Residual dynamics and dietary exposure risk of dimethoate and its metabolite in greenhouse celery

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In recent years, residues of the insecticide dimethoate and its metabolites in fruits and vegetables, especially celery, have drawn attention to public health risks. We studied the residual dynamics and dietary risk of dimethoate and its related metabolite omethoate in celery grown in a greenhouse in Shenyang, northern China. We sprayed celery with 40% dimethoate EC at either a low concentration of 600 g a.i./ha or a high concentration of 900 g a.i./ha. Plants at the seedling, transplanting or middle growth stages were sprayed once, and samples were collected 90 days after transplantation. Plants at the harvesting stage were sprayed 2 or 3 times, samples were collected on days 3, 5, 7, 10, 14 and 21 after the last pesticide application. Finally, we extracted the dimethoate and omethoate compounds from the celery samples in acetonitrile and detected their concentrations by ultra performance liquid chromatography-tandem mass spectrometry. We also conducted dietary risk assessments of dimethoate and omethoate in various populations and different foods in China. The results show that the omethoate present in the celery was made by the metabolism of dimethoate. Notably, the degradation dynamics of dimethoate and total residues in greenhouse celery were in accordance with the first-order kinetic equation and the half-lives of the compounds were 2.42 days and 2.92 days, respectively. The celery sprayed once during the harvesting stage had a final residue of dimethoate after 14 days that was lower than the maximum residue limit (MRL) 0.5 mg kg^{-1} for Chinese celery, and the final residue of the metabolite omethoate after 28 days was less than the MRL 0.02 mg kg^{-1} for Chinese celery. Furthermore, after day 21, the RQs of dimethoate in celery were less than 1 and so the level of chronic risk was acceptable. Only children aged 2-7 years had an HQ of dimethoate over 1 (an unacceptable level of acute risk), while the acute dietary risks to other populations were within acceptable levels. We recommend that any applications of dimethoate to celery in greenhouses should happen before the celery reaches the harvesting stage, with a safety interval of 28 days.

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ABSTRACT

In recent years, residues of the insecticide dimethoate and its metabolites in fruits and vegetables, especially celery, have drawn attention to public health risks. We studied the residual dynamics and dietary risk of dimethoate and its related metabolite omethoate in celery grown in a greenhouse in Shenyang, northern China. We sprayed celery with 40% dimethoate EC at either a low concentration of 600 g a.i./ha or a high concentration of 900 g a.i./ha. Plants at the seedling, transplanting or middle growth stages were sprayed once, and samples were collected 90 days after transplantation. Plants at the harvesting stage were sprayed 2 or 3 times, samples were collected on days 3, 5, 7, 10, 14 and 21 after the last pesticide application. Finally, we extracted the dimethoate and omethoate compounds from the celery samples in acetonitrile and detected their concentrations by ultra performance liquid chromatography-tandem mass spectrometry. We also conducted dietary risk assessments of dimethoate and omethoate in various populations and different foods in China. The results show that the omethoate present in the celery was made by the metabolism of dimethoate. Notably, the degradation dynamics of dimethoate and total residues in greenhouse celery were in accordance with the first-order kinetic equation and the half-lives of the compounds were 2.42 days and 2.92 days, respectively. The celery sprayed once during the harvesting stage had a final residue of dimethoate after 14 days that was lower than the maximum residue limit (MRL) 0.5 mg kg^{-1} for Chinese celery, and the final residue of the metabolite omethoate after 28 days was less than the MRL 0.02 mg kg^{-1} for Chinese celery. Furthermore, after day 21, the RQs of dimethoate in celery were less than 1 and so the level of chronic risk was acceptable. Only children aged 2-7 years had an HQ of dimethoate over 1 (an unacceptable level of acute risk), while the acute dietary risks to other populations were within acceptable levels. We recommend that any applications of dimethoate to celery in greenhouses should happen before the celery reaches the harvesting stage, with a safety interval of 28 days.

Keywords Celery, Dimethoate, Omethoate, Pesticide residues, Dietary risk assessment

INTRODUCTION

Celery is a good source of vitamin C, folic acid, carotene, phenols and flavonoids (*Liang et al., 2018*) – which are known to lower blood pressure (*Madhavi et al., 2013*), and have anti-inflammatory and antioxidant effects in humans and other mammals (*Kooti et al., 2017*; *Powanda et al., 2011*). China ranks first in the world for celery production with a planting area of around 550000 ha (*Gao et al., 2014*; *Madhavi et al., 2013*). Pesticides are commonly used in celery production to increase the crop yield and quality by preventing and reducing the damage caused by diseases and insect pests. However, the application of pesticides has potential risks to the environment and human health, so risk assessments of pesticide residues have received increasing attention (*Dai et al., 2019*; *Dominiak 2019*; *Kranawetvogl et al.*, 2018; Rezaei & Mahdi, 2018).

Omethoate is a highly toxic pesticide with strong contact and penetration effects (*Eddleston et al.*, *2016*; *Zhang et al*., *2017*) and it has been banned from use on vegetables in China. However, recent investigations found that the detection rate and over standard rate of the residues of this pesticide are relatively high in celery (*Liu*, *2017*; *Sun et al*., *2014*; *Yaojun et al*., *2016*). The investigation concluded that the major cause of this problem may be that celery sprayed with dimethoate produce omethoate as a metabolite. Dimethoate, a broad-spectrum systemic insecticide and acaricide, is widely used in the control of insect pests in vegetables, fruits, tea trees, wheat and rice (*Zheng & Sun*, *2014*).

Omethoate is a metabolite of dimethoate, its toxicity is much higher. In China, the safety interval after dimethoate application is 14 days. Notably, previous research showed that, in order for the residue of omethoate to be below the maximum residue limit (MRL), the safety interval for celery sprayed with dimethoate should be 21 d (*Guo et al.*, *2017*). Nevertheless, with the improvement of peoples' standard of living, the demand for fresh vegetables in winter is increasing, resulting in the expansion of the celery planting area in northern greenhouses and greater use of dimethoate. In addition, whether the current safety interval for dimethoate application ensures the residue of its metabolite omethoate below the MRL is not clear. Therefore, it is vital to monitor dimethoate and omethoate residues in greenhouses to assess the risks to human health (EFSA, *2016*; *Van et al.*, *2016*; *Zhu et al*., *2015*).

At present, although efforts have been put into studying the dynamics of dimethoate in celery (*Chen et al.*, *2018*; *Lu et al*., *2017*; *Yuan et al*., *2014*), there are few reports on the degradation dynamics of omethoate residues. Here, we investigated the dissipation dynamics and residues of dimethoate and omethoate in greenhouse celery. Based on the experimental data, we conducted dietary risk assessments for different populations in China, and the safe application of dimethoate in celery was explored.

MATERIALS AND METHODS

Test materials

Celery was used as the test crop. The field test was carried out in the vegetable production base in Liaozhong district of Shenyang City. During the pesticide applications, there were no extreme weather events, such as heavy rain and hail, and the climatic conditions were normal. The test pesticide was 40% Dimethoate EC, the maximum recommended dose is 600 g a.i./ha in China, Hebei Zhongtian Bangzheng Biologic Science Co., Ltd., Before application, the formulation of dimethoate was analyzed. The content of dimethoate met the requirements and no omethoate was detected in it.

Instruments

Waters UPLC TQ Ultra Performance Liquid Chromatography Tandem Mass Spectrometer, Waters, USA; Zhongjia HC 3514 High Speed Centrifuge, Anhui USTC Zonkia Scientific Instrument Co., Ltd.; Ding Haoyuan RS-1 Vortex Mixer, Beijing Ding Hao Yuan Technology Co., Ltd.; Pine-tree ultra pure water machine, Beijing Xiangshunyuan Technology Co., Ltd.; JACTO HD400 Backpack Sprayer, JACTO Agricultural Machinery Co., Ltd.; 0.22 μm needle filter, 50 mL polypropylene plastic centrifuge tube, Xinkang Medical Equipment Co., Ltd.

Reagents

Methanol, acetonitrile (chromatographically pure), Merck. Wondapak QuEchERS extraction and separation kit, Shimadzu Kojima (Shanghai) Trading Co., Ltd. Dimethoate and omethoate were purchased from the Environmental Quality Supervision and Testing Center of the Ministry of Agriculture (Tianjin).

Standard solutions

Standard stock solutions (100 mg L^{-1}) of dimethoate and omethoate was diluted with acetonitrile to make the working standard solution comprised (0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 mg L^{-1}) . Additionally, celery samples cultivated in control plots were used as blanks. The stock solution was diluted with the clean control extract to generate the matrix standard solution (0.005, 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 mg L^{-1}). Standard solutions were stored in the dark at -20℃. Blanks with solution of dimethoate and omethoate at three concentration levels (0.01, 0.1, and 1 mg kg^{-1}) were employed for the recovery assay. In addition to recovery rates, performance parameters of the analytical method were determined such as linear ranges, LOQ and LOD.

Field test design

According to the requirements of Guideline on pesticide residues trials (NY/T 788-2004, *2004*) the test plot was designed with a plot area of 30 m^2, an buffer zone of 2 m and three repeat plots, which were randomly arranged. A control area of 30 m^2 without pesticide application was also set up to collect control samples.

Dissipation dynamics: Dimethoate sprayed at 900 g a.i./ha (1.5 times the maximum recommended dose) using a knapsack sprayer on the surface of celery at the middle growth stage and the experiment were repeated on three plots. Samples were collected at 2 h, 1 d, 3 d, 5 d, 7 d, 10 d, 14 d, 21 d, 28 d and 42 d after pesticide application.

Final residual dynamics: The pesticide application dose was 600 g a.i./ha (the maximum recommended dose) and 900 g a.i./ha (1.5 times the maximum recommended dose), respectively. Dimethoate sprayed once using a knapsack sprayer on the soil at the seedling stage, and samples of ripe celery were collected at 145 days after the pesticide application. Dimethoate sprayed once using a knapsack sprayer on the surface of celery at the transplanting stage and samples of ripe celery were collected at 90 days after the pesticide application. Dimethoate sprayed once using a knapsack sprayer on the surface of celery at the middle growth stage and samples of ripe celery were collected at 45 days after the pesticide application.. In addition, dimethoate sprayed using a knapsack sprayer on the surface of celery 2 and 3 times during the harvesting stage with intervals of 7 d between applications, and the experiment were repeated on three plots. Samples were collected at 3 d, 5 d, 7 d, 10 d, 14 d and 21 d after the last pesticide application.

The seedling stage is the day of sowing, the transplanting stage is 55 days after sowing, while the middle growth stage is 45 days after transplantation. Finally, ripe celery was collected 90 days after transplantation. The harvesting stage is 62-97 days after transplantation. Samples were collected at 3 d, 5 d, 7 d, 10 d, 14 d and 21 d after the last pesticide application. The growing stage, day of the pesticide application and sampling is shown in Figure 1.

Sampling: 2 kg of normal, damage-free celery samples of 2 centimeters above the ground were randomly collected from 5-12 points in each plot each time, and no samples were collected within 0.5 m of the edge of the plot. The samples were placed in polyethylene bags and transported to the laboratory for the next stage of the study. Samples were homogenized using a blender (Foer Group, Hong Kong Special Administrative Region, China) and stored in a refrigerator at -18℃ until use.

Sample analysis

Extraction: Firstly, 10.0 g of the sample to be tested was weighed and placed in a 50 mL centrifuge tube. Secondly, 20.0 mL acetonitrile was added into the centrifuge tube and homogenized for 2 min. Then the QuEChERS extraction separation bag was added with vigorously shaking for 2 min and centrifuged at 10, 000 r/min for 5 min. Lastly, the solution supernatant was filtered with 0.22 μm filter membrane, and the filtrate was ready to be tested.

Detection

Chromatographic conditions: Acquity UPLC HSS T3 column (100 mm × 2.1 mm, 1.8 μm), column temperature 25 ℃, injection volume 5 μL, flow rate 0.38 mL min^{-1}, mobile phase A is water, and B is methanol. Gradient elution conditions: 0 - 0.25 min, 90% - 5% A; 0.25 - 5.00 min, 5% - 90% A. Mass spectrometry conditions: electron spray ion source positive ion mode (ESI +), ion source temperature 500 ℃, capillary voltage 1.0 kV, nebulizing gas flow rate 900 L h^{-1}, taper hole antiblow air flow rate 50 L h^{-1}, and the scanning method was the multiple reaction monitoring (MRM) mode. The other MS/MS parameters were separately optimized for each target compound and are listed in Table 1.

Dissipation dynamics

The first-order kinetic equation was used to express the dissolution dynamics of dimethoate and omethoate in celery over time.

$$c_t = c_0 e^{-kt} \quad (1)$$

$$t_{1/2} = \frac{Ln2}{k} \quad (2)$$

Where t is time (day), c_t is the concentration (mg kg^{-1}) at time t (days), c_0 is the initial concentration (mg kg^{-1}), k is the degradation rate constant (day^{-1}), and $t_{1/2}$ is the half-life (d).

Final residue

The toxicological endpoints of dimethoate and its metabolite are the same, so the sum of residues of dimethoate and omethoate should be considered together for both acute and chronic dietary intake. Omethoate is more toxic than dimethoate and the relative toxicity of omethoate compared to dimethoate following chronic and acute were found to be about ~3:1 and ~6:1, respectively (None, 2009).

Sum of dimethoate and 6*omethoate, expressed as dimethoate (for acute risk assessment);

Sum of dimethoate and 3*omethoate, expressed as dimethoate (for chronic risk assessment).

The risk of acute dietary exposure consists of a WHO template for the evaluation of acute exposure (IESTI), while the risk of chronic dietary exposure uses a WHO template for the evaluation of chronic exposure (IEDI). (http://www.who.int/foodsafety/areas_work/chemical-

risks/gems-food/en/).
The following formula (*Geng et al.*, *2018*) was used to calculate the risk of chronic dietary exposure of dimethoate and omethoate.

$$NEDI = F \times STMR / bw \quad (3)$$

$$RQ = NEDI / ADI \quad (4)$$

Where $NEDI$ is the country's estimated daily intake (mg kg^{-1} bw day^{-1}), $STMR$ is the median residue of the standard test (mg kg^{-1}), F is the average food consumption (kg d^{-1}), bw is the bodyweight (kg), and ADI is the acceptable daily intake (mg kg^{-1} bw day^{-1}). RQ is chronic risk assessment, $RQ > 1$ indicates that the chronic dietary intake risk is unacceptable; $RQ < 1$ indicates that the chronic dietary intake risk is acceptable, and the smaller the smaller the risk.

The following formula was used to calculate the risk of acute dietary exposure of dimethoate (the single weight of unprocessed food was over 25 g, and the single weight of the edible portion was over or equal to the consumption of most individuals) (Geng et al., 2018).

$$IESTI = LP \times HR \times v / bw \quad (5)$$

$$HQ = IESTI / ARfD \quad (6)$$

Where $IESTI$ is the estimated short-term intake(mg kg^{-1} bw day^{-1}), LP is the average food consumption(kg d^{-1}), HR is the highest residue obtained in the test (mg kg^{-1}), v is the variability factor and was assigned a value of 3 according to JMPR (*Gao et al.*, *2007*), bw is the bodyweight (kg), and $ARfD$ is the acute reference dosemg (mg kg^{-1} bw day^{-1}). HQ is acute risk assessment， when $HQ < 1$, which means that the risk of acute dietary intake is acceptable. $HQ > 1$, it means that there is an unacceptable acute risk.

RESULTS

Method validation

The limits of detection (LODs) and the limits of quantification (LOQs) for dimethoate and omethoate were considered to be the concentrations produced at a signal-to-noise (S/N) ratio of 3 and 10, respectively. The LODs for the two target chemicals were 0.003 mg kg^{-1}, and the LOQs were 0.01 mg kg^{-1}. Good linear calibration curves were obtained over the concen tration range of 0.005 - 0.5 mg L^{-1} for dimethoate and omethoate and the correlation coefficient r was higher than 0.99 (Table 2). The sample concentrations outside the linear range are diluted to the appropriate analytical concentration. The matrix effect (ME) was calculated:

$$\text{ME (\%)} = (\text{slope}_{\text{ratio}} - 1) \times 100\% \qquad (7)$$

$$\text{slope}_{\text{ratio}} = \text{slope}_{\text{matrix}} / \text{slope}_{\text{solvent}} \qquad (8)$$

where slope matrix and slope solvent are the calibration curve slopes of the celery and acetonitrile standard, respectively. The matrix effects (MEs) were -4% (Table 2), which caused the suppression of the signal. Thus, matrix-matched calibration solutions were used to compensate for errors associated with matrix-induced calibration.

The accuracy was evaluated by determining the recovery assay at three levels in celery. No dimethoate and omethoate were detected in the blanks. The mean recov eries were in the range of 83.4%-92.9% and 80.4%-94.6% for dimethoate and omethoate, with RSD in the range of 3.7%-4.5% and 4.0%-7.3%, respectively (Table 3). This evidence demonstrates that the method of analysis is accurate and precise.

Dimethoate dissipation dynamics in celery

The results of dimethoate detection are given as average values of three repeat plots. As shown in Figure 2 (when the safety interval was over 28 d, the concentration of dimethoate was lower than the LOQ.), the degradation of dimethoate met the first-order kinetic equation, $Ct = 4.0499\ e^{-0.286t}$, and the correlation coefficient R^2 was 0.9943 and the half-life was 2.42 d, it indicates dimethoate is an easily degradable pesticide. In addition, 10 days later, the dissipation rate reached 94.6%, and the residual concentration of dimethoate decreased below 0.5 mg kg^{-1} (the MRL of dimethoate on celery is 0.5 mg kg^{-1}) , which is lower than the MRL. Furthermore, the dissipation rate reached 99% after 16.1 d.

Omethoate dissipation dynamics in celery

The results of omethoate detection are given as average values of three repeat plots. The fitting of the dissipation data is shown in Figure 3 (when the safety interval was over 42 d, the concentration of omethoate was lower than the LOQ.). Before application, the formulation of dimethoate had been analyzed and no omethoate was detected in it. But omethoate was detected in the celery. After the application of dimethoate, the concentration of omethoate increased to 0.19 mg kg^{-1} on day 3 and gradually decrease after 3 days. This indicated that the high levels of omethoate present in the celery were made by the metabolism of dimethoate. After day 28, the concentration of omethoate was below 0.02 mg kg^{-1}, which is lower than the allowable MRL of omethoate in celery. These findings demonstrate that a 10 d safety interval is sufficient to ensure the dimethoate concentration in celery declines to safe levels but is not sufficient for the omethoate concentration to reach safe levels. Based on the MRL (0.02 mg kg^{-1}) of omethoate in Chinese celery, we recommend a safety interval of 28 d after dimethoate application.

As shown in Figure 4, the dissipation behavior of total residues of dimethoate and its metabolite omethoate conformed to the first-order kinetic equation, $C_t = 3.7599e^{-0.237t}$, the correlation coefficient r^2 was 0.9814. The half-life was 2.92 d, which is 20.1% longer than that of parent compound dimethoate. This indicated that as a metabolite of dimethoate, omethaote should be taken into account in risk assessment..

Final residues following pesticide treatments **in seedling, transplanting and middle growth stage**

The final residues of dimethoate and its metabolite omethoate after application during seedling stage, transplanting stage and middle stage of growth the celery are shown in Table 4. The data show that both residues of dimethoate and omethoate in celery were lower than the LOQ and the MRLs (the MRL of dimethoate is 0.5 mg kg^{-1} and the MRL of omethoate is 0.02 mg kg^{-1}).

Final residues following pesticide treatments in **harvesting stage**

Samples were collected at 3 d, 5 d, 7 d, 10 d, 14 d and 21 d after the last pesticide application. The final residues of dimethoate and omethoate are shown in Table 5–6. The data show that, when 2 different dosages of dimethoate were sprayed 2 or 3 times, the residue of dimethoate in celery was lower than the allowable MRL of 0.5 mg kg^{-1} at 10 d, but the concentration of omethoate was still higher than the allowable MRL of 0.02 mg kg^{-1} at 21 d. Additionally, celery sprayed 3 times with the same concentration of dimethoate had higher residues of dimethoate and omethoate than celery that was only sprayed twice, showing a cumulative effect of repeated pesticide application. However, because we did not collect a sample of celery 28 d after the final pesticide application, we were unable to find out that whether the concentration of omethoate had declined to a level below the MRL by this stage.

Chronic dietary risk assessment

Although we recommend the safety interval (based on the MRL of omethoate in Chinese celery, we recommend a safety interval of 28 d after dimethoate application), the dietary intake risk had not been calculated at different times. Based on our test data, the standard median residue test (STMR) of total of dimethoate and omethoate in celery is shown in Table 7. The allowable daily intake (ADI) of dimethoate is 0.002 mg kg^{-1} bw (*GB 2763-2016, 2016*). The daily consumption of vegetables is known based on the Chinese dietary structure (*Wu et al., 2018; Liu et al., 2018*). The daily intake of celery was lower than total vegetable intake. If the daily total vegetable intake replaces the celery intake, the calculated dietary risk of total residual of dimethoate and omethoate is acceptable in vegetable, then the dietary risk of total residual of dimethoate and omethoate in celery is acceptable.

The risk quotient (RQ) was calculated according to the chronic dietary risk formula 3 and 4. The results show (Table 7) that day 10, the RQs of dimethoate were both more than 1 and therefore the risks were the unacceptable. Day 14, some RQs of dimethoate were more than 1 (2-12 years and 51-65 years / female), and the risks were considered to be unacceptable. After day 21, the RQs of dimethoate in celery were less than 1 and so the level of chronic risk was acceptable.

Acute dietary risk assessment

The acute reference dosages (ARfD) of dimethoate is 0.01 mg kg^{-1} bw (*Geng et al*., *2018; Utture et al*., *2012*). Based on the dietary structures of different populations in China (*Wu et al.*, *2018*), the HQ was calculated according to the acute dietary risk assessment formula 5 and 6 to judge the level of acute dietary risk (Table 8). The results show that on the 10th day, the HQ range of dimethoate was 2.42-4.15. Day 14, the range of HQ of dimethoate was 1.22-2.09. Day 21, the HQ range of dimethoate was 0.67-1.14. Day 10 and 14, the HQs of dimethoate were both more than 1 and the acute risks were the unacceptable. Day 21, only children aged 2-7 years had an HQ of dimethoate over 1 (an unacceptable level of risk), while the acute dietary risks to other populations were within acceptable levels. As a precaution, we recommend that diets for children aged 2-7 avoid large amounts of single types of food in the short term in order to reduce acute dietary risk.

DISCUSSION

This study found that the dissipation of dimethoate and total residues in greenhouse celery conforms to the first-order kinetic equation, with R^2 equal to 0.9943 and 0.9814, respectively, and half-lives of 2.42 d and 2.92 d, respectively.

Previous studies found that the half-lives of dimethoate in the open field is 2.5 d (*Guo et al*., *2017*), which indicates that the residual periods of dimethoate was no significant difference in greenhouse and open field. According to reports, the half-life of dimethoate in mango is 2 d (*Bhattacherjee et al*., *2016*), and the half-life in cucumber is 5.2 d (*Geng et al*., *2018*), which indicates that the dissipation of dimethoate is related to the matrix it is applied to. The half-life of dimethoate in celery grown in Guizhou is 5.4 d, and the half-life of celery in Anhui is 3.5 d (*Chen et al*., *2018*). Nevertheless, 7 d after application, the dissipation rate of dimethoate is faster in Liaoning (85%) than in Guizhou (75%) and Anhui (70.27%), indicating that the half-life of dimethoate is also related to region and climate.

As shown in the final residue results, the safety risks of spraying dimethoate during the seedling, transplanting and middle growth stages are within acceptable limits. Specifically, 14 d after the last application during the harvesting stage, the residue of dimethoate dropped below its MRL, but the residue of the dimethoate metabolite omethoate remained far higher than its MRL. Hence, the safety interval of dimethoate application should be at least 28 d, which is similar to the respective safety intervals of 27 d for cucumber (*Geng et al*., *2018*), and 30 d for pomegranate (*Utture et al*., *2012*).

As shown by the results of the dietary risk assessments, after day 21, the RQs of dimethoate in celery were less than 1 and so the level of chronic risk was acceptable. Only children aged 2-7 years had an HQ of dimethoate over 1 (an unacceptable level of acute risk), while the acute dietary risks to other populations were within acceptable levels. Furthermore, from a toxicology perspective, at this safety interval the celery would be safe to eat even if the residual concentration of omethoate in celery was higher than the corresponding MRL. Poland and France have made similar assessments of the risks of exposure to dimethoate and omethoate in other foods (*Nougadère et al*., *2014*; *Paweł et al*., *2015*).

CONCLUSION

This study shows that the application of dimethoate to greenhouse-grown celery results in omethoate residues that exceed acceptable levels after the current standard safety interval. Any applications of dimethoate to celery in greenhouses will occur with a 28-day safety interval, that ensures acceptable of residue omethoate. It is recommended, as a precaution, that diets for children 2-7 years of age avoid large amounts of single types of food in order to reduce their dietary risk. Notably, this result provides data to support risk assessments of dimethoate and omethoate in celery and other foods. Although the standard residue test in this study was conducted in Liaoning district, it provides a reference for other regions in northern China. More importantly, the multi-year residual data in many places may be combined to make these assessments more accurate.

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Figure 1

Growing stage, day of the pesticide application and sampling

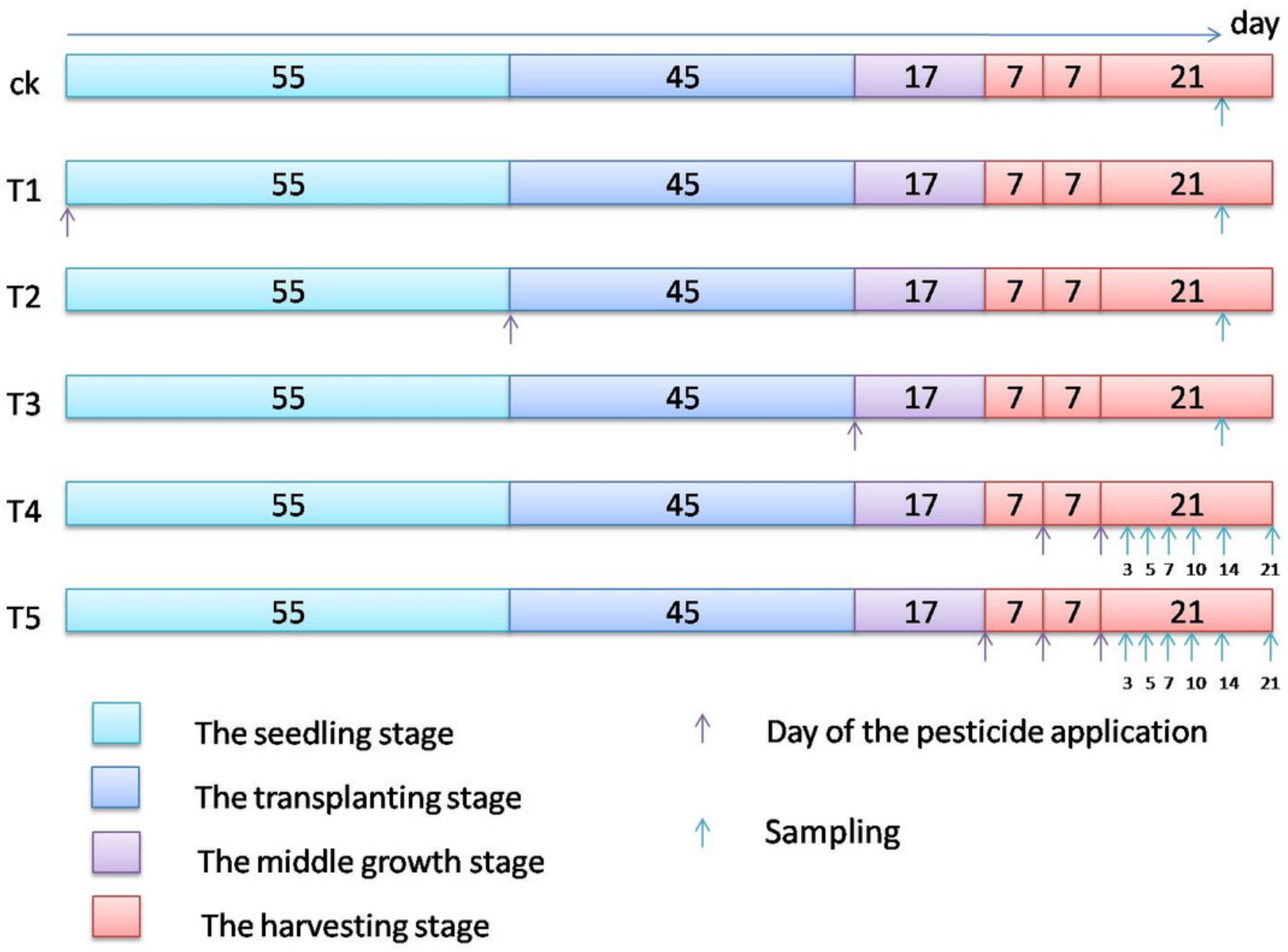

Figure 2

Level of dimethoate in celery

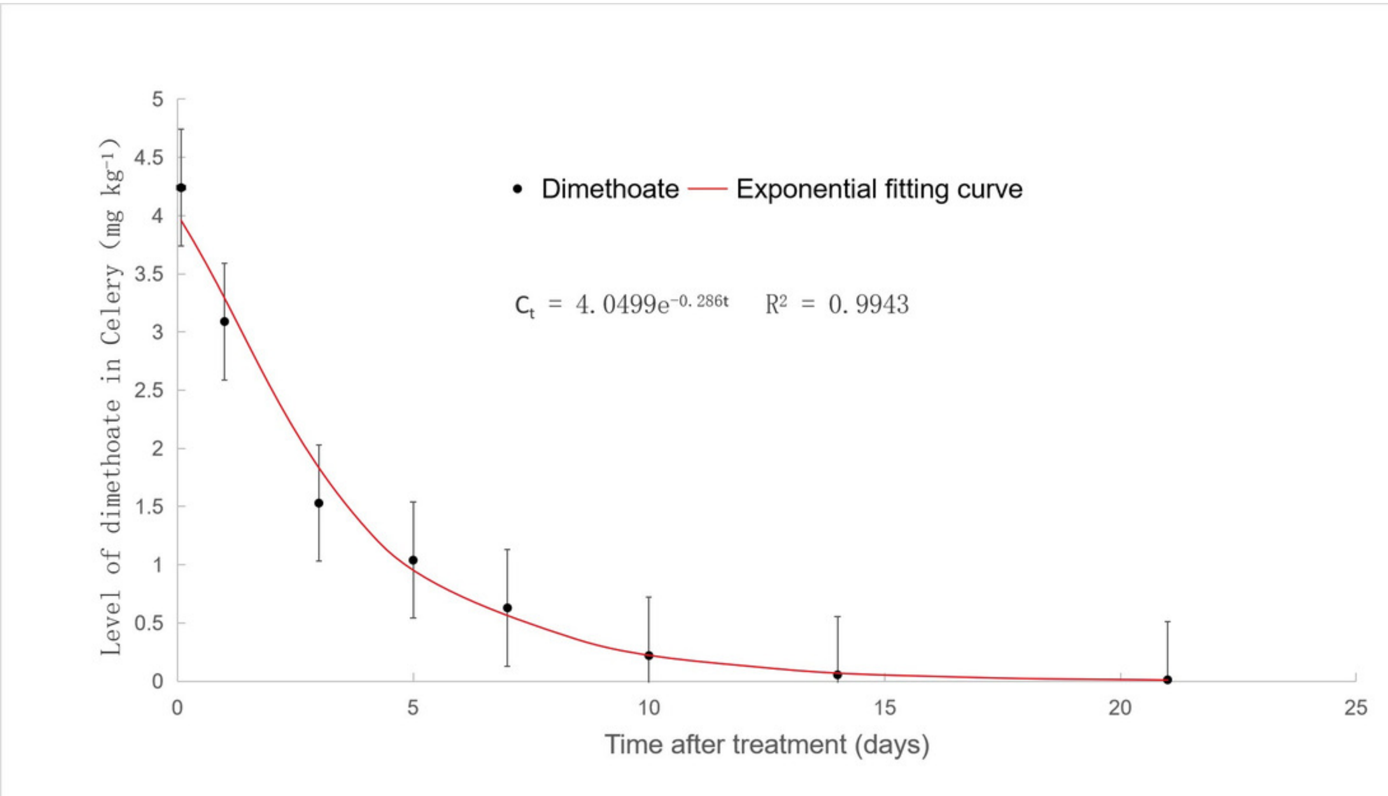

Figure 3

Level of omethoate in celery

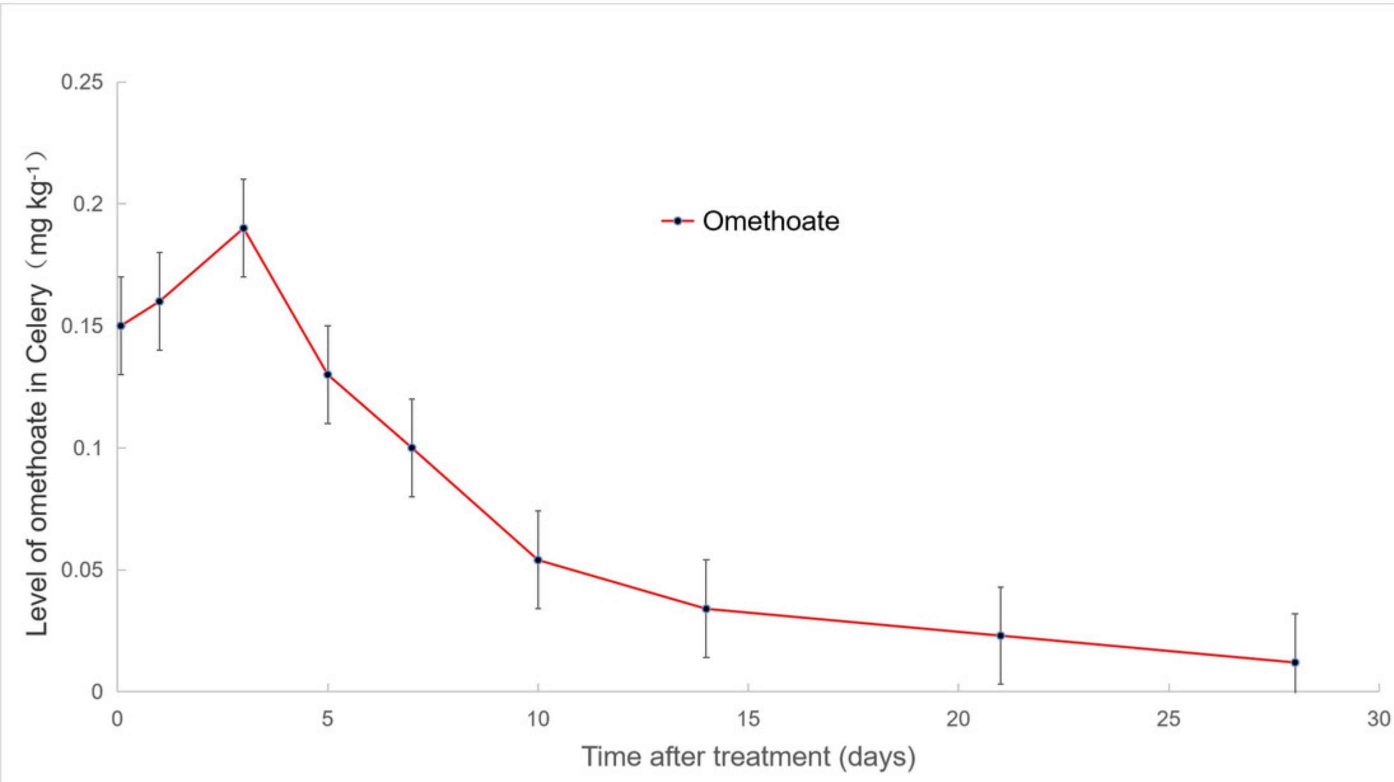

Figure 4

Level of dimethoate and its metabolite in celery

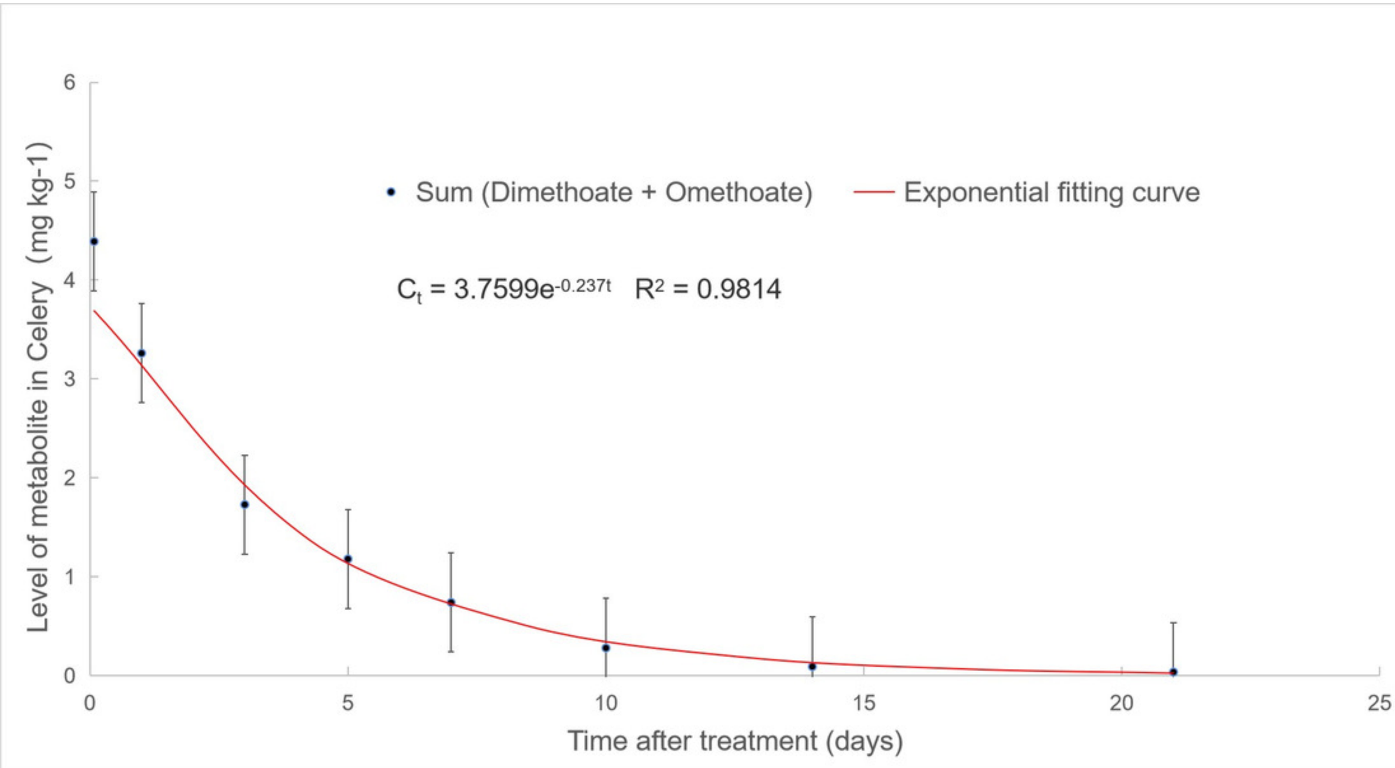

Table 1 (on next page)

Details of tandem mass spectrometry parameters of dimethoate and omethoate

Pesticide	Precursor ion, m/z	Product ion, m/z	Collision energy, eV	Declustering potential, V
Dimethoate	230.0	125.2	12	20
	230.0	199.3	12	10
Omethoate	214.4	125.1	15	20
	214.4	183.2	15	11

Table 2(on next page)

Linear regression parameters of the calibration curve for dimethoate and omethoate in pure solvent and matrices

Compounds	Matrix	Range (mg L^{-1})	Regression equation	R	Slope ratio	ME (%)
Dimethoate	acetonitrile	0.005-500	y=146.345x+41.4	0.9992	-	-
	Celery*	0.005-500	y=141.177x+226	0.9993	0.96	-4
Omethoate	acetonitrile	0.005-500	y=35.019x+64.79	0.9986	-	-
	Celery*	0.005-500	y=33.5158x+172	0.9960	0.96	-4

*Celery samples cultivated in control plots were used as blanks. The stock solution was diluted with the clean control extract to generate the matrix standard solution.

Table 3 (on next page)

Recoveries and relative standard deviations (RSDs) of dimethoate, and omethoate in celery at different fortification levels (n = 6)

Pesticide	Fortification (mg kg^{-1})	Celery	
		Mean Recovery (%)	RSD (%)
Dimethoate	0.01	83.4	3.7
	0.1	86.6	4.5
	1	92.9	4.0
Omethoate	0.01	80.4	4.0
	0.1	88.8	7.2
	1	94.6	7.3

Table 4 (on next page)

Residues of dimethoate and its metabolite omethoate after application during seedling stage, transplanting stage and middle stage of growth the celery*

Pesticide	Dosage (g a.i./ha)	Final residue during seedling stage (mg kg^{-1})	Final residue during transplanting stage (mg kg^{-1})	Final residue during middle stage of growth (mg kg^{-1})
Dimethoate	600	<0.01	<0.01	<0.01
	900	<0.01	<0.01	<0.01
Omethoate	600	<0.01	<0.01	<0.01
	900	<0.01	<0.01	<0.01

* Seedling stage (145 days), transplanting stage (90 days) and middle stage of growth the celery (45 days)

Table 5(on next page)

Residues of dimethoate and its metabolite omethoate after the application of dimethoate two times during harvesting stage of growth the celery

Pesticide	Dosage(g a.i./ha)	Final residue (mg kg^{-1}) （Days after the last application）					
		3	5	7	10	14	21
Dimethoate	600	1.60	1.15	0.78	0.35	0.064	0.014
		1.61	1.16	0.74	0.33	0.058	0.015
		1.58	1.13	0.75	0.35	0.062	0.018
	RSD (%)	1.5	1.5	2.1	1.2	0.31	0.21
	900	1.87	1.26	0.87	0.35	0.081	0.023
		1.86	1.23	0.81	0.35	0.082	0.022
		1.89	1.31	0.92	0.37	0.091	0.024
	RSD (%)	1.5	4.0	5.5	1.2	0.55	0.1
Omethoate	600	0.19	0.15	0.13	0.11	0.041	0.031
		0.18	0.15	0.12	0.11	0.043	0.032
		0.20	0.14	0.13	0.12	0.039	0.028
	RSD (%)	1.0	0.58	0.58	0.58	0.20	0.21
	900	0.21	0.16	0.14	0.10	0.058	0.041
		0.20	0.16	0.14	0.11	0.054	0.041
		0.22	0.17	0.13	0.15	0.059	0.046
	RSD (%)	1.0	0.58	0.58	2.6	0.26	0.29

Table 6(on next page)

Residues of dimethoate and its metabolite omethoate after the application of dimethoate three times during harvesting stage of growth the celery

Pesticide	Dosage (g a.i./ha)	Final residue (mg kg^{-1}) （Days after the last application）					
		3	5	7	10	14	21
Dimethoate	600	1.73	1.21	0.82	0.41	0.074	0.035
		1.73	1.22	0.80	0.43	0.075	0.031
		1.72	1.21	0.83	0.40	0.078	0.036
	RSD (%)	0.58	0.58	1.5	1.5	0.21	0.26
	900	2.01	1.39	0.89	0.46	0.11	0.062
		1.98	1.39	0.91	0.47	0.12	0.063
		2.05	1.38	0.87	0.44	0.15	0.058
	RSD (%)	3.5	0.58	2.0	1.5	2.1	0.26
Omethoate	600	0.21	0.19	0.14	0.11	0.062	0.033
		0.21	0.19	0.15	0.10	0.056	0.042
		0.22	0.20	0.13	0.11	0.061	0.039
	RSD (%)	0.58	0.58	1.0	0.58	0.32	0.46
	900	0.22	0.18	0.15	0.11	0.071	0.047
		0.21	0.19	0.16	0.12	0.075	0.041
		0.22	0.18	0.14	0.11	0.081	0.048
	RSD (%)	0.58	0.58	1.0	0.58	0.5	0.38

Table 7(on next page)

Chronic risk quotient (RQ) of total residualof dimethoate and omethoate (expressed as dimethoate) of different populations in China

Age (year) /Sex	Body weight (kg)	Vegetable intake (F) (g d^{-1})	Median residue (STMR)* (mg kg^{-1})			chronic risk quotient (RQ)		
			10 d	14 d	21 d	10 d	14 d	21 d
2-7/irrespective	17.9	194.8	0.73	0.26	0.15	3.97	1.41	0.82
8-12/irrespective	33.1	272.4	0.73	0.26	0.15	3.00	1.07	0.62
13-19/male	56.4	396.7	0.73	0.26	0.15	2.57	0.91	0.53
13-19/female	50.0	317.9	0.73	0.26	0.15	2.32	0.83	0.48
20-50/male	63.0	436.4	0.73	0.26	0.15	2.53	0.90	0.52
20-50/female	56.0	412.1	0.73	0.26	0.15	2.69	0.96	0.55
51-65/male	65.0	477.9	0.73	0.26	0.15	2.68	0.96	0.55
51-65/female	58.0	447.0	0.73	0.26	0.15	2.81	1.00	0.58
>65/male	59.5	413.3	0.73	0.26	0.15	2.54	0.90	0.52
>65/female	52.0	364.1	0.73	0.26	0.15	2.56	0.91	0.53

*STMR is the median residue of dimethoate (sum of dimethoate and 3*omethoate, expresses as dimethoate) of the standard test in Table 5 and 6.

Table 8(on next page)

Acute risk quotient (HQ) of total residualof dimethoate and omethoate (expressed as dimethoate) of different populations in China

Age (year) /Sex	Body weight (kg)	Vegetable intake (F) (g d^{-1})	Highest residue (HR)* (mg kg^{-1})			acute risk quotient (HQ)		
			10 d	14 d	21 d	10 d	14 d	21 d
2-7/irrespective	17.9	194.8	1.27	0.64	0.35	4.15	2.09	1.14
8-12/irrespective	33.1	272.4	1.27	0.64	0.35	3.14	1.58	0.86
13-19/male	56.4	396.7	1.27	0.64	0.35	2.68	1.35	0.74
13-19/female	50.0	317.9	1.27	0.64	0.35	2.42	1.22	0.67
20-50/male	63.0	436.4	1.27	0.64	0.35	2.64	1.33	0.73
20-50/female	56.0	412.1	1.27	0.64	0.35	2.80	1.41	0.77
51-65/male	65.0	477.9	1.27	0.64	0.35	2.80	1.41	0.77
51-65/female	58.0	447.0	1.27	0.64	0.35	2.94	1.48	0.81
>65/male	59.5	413.3	1.27	0.64	0.35	2.65	1.33	0.73
>65/female	52.0	364.1	1.27	0.64	0.35	2.67	1.34	0.74

* HR is the highest residue of dimethoate (sum of dimethoate and 6*omethoate, expresses as dimethoate) of the standard test in Table 5 and 6.