Effects of multiple environmental factors on the elimination of methomyl in aquaculture water

Longxiang Fang[1,2,3]**, Chao Song**[1,2,3]**, Jingwei Zhang**[1,2,3]**, Shiyun Zhang**[1,2,3]**,
Cong Zhang**[1,2,3]**, Jiazhang Chen**[1,2,3]**, Shunlong Meng**[1,2,3,*]

[1]**Freshwater Fisheries Research Center, Chinese Academy of Fishery Sciences, 214081 Wuxi, PR China**

[2]**Laboratory of Quality & Safety Risk Assessment for Aquatic Products on Environmental Factors (Wuxi),
Ministry of Agriculture and Rural Affairs, 214081 Wuxi, PR China**

[3]**Key Laboratory of Control of Quality and Safety for Aquatic Products, Ministry of Agriculture and Rural Affairs,
100000 Beijing, PR China**

ABSTRACT: Methomyl is a highly effective broad-spectrum carbamate pesticide that is widely used in the control of pests and diseases in crops. However, few studies have assessed the degradation of methomyl residues in aquaculture environments. In this study, the effects of pH, temperature, illumination, and aerobic/anaerobic conditions in pond water were analyzed to study the degradation pattern of methomyl. The pesticide residues in all treatments were extracted per solid-phase extraction technique and analyzed using liquid chromatography-mass spectrometry. The results showed that the degradation process of methomyl satisfied the first-order kinetics reaction, and the half-life and percent degradation of methomyl ranged from 6.19–49.33 d and 21–97 %, respectively. Simultaneous variance analysis indicated that all the tested experimental factors had a significant effect on the results, with pH being the most significant. We conclude that methomyl was used frequently in summer, and that high water temperature and long illumination contribute to the degradation of methomyl. We provide theoretical guidance for the safer use of methomyl in production by further reducing the risk from methomyl residues and further ensuring the safety of products from aquaculture.

KEY WORDS: Methomyl · Aquaculture water · Environmental factors · Degradation dynamics

1. INTRODUCTION

Methomyl ($C_5H_{10}N_2O_2S$) is a white, crystalline carboximidic acid with a sulfurous odor and a water solubility of 57.9 g l^{-1} (Bonatti et al. 1994, Tomašević et al. 2010). It is a carbamate insecticide, and is also an environmental estrogen that is soluble in most organic solvents and has stable chemical properties (Howard 1990, Amer et al. 1996). It can be combined with numerous insecticides for the production of compound insecticides and is widely used in the prevention and control of cotton bollworm, cotton aphid, and phasmids, to name a few (Meng et al. 2013a). The insecticidal toxic mechanism is the inhibition of acetylcholinesterase activity in the insect body (Elaswad & Badawy 2015), resulting in the excessive excitement and paralysis, and ultimately death, of insect pests. The insecticide acts quickly, can kill both insects and eggs, and is widely used in agricultural and forestry production (Litchfield 1996, Meng et al. 2013a). Globally, methomyl is significant in the prevention and control of pests and is also associated with increased agricultural production and profits (Litchfield 1996).

Only about 1 % of applied pesticide reaches the targeted organisms, while the rest remains in the soil or enters water bodies through direct drainage, surface runoff, leaching, or dry and wet deposition, and this is believed to adversely affect soil and aquatic organisms (Meng et al. 2016). Due to the high solubility of

methomyl in water and its unregulated discharge in agricultural production, methomyl residues have been detected in water and aquacultural products. These residues may be harming the aquatic ecosystem, and thus pose a threat to water for human use and to fisheries (Strathmann & Stone 2001, Munshi et al. 2012). Once methomyl enters into the water, it can affect the early growth, sexual differentiation, reproduction, and resource distribution in fish (Meng et al. 2013a). For instance, Meng et al. (2014a) reported that methomyl is highly toxic to tilapia *Tilapia mossambica* and disrupts endocrine functioning, resulting in abnormal reproductive organs, reproductive functioning and reproductive behavior, thereby causing declines in fertility and damage to biological reproductive functioning. This may lead to population decrease and ultimately species extinction (Gupta et al. 1994, Meng et al. 2013a, Meng et al. 2014b).

The level of pesticide residues in soil and water depends primarily on the pesticide half-life, its water solubility, soil migration, and the amount of pesticide applied. The T0.5 (half-life) of methomyl in soil varies with soil properties and other factors, generally ranging from a few days to 50 d (Leistra et al. 1984, Scoy et al. 2013). Furthermore, soil properties also have an impact on the migration and adsorption capacity of methomyl in the soil. Typically, humus has a higher adsorption capacity than clay (Cox et al. 1993). Field experimental studies indicated that only 2% of methomyl remained 1 month after application (Leistra et al. 1984). This suggests that it may not be present as a residue for a long period of time or in a large quantity in the soil in the areas where it is applied. Due to its strong migration and long half-life in soil, it may enter the water via surface water runoff or groundwater (Xu et al. 2016). Studies have found that the half-life of methomyl is greater in water than in soil, and the hydrolyzed half-life in 3 different aqueous solutions (pH of 6, 7, and 8) were 54, 38, and 20 wk, respectively (Yang et al. 2005a, Scoy et al. 2013). This indicates that it may exist in water for a long period of time, causing large quantities of residues in water, which may be harmful to aquacultural products.

Studies have increasingly focused on the techniques for monitoring and measuring methomyl, such as the inspection measurement method (Fernandes et al. 2011, Mirmohseni & Houjaghan 2013), as well as techniques for removal (Micó et al. 2010, El-Geundi et al. 2012). Further, the toxicological effects and the complex changes in soil and its residues in aquacultural products (Hu et al. 2010, Kim et al. 2013), and the combined effect of its toxicity with other pesti-

cides (Meng et al. 2014c, Meng et al. 2016) have also been studied. The present study evaluated the degradation dynamics of methomyl using orthogonal experimental analysis of environmental factors. In this experiment, pH, temperature, covered or open types of experimental glass cylinder, and illumination time were used as impact factors, and the corresponding levels were set based on the breeding cycle and environmental conditions. Liquid chromatography-mass spectrometry (LC-MS) was then used to assess the real-time quantitative degradation. In addition, we explored the relationship between various factors and the elimination rate of methomyl in attempt to find a fast and effective way to reduce the residue of methomyl in water and ensure the safety of aquatic products.

2. MATERIALS AND METHODS

2.1. Instruments and reagents

The instruments used in this study included an LC-MS (Waters), a precision acidity meter (pHS-3C, Shanghai INESA Scientific Instrument), and a solid-phase extraction (SPE) system with vacuum manifolds (Shanghai ANPEL Laboratory Technology).

Standard of methomyl (purity > 97%) was purchased from Shanghai Focus Biotechnology. The methanol used in this study was chromatography-grade and was purchased from Merck. All the standards used in this study were dissolved in methanol and stored at −20°C. HCl (1 and 5 mol l⁻¹) and NaOH (1 and 5 mol l⁻¹) solutions were used to adjust the pH value of the water used in the experiment.

2.2. Orthogonal experimental design

Considering that dissolved oxygen, pH, water temperature and illumination are the main factors affecting the duration of methomyl residues in the environment (Gundersen et al. 1997, Tao & Tang 2004, Zhao 2009,), we selected an open or covered system, pH, temperature and illumination as the influencing factors. The levels of the selected factors were determined based on the pond environmental factors during the experimental period. The orthogonal table was designed using Minitab software, with 2 systems (open or covered) and 3 environmental factors (pH, temperature, illumination), each at 3 levels, creating a total of 18 treatments, i.e. L18(2 × 3³); see Table 1.

The covered treatments were covered with trans-

Table 1. L18 (2×3^3) Orthogonal experimental design scheme and the experimental conditions of 18 groups. Each group had 3 replicates

Treatment	System	pH	Temp. (°C)	Illumination (h)
1	Open	5	20	4
2	Open	5	25	12
3	Open	5	30	20
4	Open	7.5	20	4
5	Open	7.5	25	12
6	Open	7.5	30	20
7	Open	10	20	12
8	Open	10	25	20
9	Open	10	30	4
10	Covered	5	20	20
11	Covered	5	25	4
12	Covered	5	30	12
13	Covered	7.5	20	12
14	Covered	7.5	25	20
15	Covered	7.5	30	4
16	Covered	10	20	20
17	Covered	10	25	4
18	Covered	10	30	12

parent plastic wrap to create an anaerobic environment, whereas the open treatments were not covered (aerobic environment). The pH value of the water was adjusted using NaOH and HCl solution, and the pH of the water was corrected daily. Furthermore, water temperature was controlled by a heating device (50 W heating rod), and air conditioning was used to reduce water temperature fluctuation. Lighting was controlled by an external lighting device (30 W fluorescent lamp, cool white light, wavelength 450 peak nm) at around 2500 lux, and the lighting period was controlled using a timing converter. According to the orthogonal design of the software (Minitab 16), there was a total of 18 experimental trials (Table 1), and each treatment was set up in 3 parallel groups, resulting in 54 cylinders. The initial concentration of methomyl in each cylinder was 20 µg l^{-1}. The water samples were sampled 7 times within 31 d (sampled at 0, 7, 14, 18, 23, 27 and 31 d) to determine the changes in methomyl concentration in the water using LC-MS.

2.3. Sample analysis

To ensure a uniform sample, we mixed the experimental water evenly and filled a 20 ml water sample from 10 cm below the surface in each glass cylinder and placed it in a 50 ml centrifugal tube. Each time

54 water samples were collected. In the covered system, only part of the plastic wrap was opened, thus the dissolved oxygen content was not affected by the rapid stirring and sampling. Then, all the samples were extracted and concentrated using SPE. A Waters HLB extraction column was used and activated with 5 ml of methanol and 5 ml pure water, the water samples were added, and finally, the column was eluted twice with 2 ml methanol and 3 ml methanol. The eluent was collected and shaken well and diluted with methanol once, filtered using a 0.22 µm organic phase filter membrane, and transferred into the 1.5 ml Waters sample vial, in preparation for analysis.

The pesticide residues in all samples were analyzed by LC-MS. The chromatographic separation method was as follows. Chromatographic column: ACQUITY UPLC BEH C18 column, 2.1 × 100 mm, i.d. = 1.7 µm; column temperature: 30°C; flow: 0.3 ml min^{-1}; injection volume: 5 µl. The liquid phase was as follows: Solution A: 0.1% formic acid water, Solution B: acetonitrile. The gradient conditions are given in Table 2.

Scanning by mass spectrometry and sample ion collision, we obtained the parent ion (163.136) and 2 daughter ion (88.062 and 106.088) fragments of our target compound; one of them (88.062) was selected as the quantitative ion. The cone voltage was 22 V, and the collision was 14 V and 12 V, the retention time was 1.24 min. The LC-MS TIC (total ion mass spectrometry) and quantitative ion spectra are shown in Fig. 1.

Mass tuning parameters were as follows. Ion source: positive electrospray ionization (ESI +); detection pattern: multiple reaction monitoring (MRM); capillary voltage: 3.5 kV; cone voltage: 30 V; source temperature: 450°C; desolvation temperature: 450°C; desolvation: 800 l h^{-1}; cone: 50 l h^{-1}.

Considering the degradation of methomyl in water during the experiment, the gradient standard solution was prepared in the range of 1–50 µg l^{-1}. A

Table 2. Flow phase and gradient elution conditions of LC-MS. A: 0.1% formic acid water; B: acetonitrile

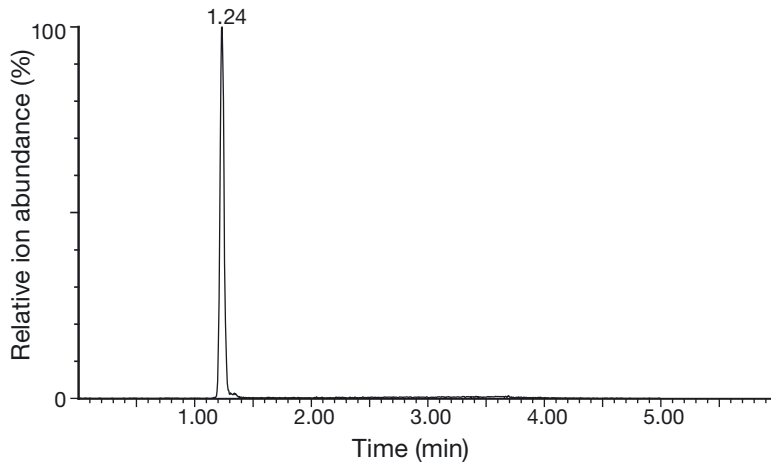| Time (min)	Flow (ml min^{-1})	A%	B%	Curve
Initial	0.3	90	10	Initial
2.5	0.3	10	90	3
3	0.3	50	50	6
3.5	0.3	90	10	6
5	0.3	90	10	6

Fig. 1. Liquid chromatography-mass spectograph of methomyl showing the total ion mass spectrum. Concentration of methomyl is 20 µg l^{-1}

blank sample was run both before and after the treatment, the standard recovery range was 78.3–115.3%. The selected daughter ion 88.062, corresponding to the response peak area for ion quantitation, was monitored, and external standards were used for the quantitative calculation of the samples.

2.4. Statistical analysis

Based on the mass detection, the first-order reaction kinetics equation was used to calculate the methomyl concentration in the water at various time periods. If a reaction has a single reactant and the value of the exponent is 1, then it is said to be a first-order reaction. First-order reactions have many applications, such as in human body drug absorption and elimination and in pollutant degradation (Rehbein et al. 2017). The equation is as follows:

$$C_t = C_0 e^{-kt} \tag{1}$$

where C_t represents the concentration of methomyl at time t, C_0 is the initial concentration of methomyl, t is the duration, and k is the elimination rate constant. T0.5 is calculated by the following equation:

$$T0.5 = (\ln 2) k^{-1} \tag{2}$$

Finally, a range analysis was carried out on the results using the Rj values to determine the factors influencing the degradation situation of methomyl (K1, K2 and K3 are the averages of the different levels under the same conditions, Rj presents extreme differences in the data under the same treatment condition, namely as maximum K-value minus the minimum K-values).

Statistical analyses were done using SPSS19.0. All data are expressed as mean ± SE (n = 3), significance differences were analyzed with a general linear model (ANOVA), the response value was 54 sets of half-life data, and the model was composed of 4 factors, pH, temperature, illumination and open or covered system. The analytical results of half-life data were calculated, and the adjusted SS was used in the test. Data were tested for normality of distribution (Shapiro-Wilk test) and homogeneity of variance (Levene's test) prior to analysis. Data that did not meet assumption of normality and homoscedasticity were transformed (log$_{10}$) and then analyzed by a general linear model ANOVA, and the orthogonal results were analyzed using Minitab at a 95% confidence level (α = 0.05). We expressed the average results of each treatment; the figure data were processed and analyzed using Origin 9.1 (https://baike.baidu.com/item/origin/503423?fr=aladdin).

3. RESULTS

3.1. Degradation

Under the experimental conditions, T0.5 and elimination rate of methomyl ranged from 6.19 to 49.33 d and 0.34 to 0.96 (Fig. 2), respectively. The degradation effect of Treatment 18 (pH = 10, temperature = 30°C, illumination = 12 h) was the most obvious, with T0.5 = 6.19 d and average elimination rate of 0.96. Treatment 4 (pH = 7.5, temperature = 0°C, illumination = 4 h) showed the slowest degradation rate, with T0.5 = 49.33 d and average elimination rate of 0.34. The other treatments showed different degrees of degradation. Most of the experimental groups reached T0.5 within 30 d. It is thus evident that the treatment had a significant effect on the degradation rate of methomyl.

3.2. Environmental factors

As shown in Table 3, T0.5 of the Rj values were as follows: within the scope of the level set by the experiment, pH had the greatest effect on degradation, followed by temperature and illumination, while the open or covered treatments had the smallest effect. ANOVA indicated that the influence of pH on
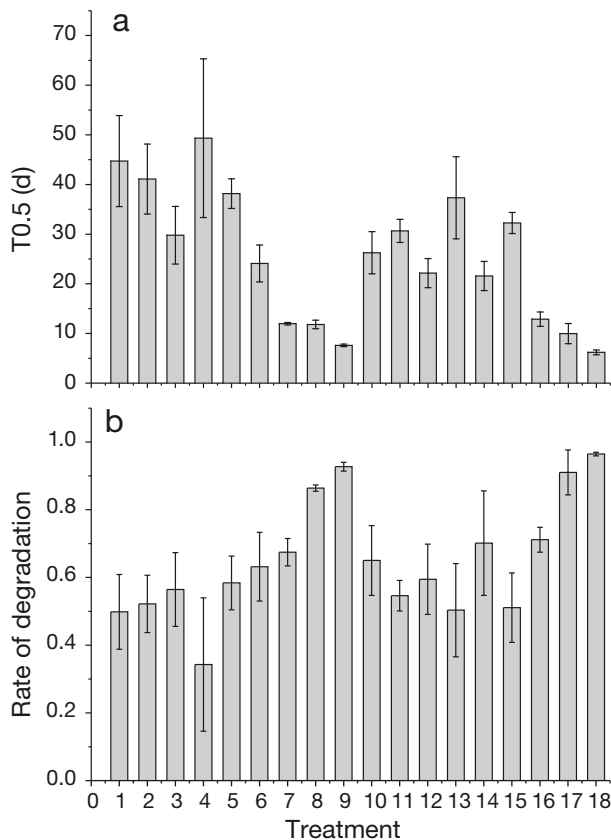
Fig. 2. (a) The half-life (T0.5) and (b) elimination rate of methomyl according to treatment. See Table 1 for treatment details

Table 3. Analysis of the half-life data (d) of the L18 (2×3^3) orthogonal experiment. K1, K2 and K3 are the averages of the different levels under the same conditions, Rj presents extreme differences in the data under the same treatment condition

	Open or covered	pH	Temp.	Illumination
K1	28.733	32.449	30.413	29.091
K2	22.144	33.795	25.549	26.154
K3	–	10.071	20.353	21.070
Rj	6.589	22.378	10.060	8.021

Table 4. ANOVA of the half-life data of the L18 (2×3^3) orthogonal experiment. SeqSS: continuous SS; adjSS: adjusted SS; adjMS: adjusted MS. Data are significant at $p < 0.05$

Factor	df	SeqSS	AdjSS	AdjMS	F	p
Open	1,10	195.36	195.36	195.36	8.24	0.017
pH	2,10	2130.76	2130.76	1065.38	44.94	0
Temperature	2,10	303.77	303.77	151.88	6.41	0.016
Illumination	2,10	197.62	197.62	98.81	4.17	0.048

methomyl degradation was highly significant ($p < 0.05$). The effects of illumination, temperature and the type of system (open or covered) were also significant, as shown in Table 4.

4. DISCUSSION

The T0.5 of methomyl ranged between 6.19 and 49.33 d and varied with treatment. The factors influencing degradation were in the following order of importance: pH > temperature > open or covered > illumination (Table 3). It is evident that all the 4 environmental factors had significant effects on the rate of degradation (Table 4). The effect of pH on methomyl degradation was particularly significant and was consistent with range analysis results.

4.1. pH

The concentration of acid and alkali can significantly affect the mobility of ions in water systems (Chen et al. 2004). In the present study, 3 pH values (5, 7.5, and 10) were selected to elucidate the effect of pH on the degradation of pesticide in fishpond water. Tables 3 & 4 show that pH has a significant influence on the degradation rate of methomyl. The degradation of methomyl in alkaline water was faster (Table 3). This is in agreement with Yang et al. (2005a,b) who found that the amount of degradation of an organic compound in water is strongly dependent on its existing form (Gundersen et al. 1997). Methomyl is a polar carbamate pesticide that easily hydrolyzes at high pH values (Elaswad & Badawy 2015). A hydrolyzed molecule is more easily adsorbed in water due to its higher hydrophobicity compared to an unhydrolyzed molecule.

The effect of pH as observed in this study can also be explained by the fact that an increase in pH may enhance the release of organic matter into the solution and consequently result in an increasing rate of pesticide degradation (Tao & Tang 2004). In addition, a high pH value, or presence of Na^+ and other cationic species, provides more cation-exchange sites in the water compared to water with low pH, where H^+ is the dominant species (Gundersen et al. 1997). This would increase relative availability and increase the degradation rate of methomyl under higher pH values.

In an aquaculture system, the pH of water is reduced by the CO_2 emitted by aquatic animals such as fish and the acid produced by nitrifica-

tion reactions, and a low pH will have a very adverse effect on fish growth (Sipaúbatavares et al. 2016, Kurzbaum et al. 2017). Therefore, pH plays an important role in maintaining the stable operation of fishpond systems. This is consistent with the common practice in fish farms of sprinkling quicklime into a pond at the end of the farming season (Keiblinger et al. 2016), which not only rapidly kills various pathogenic bacteria and promotes the rapid degradation of residual pesticides, but also neutralizes the acidic environment, keeps the pond slightly alkaline, and provides calcium ions for the nutrition of aquatic plants and animals.

4.2. Temperature

Three water temperatures (20, 25, and 30°C) were used to assess how temperature influences the degradation behavior of methomyl (Table 1). Our results showed that the rate of degradation of methomyl in water increased with temperature (Table 3). It is well known that pesticide degradation is a process whereby activation energy is released. The increase in temperature destroys the former steady-state equilibrium, resulting in the degradation equilibrium shifting to the elimination reaction in which a lot of energy is absorbed (Tao & Tang 2004, Pookmanee et al. 2014). As a result, the amount of methomyl decreased with increasing temperature. Zhao (2009) reported a similar phenomenon whereby the elimination rate was positively correlated with temperature within a certain range of pesticide concentrations. Additionally, the dissolvable organic components in water increase because chemicals are generally easily dissolved into solution under increased temperature (Zhao et al. 2003).

4.3. Open or covered cylinders

In this experiment, open (aerobic) and covered (anaerobic) cylinders were used to compare the differences in biodegradation between aerobic and anaerobic systems. When organic pollutants undergo biodegradation, oxygen is one of the important factors that participates in and promotes biodegradation. Our results indicated that the degradation rate in covered cylinders was higher than in the open cylinders, which was unexpected. This is in contrasts with the results of Tai et al. (2018), who found that dissolved oxygen was necessary for the biodegradation of methomyl in aquatic water. One possible ex-

planation is that anaerobic bacteria were the dominant species in this system, and thus the biodegradation pathway was more suitable (Chen et al. 2015, Kulkarni & Kaliwal 2018, Parween et al. 2018). This phenomenon deserves further investigation.

4.4. Illumination period

Our results indicated that the illumination period greatly influenced the elimination rate and T0.5. Other studies (Tomašević et al. 2010, Abaamrane et al. 2012, Benhamouda et al. 2017) also found that pesticides were significantly degraded under UV radiation, and no obvious photolysis of methomyl was observed under natural light and in the dark.

5. CONCLUSIONS

In the present study, the influence of pH, temperature, illumination, and an open (aerobic) or covered (anaerobic) system on the degradation of methomyl was investigated. We discovered that these 4 environmental factors distinctly influenced the degradation of methomyl. When these factors are properly adjusted according to the natural environmental conditions, this can effectively reduce the amount of pesticide residues in water and ensure better water quality. In view of the complexity of factors affecting ponds, as well as the various sources of methomyl, the ecological effects of methomyl residues in ponds still deserve further investigation. After understanding the effects of natural factors on the elimination dynamics of methomyl in aquaculture ponds, studies should be conducted to investigate the effects of various culture dynamics on the elimination of methomyl to better reduce the risk from methomyl residues and to further ensure the safety of aquacultural products.

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