

Article

Effects of Granule Size Ranges on Dazomet Degradation and Its Persistence with Different Environmental Factors

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Abstract: Pesticides are considered the most effective way to protect crops. However, irrational use has caused resources waste and environmental pollution. Dazomet (DZ) is a soil fumigant that has been used in many countries for decades, although it has caused occasional crop damage or insufficient control efficacy in some circumstances. In this study, the effects of DZ's granule size and exposure to various environmental conditions on DZ degradation when used as a fumigant were demonstrated. The degradation rate of DZ was closely related to granule size. The half-life of larger DZ granules was longer than smaller granules with all studied environmental factors. The degradation rate decreased as the DZ usage (90–360 mg/kg) increased and different granule sizes showed the same variation trend. The half-life in each of the five granule size ranges tested decreased significantly as the temperature increased. DZ half-life decreased by 4.67–6.59 times as the temperature increased from 4 to 35 °C. Moreover, DZ usage and temperature affected the half-life of granules >400 and 300–400 µm in diameter significantly more than <100 µm granules. The half-life of all DZ granule sizes was reduced by 13.9–47.4% in alkaline compared to acidic conditions (pH from 9 to 5). Moreover, elevated temperatures could not only promote the production of methyl isothiocyanate (MITC) but accelerate its dissipation. The interactions between DZ granule size, dosage, temperature, and pH provide practical guidance on methods to improve DZ's efficacy against pests and reduce the risk of phytotoxicity.

Keywords: dazomet; degradation rate; granule size range; environmental factor; methyl isothiocyanate



Citation: Ren, L.; Li, W.; Li, Q.; Zhang, D.; Fang, W.; Li, Y.; Wang, Q.; Jin, X.; Yan, D.; Cao, A. Effects of Granule Size Ranges on Dazomet Degradation and Its Persistence with Different Environmental Factors. *Agriculture* **2022**, *12*, 674. <https://doi.org/10.3390/agriculture12050674>

Academic Editor: Borbála Biró

Received: 13 April 2022

Accepted: 7 May 2022

Published: 9 May 2022

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1. Introduction

Pesticides are widely used to control weeds, insects, and plant diseases in modern agriculture. However, the irrational and excessive use of pesticides also causes a series of ecological, environmental, and public health issues. Consequently, improving the utilization efficiency of pesticides and minimizing their potential risk to non-target species is highly desirable in both agriculture and the environment. Soil fumigants are widely used as a pesticide to control soil-borne pests that would otherwise reduce crop production and quality. Moreover, it is often necessary to fumigate soils in glass or plastic structures to prevent the year-on-year accumulation of pests and diseases in soil so that crops can be continually produced for many years [1–4].

Methyl bromide (MB) was a commonly used soil fumigant until its use was completely phased out globally due to its stratospheric ozone-depleting properties. Dazomet (3,5-dimethyl-1,3,5-thiadiazinane-2-thione; DZ) is one of many alternatives that has replaced MB [5–8]. It has been extensively used to control soil-borne plant diseases that affect

high-value crops such as strawberries, tomatoes, flowers, ginger, and cucumbers [9,10]. DZ releases methyl isothiocyanate (MITC) when exposed to moisture, which is toxic to soil-borne fungi, weeds, some soil arthropods, and nematodes [11–13]. Once released, abiotic degradation of MITC by hydrolysis is slow and takes place over months [14]. DZ is a solid microgranule that can safely spread or be mixed into the soil by hand or machine. However, DZ's many decades of use have not been without problems. Growers reported DZ's persistent fumigant residues were sometimes phytotoxic to crops [15]. A survey of seedbed operators in the southern United States showed that nearly 40% of farmers were not satisfied with the performance of DZ [16]. This is because the soil conditions such as temperature, humidity, dosage, soil conditioner, sowing time, application method, and season all affect the fumigation effect of DZ. In addition, the uneven distribution of DZ caused by hand application can result in high concentrations being phytotoxic to emerging crops and low concentrations being insufficient pest control. Moreover, the decomposition rate of DZ into MITC was slow in cold wintery conditions, which reduced fumigation efficacy [17]. Therefore, it is of great significance to clarify the factors that influence the decomposition, migration, and diffusion of DZ. Fang reported that the decomposition rates of DZ differed greatly in various soils, depending mainly on soil physicochemical properties such as pH and organic matter content. This study also pointed out that DZ was degraded in soil mainly by hydrolysis [18].

In commercial practice, we observed some evidence of phytotoxicity after DZ fumigation, such as a lack of seed germination or young plants with yellow leaves and limited plant growth, which caused major losses in agricultural production. Unfortunately, there were DZ residues in the soil more than a month after fumigation in conditions where the soil environmental factors and application dose appeared suitable. DZ produced commercially is required to have more than 85% of its granules between 100–400 microns in diameter [19]. It is possible that the DZ granular size applied to the soil was inappropriate under the circumstances at that time, which prolonged the half-life of DZ in the soil and lead to crop phytotoxicity.

The current researches mainly focus on the impact of environmental factors and application methods on the degradation of DZ [18,20] but the influence of granule size on its dissipation has not been investigated. Therefore, the objective of this study was first to determine the effects of DZ granule size on the degradation rate in water under different environmental conditions, including DZ dose, pH, and temperature. This research seeks to provide a scientific basis for improving the effective utilization rate of DZ based on choosing a suitable granule size according to the practical environmental factors and avoiding crop damage.

2. Material and Methods

2.1. Chemicals and Reagents

DZ with granule size ranges of >400, 300–400, 100–300, and <100 μm diameter were obtained from the Nantong Shizhuang Chemical Company (Nantong, China). MITC (98%, chromatographic pure) was purchased from Macklin Biochemical Technology Co., Ltd. (Shanghai, China). Acetonitrile, anhydrous sodium sulfate, ethyl acetate, H_3PO_4 , NaOH, and glacial acetic acid (all analytical grade) were purchased from the Beijing Chemical Industry Group Company (Beijing, China).

2.2. Effects of Granule Size on the Hydrolysis of DZ under Different Dosages

Different sizes of DZ particles (>400, 300–400, 100–300, <100, and stock solution with DZ dissolved in acetone, denoted as SD) were added into deionized water to make DZ concentrations of 90, 180, and 360 mg/kg, respectively (SD preparation was to explore the hydrolysis behavior of DZ in the molecular state). The dose of DZ was as reported in the previous study [18], and on this basis, low and high were set for a total of three concentrations. Then the DZ aqueous solution was added into a 20 mL clear headspace. The vials were capped and incubated for 2 h, 1, 2, 3, 5, 7 and 11 days (d) at 25 °C. At each

time interval, 10 mL acetonitrile was added to the vials, which were then shaken vigorously for 10 min at 2500 rpm/min before 2 g sodium chloride was added and then shaken for 5 min. Thereafter, the mixture was centrifuged for 5 min at 4000 rpm/min. The supernatant was filtered through a 0.22 μm nylon filter into a 2 mL glass vial for high-performance liquid chromatography (HPLC) analysis. The recovery efficiency of DZ in water ranged from 94% to 105% using HPLC analysis. Data were expressed as the mean value of three independent experiments with a reported standard deviation.

The concentration of DZ was analyzed by HPLC with a Venusil XBP-C8 column (4.6 \times 150 mm, 5 μm ; Agela Technologies Inc.; Wilmington, DE, USA) set in diode array detection (HPLC-DAD). The operating conditions followed those described by Di Primo et al. and Petanovska-Ilievska et al. [21,22]. Specifically, the mobile phase was water that contained 0.2% glacial acetic acid (A) and acetonitrile (B) at the mobile phase ratio of 45:55 (*v/v*); the flow rate was 1.0 mL/min with 20 μL injection volume; the temperatures of column box was maintained at 30 $^{\circ}\text{C}$; and the detection wavelength was 282 nm. The retention time of DZ in the column was 2.4 min. The limit of quantification for DZ in water was 0.05 mg/kg. The dissipation kinetics of dazomet were fitted with the first-order kinetic model:

$$C_t = C_0 \exp(-kt) \quad (1)$$

where, C_t is the DZ concentrations in water at incubation time t , C_0 is the concentration at time zero ($t = 0$), and k (h^{-1}) is the first-order rate constant. The half-life value ($t_{1/2}$) was calculated:

$$t_{1/2} = \ln 2/k \quad (2)$$

2.3. Effects of Granule Size on the Hydrolysis of DZ under Different Temperatures

Deionized water, amended with 180 mg/kg DZ containing the DZ granule size ranges described in Section 2.2, was incubated for 2 h and 1, 2, 3, 5, 7 and 11 d at 5, 15, 25 and 35 $^{\circ}\text{C}$. The DZ extraction and residue quantification procedures followed those described in Section 2.2.

2.4. Effects of Granule Size on the Hydrolysis of DZ under Different pH Values

The hydrolysis study was investigated under three different pH values of 5, 7 and 9. Typically, the pH of the water was adjusted to those levels by adding H_3PO_4 or NaOH. Then, the added DZ in the granule size ranges described in Section 2.2 were incubated for 2 h, and 1, 2, 3, 5, 7, 9 and 11 d at 25 $^{\circ}\text{C}$. The DZ extraction and residue quantification procedures followed those described in Section 2.2.

2.5. Quantification of MITC as a Result of the Hydrolysis of DZ

In order to clarify the production and degradation of MITC in water under different conditions, SD was added into 20 mL clear headspaces containing 5 mL of deionized water to obtain 90, 180, and 360 mg/kg solutions, respectively, which were then placed in an incubator at 25 $^{\circ}\text{C}$. Simultaneously, another 180 mg/kg solution was incubated at 4, 15, 25 and 35 $^{\circ}\text{C}$, respectively. Samples were removed at selected times to determine the MITC concentration.

MITC production was quantified by gas chromatography-mass spectrometry (GC-MS) after first performing liquid-liquid extraction. At each time interval, 0.5 mL of the DZ incubation solution was transferred to a 20 mL headspace vial. Ethyl acetate (5 mL) and anhydrous sodium sulfate (8 g) were added to the solution. Then, the headspace vial was sealed with a Teflon[®]-faced butyl rubber septum and an aluminum crimp. The vial was shaken for 1 min followed by static extraction for 1 h. Subsequently, \sim 1 mL of the supernatant was transferred to a 2 mL vial through a 0.22 pore size filter. GC-MS (5977B GC/MCD, Agilent Technologies Inc., Santa Clara, CA, USA) was performed using the RTX-5MS column (30 m long, 0.25 mm ID, 0.25 μm film thickness, Agilent Technologies Inc.) in the selected ion monitoring (SIM) mode to measure MITC concentration. Helium (99.9999% purity) was used as the carrier gas at a flow rate of 1.5 mL min^{-1} and an inlet temperature

of 250 °C. The oven temperature program was initially set at 50 °C, increased to 100 °C at 10 °C/min, and then held at 100 °C for 2 min. The mass spectrometer program was set in the electron ionization mode at 70 eV. The transfer line and ion source temperature were 230 °C. The qualifier ions were determined to be 45 *m/z* and 73 *m/z*, respectively. The retention time of MITC was 3.5 min.

2.6. Statistical Analysis

The data fitting first-order kinetic equation of DZ degradation was performed by Origin 2019 software (OriginLab Corp., Northampton, MA, USA). The data analyses were performed by the SPSS software (SPSS Inc., Armonk, NY, USA) for ANOVA and the Duncan's new multiple range test for significance analysis. All values reported were the mean of three independent experiments.

3. Results and Discussion

3.1. Effects of Granule Size on the Dissipation Kinetics of DZ Using Different Application Dosages

Currently, the excessive use of pesticides has caused a series of resource waste issues and environmental pollution [23]. Therefore, improving pesticide utilization efficiency and minimizing the potential risk to the environment and non-target organisms has garnered considerable attention in agriculture. Herein, it is highly desirable to study the correlation between DZ dose and granule size. In this study, the DZ degradation data showed a good fit to first-order kinetics (all r^2 values mostly greater than 0.86) with five granule sizes under three application doses (Table 1). The half-life increased with an increased dose within each granule size range. The degradation rates (*k*) of DZ with granule sizes 300–400 and >400 µm were significantly less than those in the <100 µm granule size and SD at DZ application doses of 180 and 360 mg/kg. The degradation rates (*k*) of DZ were statistically similar in all the granule size ranges tested when the DZ application dose was 90 mg/kg. The largest granule size range of >400 µm had the longest half-life of 1.16–4.71 d. On the other hand, SD dissipated the fastest, with a half-life of 1.21–2.86 d at the same application dose. Figure 1 shows the difference comparisons of half-life with five granule sizes between the three usage values. The difference in half-life of granule sizes including >400 and 300–400 µm was significantly greater than that of the granule sizes with <100 µm and SD, indicating that the effect of the usage change on the degradation in half-life in the large granule size range was greater than in the small ones.

Table 1. Degradation characteristics of DZ with different granule sizes in deionized water according to application dose.

Dosage (mg/kg)	Granule Size Ranges (µm)	Rate Constant (<i>k</i>)	Half-Life $t_{1/2}$ (d)	Correlation Coefficient (r^2)
360	>400	0.147 ± 0.003 d	4.714	0.9571
	300–400	0.169 ± 0.012 c	4.101	0.9777
	100–300	0.203 ± 0.015 b	3.414	0.9317
	<100	0.206 ± 0.015 b	3.364	0.9436
	SD	0.242 ± 0.017 a	2.864	0.8680
180	>400	0.308 ± 0.009 d	2.250	0.9362
	300–400	0.332 ± 0.020 d	2.087	0.9380
	100–300	0.439 ± 0.022 c	1.579	0.8983
	<100	0.570 ± 0.080 b	1.216	0.8622
	SD	0.857 ± 0.006 a	0.809	0.9923
90	>400	0.597 ± 0.025 c	1.161	0.9138
	300–400	0.475 ± 0.022 bc	1.459	0.9657
	100–300	0.512 ± 0.024 bc	1.354	0.9512
	<100	0.575 ± 0.043 b	1.205	0.8623
	SD	1.005 ± 0.111 a	0.690	0.9901

Means (N = 3) within the same column followed by the same letter are not statistically different ($p < 0.05$) according to Duncan's new multiple range test.

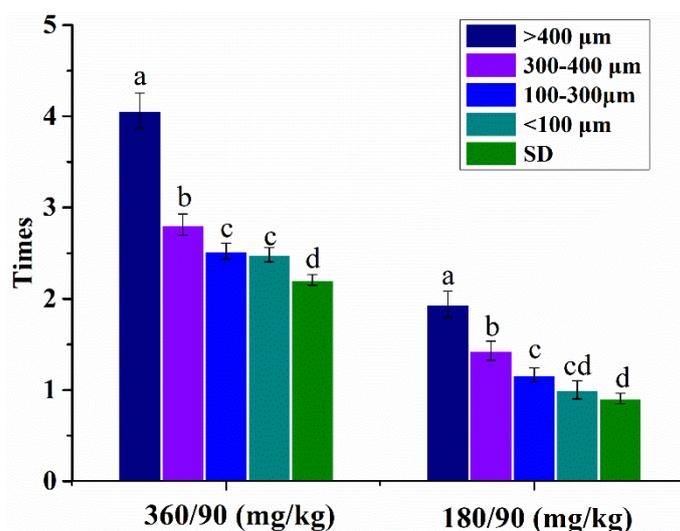


Figure 1. The ratios of DZ half-life values at 360 and 180 mg/kg compared to 90 mg/kg under different DZ particle sizes. Different letters within the same graph indicate a significant difference at $p < 0.05$ level by Duncan's new multiple range test.

Previous studies have shown that hydrolysis was the primary degradation mechanism for the decomposition of DZ in soil [18]. Chemically, DZ falls into the group of dithiocarbamates, a sulfur analog to carbamates or urethanes. It is a cyclic pro-pesticide, which rapidly hydrolyzes in water to form MITC, formaldehyde, and other compounds [14,24]. Guo pointed out that the active ingredient could molecularly achieve a much smaller particle size and larger surface area, which enhances the dissolution rate [25]. Therefore, smaller granule sizes of DZ (<100 μm range and SD) were more easily dissolved in water and then hydrolyzed rapidly compared to the three larger granule size ranges.

The degradation rate decreased significantly as the dose increased, from 90 to 360 mg/kg, and the different granule sizes (Figure S1) showed a similar variation trend (Table S1). The results were consistent with previous studies that reported that increases in dosage in the fumigants allyl-isothiocyanate and dimethyl disulfide were inversely correlated with fumigant degradation [26–28]. Therefore, compared with large granules, small granules of DZ are less likely to cause phytotoxicity to crops at the same dose.

3.2. Effects of Granule Size Range on the Dissipation Kinetics of DZ at Different Temperatures

DZ is a kind of pre-plant fumigant; therefore, the application time varies greatly due to different crop planting times. When DZ was fumigated at low temperatures in winter, its decomposition rate into MITC slowed down, affecting the fumigation effect [17]. Therefore, clarifying the impact of the temperature on the decomposition, migration, and diffusion of DZ is of great significance for improving the fumigation and disinfection effect and avoiding crop phytotoxicity.

Here, DZ hydrolysis with different granule size ranges was investigated at different temperatures. The DZ degradation rate at different temperatures generally followed first-order kinetics, with r^2 ranging acceptably from 0.86 to 0.98 (Table 2). The degradation rate constant k within each granule size range increased significantly as the temperature increased from 4 to 35 °C, where the half-life decreased by 4.67–6.59 times, indicating DZ hydrolysis was sensitive to temperature. For the five granule size ranges, the half-life was a linear function of the temperature (all $r^2 > 0.85$, $p < 0.05$, Figure 2, Table S2). It is well-known that temperature governs most chemical reactions. Previous researches have reported that the degradation of fumigants in soil is strongly dependent on temperature and moisture [29,30] and that the fumigant degradation rate accelerated at elevated temperatures [31,32]. Consolazio et al. indicated that DZ dissipation critically depended on the temperature and that an increase of 23 °C quadrupled the hydrolysis rate [14]. Moreover,

Fang et al. demonstrated that the DZ degradation rate increased by 4.6 and 0.73 times in Beijing and Zhejiang soil types, respectively, at 5 and 30 °C [18].

Table 2. Degradation characteristics of DZ with different granule size ranges in deionized water exposed to temperatures from 4 to 35 °C at a DZ dosage of 180 mg/kg.

Granule Size (μm)	Temperature ($^{\circ}\text{C}$)	Rate Constant (k)	Half-Life $t_{1/2}$ (d)	Correlation Coefficient (r^2)
>400	35	0.414 ± 0.003 a	1.674	0.9317
	25	0.308 ± 0.009 b	2.250	0.9362
	15	0.098 ± 0.003 c	7.071	0.9505
	4	0.063 ± 0.003 d	11.000	0.9716
300–400	35	0.472 ± 0.018 a	1.468	0.9234
	25	0.332 ± 0.020 b	2.087	0.9380
	15	0.132 ± 0.004 c	5.250	0.9818
	4	0.078 ± 0.006 d	8.885	0.9561
100–300	35	0.578 ± 0.014 a	1.199	0.8967
	25	0.469 ± 0.022 b	1.479	0.8983
	15	0.185 ± 0.006 c	3.747	0.9825
	4	0.098 ± 0.004 d	7.071	0.9667
<100	35	0.625 ± 0.014 a	1.109	0.9289
	25	0.570 ± 0.080 a	1.216	0.8622
	15	0.215 ± 0.009 b	3.223	0.9483
	4	0.125 ± 0.008 c	5.544	0.9533
SD	35	0.912 ± 0.029 a	0.760	0.9888
	25	0.857 ± 0.006 a	0.809	0.9923
	15	0.348 ± 0.012 b	1.991	0.9416
	4	0.207 ± 0.010 c	3.354	0.8835

Means ($N = 3$) within the same column followed by the same letter are not statistically different ($p < 0.05$) according to Duncan's new multiple range test.

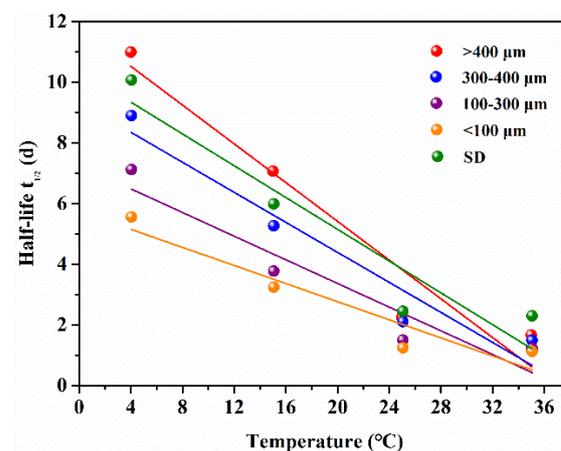


Figure 2. Half-life values of DZ granule size range as a function of temperature.

Of note, the degradation rate of the DZ granule size range $> 400 \mu\text{m}$ at 4°C was 6.57 times lower than at 35°C , whereas the SD was 4.41 times lower than the former, and this difference in the degradation rate was significantly attenuated by the decrease in granule sizes (Table 2, Figure 3), which was consistent with the effects of the usage on the degradation of the different DZ granule size ranges.

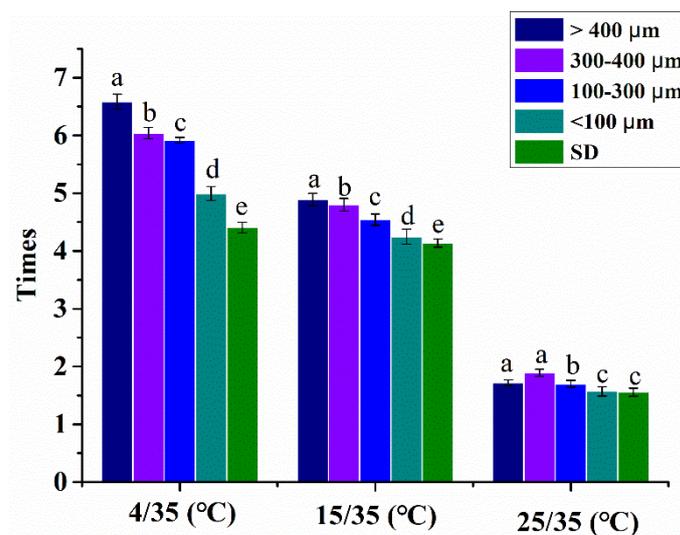


Figure 3. The ratios of DZ half-life values at 4, 15 and 25 °C compared to 35 °C under different DZ particle sizes. Different letters within the same graph indicate a significant difference at $p < 0.05$ level by Duncan's new multiple range test.

In general, temperature and solubility are positively correlated. We observed that large granule sizes of DZ exposed in water to elevated temperatures could be rapidly dissolved in water and then hydrolyzed. Although the dissolution rate was hindered after the temperature decreased and the time of complete dissolution was prolonged, the degradation was deterred. Conversely, the time for complete dissolution and the degradation rate, in the granule size range $< 100 \mu\text{m}$ or in SD, were both less influenced by temperature.

DZ decomposed faster over 5 d at 35 °C than at 4 °C (Figure S2) and the smaller size range granules dissolved faster than the larger ones. There were significant differences in the degradation rate of different granule size ranges at the same temperature, which was observed in all set temperature conditions (Table S3).

3.3. Effects of Granule Size Range on the Degradation of DZ at Different pH Conditions

It is well known that pH, as an important parameter, is often a controlling variable for the abiotic degradation of organic compounds. Therefore, in the present study, the effect of pH was performed at three values that span the range of pH expected in water: 5, 7 and 9. DZ's half-life values in all the granule size ranges decreased as the pH increased from 5 to 7 or 9 (Table 3 and Table S4). The half-life of DZ was reduced by 13.9–47.4% at pH 9 compared with pH 5, indicating that DZ was hydrolyzed more in alkaline than in acidic conditions. There were no significant differences between the DZ half-life values at pH 7 or 5 ($p < 0.05$) in all DZ granule size ranges except 100–300 μm , illustrating that neutral or acidic conditions stimulated DZ hydrolysis similarly and less than pH 9. In addition, there was no significant difference in the effects of pH change on the degradation half-life of the five granule sizes (Figure S3).

The physiochemical properties of soil largely determine the fate of pesticides in the environment, particularly its pH which has a major influence [33]. Our results are consistent with previous studies [34]. The hydrolysis of DZ is also consistent with its chemical reactivity. DZ has an isolated amine nitrogen atom only bound to alkyl groups, which is likely attacked by hydroxide (OH^-) [35]. DZ would probably be primarily protonated and susceptible to base hydrolysis at pH 9 or less. Moreover, the high solubility of DZ promotes the ionization of DZ.

Table 3. Degradation characteristics of DZ with different granule sizes in deionized water at different pH conditions.

Granule Size Range (μm)	pH	Rate Constant (k)	Half-Life $t_{1/2}$ (d)	Correlation Coefficient (r^2)
>400	5	0.272 ± 0.033 b	2.548	0.8573
	7	0.308 ± 0.009 b	2.250	0.9362
	9	0.380 ± 0.027 a	1.824	0.9040
300–400	5	0.326 ± 0.023 b	2.126	0.8920
	7	0.332 ± 0.020 b	2.087	0.9380
	9	0.436 ± 0.011 a	1.59	0.9349
100–300	5	0.449 ± 0.020 c	1.543	0.9674
	7	0.469 ± 0.022 b	1.479	0.8983
	9	0.650 ± 0.045 a	1.066	0.9747
<100	5	0.553 ± 0.019 b	1.253	0.8992
	7	0.570 ± 0.080 b	1.216	0.8622
	9	0.780 ± 0.074 a	0.888	0.8675
SD	5	0.777 ± 0.071 b	0.892	0.9298
	7	0.857 ± 0.006 b	0.809	0.9923
	9	1.129 ± 0.017 a	0.614	0.8850

Means ($N = 3$) within the same column followed by the same letter are not statistically different ($p < 0.05$) according to Duncan's new multiple range test.

3.4. Determination of MITC Produced by Hydrolysis of DZ

MITC is of excellent biological activity against weeds and pathogenic microorganisms; however, it is a sensitizer that irritates the skin, eyes, and respiratory system [36,37]. Abiotic degradation of MITC is limited, and hydrolysis occurs in the order of months [14]. There was a significant positive correlation between the production of MITC and the DZ dose for the duration of this study (Figure 4a and Table S5). Furthermore, DZ doses at 360, 180, and 90 mg/kg produced MITC at an increased rate and peaked at about 16.22, 9.26, and 5.5 mg/L, on days 10 and 6, respectively. The concentrations of MITC remained relatively constant over the remaining 10 days, indicating that the degradation product MITC was more stable in water compared with DZ at 25 °C. MITC production increased most at higher temperatures than lower temperatures (Figure 4b). MITC concentration reached a maximum of 15.9 mg/L on day 2 at 35 °C, which was 1.8–6.6 times higher than that at 4, 15, or 25 °C, and gradually decreased to only 10.3 mg/L on day 10 due to the hydrolysis. On the other hand, the production of MITC reached maxima on days 6 and 8 at 25, 15 and 4 °C, and then remained relatively stable. The result implied that the production and degradation were positively correlated with temperature. Previous studies have shown that the degradation of MITC increased by 2–6 times as the soil temperature increased from 20 to 40 °C. For every 10 °C increase, the degradation of MITC increased by 1.9–3.3 times [31]. The above results implied that the increase in temperature could not only promote the rapid production of MITC but could also accelerate the dissipation of MITC after it was released from DZ.

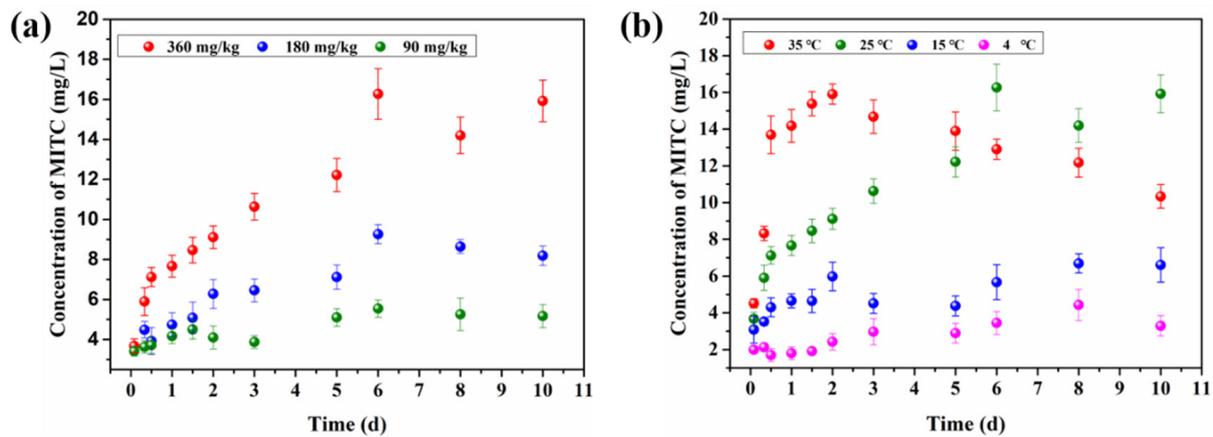


Figure 4. MITC is produced from DZ over time at (a) DZ concentrations of 90, 180, and 360 mg/kg at 25 °C or (b) at a DZ concentration of 360 mg/kg at 4, 15, 25 and 35 °C.

4. Conclusions

In the present study, the effect of DZ granule size ranges with different environmental factors, including application usage, temperature, and pH, on DZ degradation was performed. The granule size ranges had an obvious influence on the DZ degradation rate. The half-life was significantly positively correlated with the granule size range at the same DZ dosage. The half-life of >400 μm granule size was 1.16–4.71 d, whereas the SD was 1.21–2.86 d. Temperature and half-life were negatively correlated. Notably, DZ dosage and exposure temperature had more of an impact on the degradation of large granule sizes (>400 and 300–400 μm) than small ones (<100 μm and SD). The degradation rate of DZ granule size range > 400 μm at 4 °C was 6.57 times lower than at 35 °C, whereas the SD was 4.41 times lower than the former. Moreover, the DZ half-life decreased by 4.67–6.59 times as the temperature increased from 4 to 35 °C. Furthermore, the DZ persistence in all granule size ranges decreased as the pH increased. The half-life of DZ was reduced by 13.9–47.4% at pH 9 compared with pH 5. MITC increased with increasing DZ usage and it was more stable in water than DZ. In addition, increased temperatures promoted its simultaneous production and degradation. This study may be useful for DZ's further application in the field by choosing the appropriate granule size of DZ according to different environmental factors to improve its effective utilization rate and avoid phytotoxicity.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agriculture12050674/s1>, Figure S1: Image of DZ with different granule size ranges; Figure S2: Dissolution of DZ in different granule size ranges in water for 5 days at 4 °C (a) and 35 °C (b); Figure S3: Comparison of DZ half-life values at pH 5 and pH 7 compared to pH 9. Different letters within the same graph indicate a significant difference at $p < 0.05$ level by Duncan's new multiple range test. Table S1: Effects of application dosage on the degradation characteristics of DZ with different granule size ranges; Table S2: Fitting results for half-life values of DZ granule size range as a function of temperature; Table S3: Effects of temperature on the degradation characteristics of DZ with different granule size ranges; Table S4: Effects of pH on the degradation characteristics of DZ with different granule size ranges; Table S5: MITC released over time from DZ at different DZ dosages.

Author Contributions: Conceptualization, L.R. and A.C.; methodology, W.L.; software, Q.L.; validation, D.Z., and W.F.; formal analysis, Y.L.; investigation, Q.W.; data curation, X.J.; writing—original draft preparation, L.R.; writing—review and editing, A.C.; visualization, D.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation Project of China and the Hebei Technology Innovation Center for Green Management of Soil-borne Diseases, grant number 31972313 and Baoding University 2021K04.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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