2 h of the adsorption initiation, which then fluctuated between 2 and 16 h. The reason was that partial adsorption surface area of the soil was wrapped inside the particles, while the MTMC molecules bonded loosely to the soil underwent desorption. Later, the internal particles in the soil were exposed gradually, so that the free MTMC molecules had a chance to adsorb on the newly added solid surface sites, thereby resulting in a progressive increase in adsorption capacity, which peaked at 16 h. Afterwards, the adsorption process tended to equilibrium with decreasing gradient concentration.

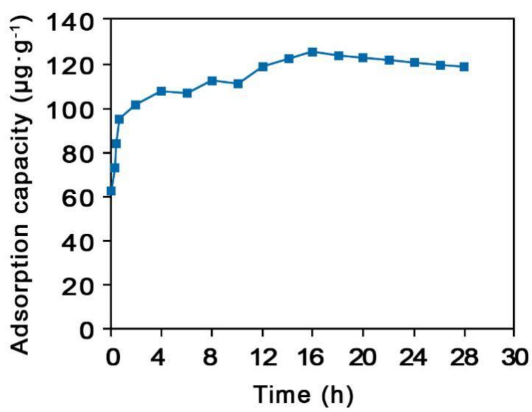

Fig. 5. The kinetic adsorption curve of MTMC on dark brown soils

Desorption defines the reverse desorption behavior of pesticides adsorbed in soil, which has an important impact on the orientation of pesticides at later stages. The equilibrium time of adsorption experiment was set to 24 h herein, in order to ensure the adsorption equilibrium of MTMC in the tested soil. As is clear from Fig. 6, the MTMC desorption capacity increased gradually within 2 h and the curve fluctuates up and down in the second to twelfth hour period. The reason for this finding is that soil particles also adsorb MTMC molecules while desorbing them. With prolongation of time, the desorption capacity tended to stabilize after 12 h, which differed insignificantly from the kinetic adsorption experiment. Nevertheless, the maximum desorption capacity was considerably lower than the adsorption capacity, which was around 12 $\mu g \cdot g^{-1}$. This suggests that the adsorption experiment was easily accomplished, without showing much reversibility. The results indicated that the desorption of MTMC in soil took place and that there was hysteresis in the desorption process. The desorption line followed the fitted curve of the Freundlich model and differed from the adsorption line because of the nature of pesticides and the migration of pesticides due to the time duration of interaction between pesticides and soil.

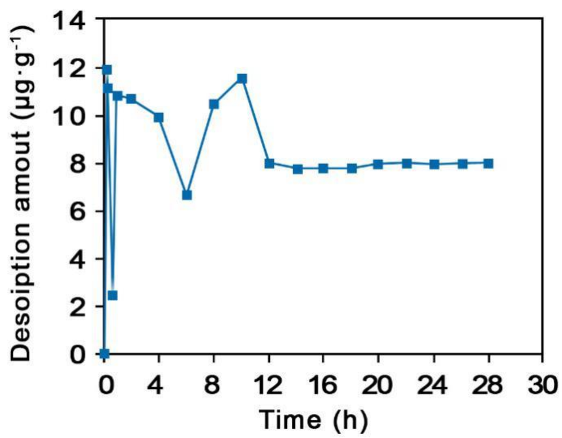

Fig. 6. The kinetic desorption curve of MTMC on dark brown soils

Mobility of 25% MTMC in Soil

The soil collected from the present experimental forest farm was dark brown soil. In Table 6, the mobility measurements of MTMC in the dark brown soil are presented. As is clear, MTMC was moderately mobile in the dark brown soil, which was probably associated with the modest sand grain content and high clay particle content in the soil. Since dark brown soil contained substantial clay particles, the MTMC adsorption by soil colloids was relatively optimal. Besides, the moderate mobility was also linked to the high pH of dark brown soil. The decrease in soil pH would increase the net charge of the pesticide, thereby enhancing the pesticide adsorption.

Table 6. Migration Behavior of MTMC in Dark Brown Soils

Type	R_f	Migration rate m/(cm•h$^{-1/2}$)	Mobility
Soil horizon A	0.38	2.36	Moderate migration (0.35 to 0.64)
Soil horizon AC	0.41	2.62	Moderate migration (0.35 to 0.64)
Soil horizon C	0.48	3.53	Moderate migration (0.35 to 0.64)

Leachability of 25% MTMC in Soil

Table 7 details the leaching properties of MTMC in dark brown soil. As is clear, the leaching extent of MTMC was a moderate 49.8%. This was attributed to the high content and good adsorption capacity of clay particles in the dark brown soil.

Table 7. Leaching of MTMC in Dark Brown Soils

Soil	Sampling frequency (50 ml of leachate per time)										Total leaching (%)
	1	2	3	4	5	6	7	8	9	10	
Dark brown soil	25.8	14.1	4.7	3.2	1.9	0.8	0.0	0.0	0.0	0.0	49.8

Effects of leachate volume on the leaching amount of 25% MTMC in soils

In Fig. 7, the effects of leachate volume on the MTMC migration in several different soils are illustrated. As is clear, the leaching amount of MTMC from soils increased with enlarging leachate volume. Nevertheless, at leachate volumes greater than 350 mL, almost no outflow of MTMC was noted from the dark brown soil, which suggested saturation of the leachate. This further proved the probable high adsorption capacity of MTMC in the dark brown soil.

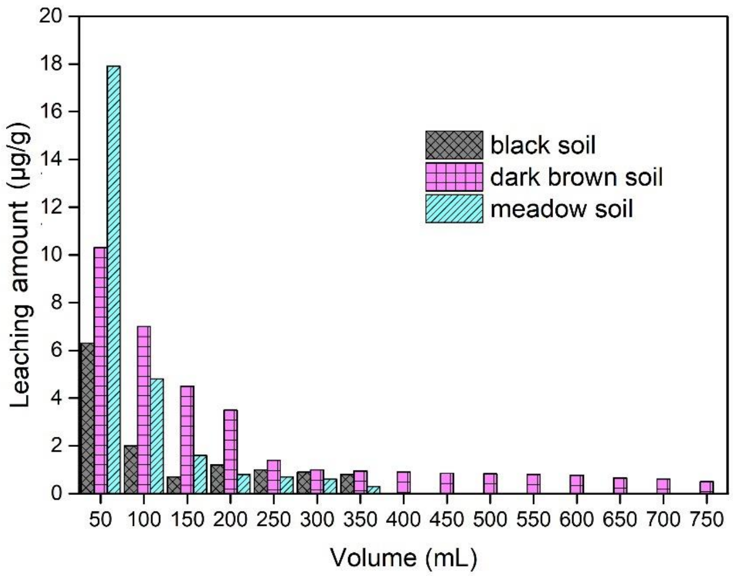

Fig. 7. Leaching amounts of MTMC on dark brown soils

Effects of leachate pH on the leaching and migration of 25% MTMC in soil

In Fig. 8, the effects of leachate pH on the leaching and migration of 25% MTMC in dark brown soil are depicted. According to the figure, the pH values of leachates were greatly influential to the MTMC leaching rates. The weakly acidic conditions in dark brown soil were conducive to the leaching of MTMC. The leaching ratio of 25% MTMC rose with deepening of soil horizon, whereas tended to drop with elevating pH. At a pH of 9, the leaching ratio was the lowest, with a value of 41.63%.

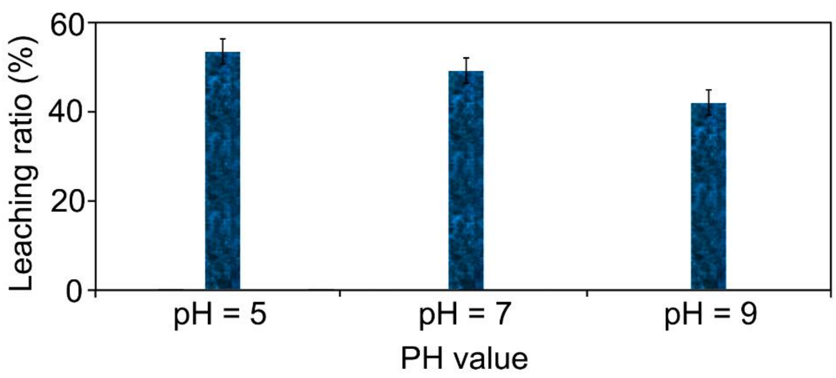

Fig. 8. Effects of leachate pH on the MTMC leaching in dark brown soils

As a molecular pesticide, the migration of MTMC was affected primarily by the content of soil organic matter after entering the soil, followed by the content of clay particles. For dark brown soil, the organic matter content was 33.85 g•kg^{-1} in the A horizon, 16.42 g•kg^{-1} in the AC horizon, and 8.21 g•kg^{-1} in the C horizon. The MTMC migration was slower during passage through the A horizon, while turned faster after entering the AC and C horizons. Thus, while capable of controlling the ACM pests from egg stage to adult stage, the application of MTMC also had moderate mobility after entering the soil, which posed a certain risk of groundwater pollution. Hence, measures such as physical adsorption or microbial and chemical degradation should be taken to mitigate the pesticide pollution of waters effectively, in order to maintain the ecological equilibrium of water environments and to ensure the sustainable development of mankind.

CONCLUSIONS

On the basis of using the best amount of meta-tolyl-N-methylcarbamate (MTMC) to kill insects, this paper discusses the migration and leaching behavior, pH value, and adsorption–desorption kinetics of MTMC in soil environment. The following conclusions were drawn:

1. *Aphrophora costalis* Matsumura (ACM) has one generation a year, and it overwinters in egg form. By late April of the following year, the overwintered eggs begin to hatch in succession. Adults appear in late June, mating begins in mid-July, and spawning ends in early October. The newly-laid eggs overwinter in the current-year shoots. The average pest period is 40.5 d for nymphs, while is 77 d for adults. With a strong flying ability, ACM adults can fly 20 to 50 m at longest and 4 to 8 m at highest.
2. Mid-May is the optimal control time, during which the root burial of 25% MTMC granules achieves best efficacy, with a mortality of up to 94.4%. In the case of root irrigation, 25% MTMC diluent (1000X) exhibits best control efficacy, with a mortality reaching 87.8%.
3. For dark brown soil, the clay minerals are primarily quartz with small amounts of agalmatolite, mica, and kaolinite. The clay mineral particles are layered structures with a distinct heterogeneity on the surfaces. The surfaces of the clay minerals are smooth.
4. The MTMC adsorption capacity by the dark brown soil rises rapidly within 2 h of the adsorption initiation, which then fluctuates between 2 and 16 h and peaks at 16 h. Afterwards, the adsorption process tends to equilibrium with decline in the gradient concentration. The desorption capacity of MTMC exhibits a gradual increase within 2 h, showing a maximum of approximately 12 $\mu g \cdot g^{-1}$, which tends to stabilize after 12 h. MTMC has moderate mobility in dark brown soil.
5. In dark brown soil, MTMC has moderate mobility, with a leaching ratio of 49.8%. With rising pH, the leaching rate tends to decline, showing a minimum of 41.63% at pH 9.

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