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RESEARCH ARTICLE

Dissipation, residue, dietary, and ecological risk assessment of atrazine in apples, grapes, tea, and their soil

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Abstract

Atrazine is one of the most used herbicides in China. It is a persistent organic pollutant but has been widely used on Chinese farmlands for a long time. To assess its dietary and ecological risks to human and environment, in this study, atrazine residues were extracted with acetonitrile and then plant samples were detected with gas chromatography coupled with mass spectrometry (GC-MS) and soil samples were determined with gas chromatography coupled with nitrogen-phosphorus detector (GC-NPD). The limit of quantification (LOQ) of the method was 0.01 mg/kg for all matrices. The recoveries ranged from 82.0 to 105.4% for plant samples and 75.6 to 85.6% for soil samples. The final residues of atrazine in all plant samples were lower than LOQ. Dietary risk assessment suggested that under good agricultural practices (GAP) conditions, intake of atrazine from apples, grapes, and tea would exhibit an acceptably low health risk on consumers. However, the final residues of atrazine in soil samples were <0.01–9.2 mg/kg, and the half-lives were 2.0–9.1 days. Based on the species sensitivity distribution (SSD) model, the potential affected fraction (PAF) of atrazine in soil samples ranges from 0.01 to 65.8%. Atrazine residues in 43.1% soil samples were higher than 0.11 mg/kg, which was the hazardous concentration for 5% of species (HC_5) of atrazine in soil. These results suggested that the ecological risks of atrazine in apples, grapes, and tea garden soil would exhibit a high risk on environmental species even under the same GAP conditions. This study could provide guidance for comprehensive risk assessment of atrazine properly used in apple, grape, and tea gardens.

Keywords Atrazine · Dissipation · Residue · Dietary risk assessment · Ecological risk assessment

Introduction

As a highly effective triazine herbicide, atrazine has been widely used in the control of long-leaf weeds in various agricultural products in China for a long time (Chen et al. 2015; Frank and Sirons 1985; Sirons et al. 1973), such as apples, grapes, and tea. But at the same time, due to the stable chemical structure of atrazine, it is difficult to degrade naturally in agricultural environment (Barchanska et al. 2014; Chen et al. 2015) and eventually caused serious pesticide residue problems. It has been proved that atrazine is irritating to human skin and eyes, and it is also an endocrine disruptor and potential carcinogen (Giersch 1993; Zhang et al. 2014). Recently, Klementova et al. (2019) reported that in the chronic toxicity assay, atrazine and its degradation product desethyl-atrazine could affect negatively the number of juveniles and clutches of microcrustacean *Daphnia magna*. Saalfeld et al. (2019) reported that at critical periods of development, the low doses of atrazine could permanently reduce the sperm quality in the wild rodent *Calomys laucha*. These studies showed that as a widely used herbicide in many countries, atrazine has different degrees of harm to human health and terrestrial and aquatic organisms. As one of the most used herbicides in China, a large number of atrazine residues in the soil also have an impact on agriculture and ecological environment (Liu et al.

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2020). Therefore, it is essential to conduct adequate research on the dissipation and residues of atrazine and reasonably assess its dietary and ecological risks.

Currently, main detection method of atrazine residue uses high-performance liquid chromatography (HPLC) and focuses on the matrix of soil (Sarmah and Sabadie 2002). There was a report about dissipation and distribution of atrazine, simazine, chlorpyrifos, and tetradifon residues in a citrus orchard plot in Valencia (Spain) by Redondo et al. Degradation half-lives were calculated, assuming zero-order kinetics: 11 days for atrazine, 12 days for simazine, 10 days for chlorpyrifos, and 18 days for tetradifon (Redondo et al. 1997). Tandon and co-workers conducted dissipation study of atrazine in the soil of winter maize in field conditions under the subtropical climatic zone of the Tarai region of India (Tandon and Singh 2015). They obtained limit of detection, 1 ng/mL, and limit of quantification for soil, straw, and cobs were 0.005, 0.007, and 0.006 μg/g, respectively. In addition, the extraction and clean-up of herbicides from complex matrixes has been considered as one of the most important steps for herbicide analysis (Lee et al. 2016; Pérez-Burgos et al. 2012). Traditional extraction method of liquid-liquid extraction (LLE) is gradually replaced by solid-phase extraction (SPE) (Sibali et al. 2009), which has higher recovery (Dorival-García et al. 2016; Shamsipur et al. 2016) and less disposal time (Nielsen et al. 2015). Therefore, in this study, all samples were cleaned up by SPE, and we chose GC-MS as detector for apples, grapes, and tea and GC-NPD as detector for soil to obtain more satisfactory detection results of atrazine.

In this study, atrazine was measured in apples, grapes, tea, and soil at six different environments during the research cycle. This method provided a compatible tool for monitoring trace amounts of atrazine in various matrixes to assess its dietary and ecological risks to human and environment. The objective of this study is to obtain adequate residue and dynamic data of atrazine in apple, grape, and tea under GAP conditions as well as to carry out dietary and ecological risk assessment, which could provide guidance for comprehensive risk assessment of atrazine properly used in apple, grape, and tea gardens.

Methods and materials

Chemicals and reagents

Atrazine (purity 99.0%) and internal standard substance of heptachlor epoxide (purity 99.0%) were provided by Dr. Ehrenstorfer GmbH. The atrazine formulation (48% atrazine wettable powder) was obtained from the Zhejiang Province Changxing First Chemical Co., Ltd. (Zhejiang Province, China). Acetonitrile (from Sinopharm Chemical Reagent Co., Ltd) was of HPLC grade and methylbenzene (Beijing Chemical Works) was guarantee reagent. Anhydrous sodium sulfate was burned at 650 °C for 4h and cooled in dryer before using. Analytical grade of sodium chloride, acetonitrile, sodium hydroxide, and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd.

Field experiment design and sampling

Field trials, including dissipation and final residue experiments, were conducted at six different geological locations in China. Apple samples were from Beijing, Anhui, Shandong, Ningxia, Liaoning, and Henan Province. Grape samples were from Beijing, Anhui, Shandong, Zhejiang, Shanxi, and Henan Province, while tea samples were obtained from Guangdong, Anhui, Hunan, Hubei, Fujian, and Zhejiang Province. There were three replicate plots in each experiment treatment with an area of 30 m^2 and one untreated plot as control area. Detailed information of field conditions is listed in Table 1.

Samples were collected haphazardly from every experiment plot to obtain reliable and representative samples. The replication of samples was three times. As required, no less than 2-kg apples, over 1-kg tea and grapes were collected. For soil samples, 1–2-kg soil with a depth of 10 cm was gathered each time. After collecting, samples were pretreated, packaged and labeled, and stored at – 20 °C freezer for further analysis in the lab.

Extraction and purification procedures

For grapes and apples, 20-g samples were weighed in 100-mL centrifuge tube, 40-mL acetonitrile was added for samples, and 2-mL sodium hydroxide solution of 2 mol/L was added for grape samples only. Then, all samples were shaken vigorously for 1 min. Five-gram NaCl was added for each sample, which was shaken again for another 1 min, and centrifuged at 3000 r/min for 5 min. About 20-mL upper layer was removed into 50-mL bottle for cleanup process. For tea, 10-g samples were weighed and added in 50-mL centrifuge tube, and 40-mL acetonitrile were added. Then, all samples were shaken vigorously for 1 min. Five-gram NaCl was added for each sample, which was shaken again for another 1 min, and centrifuged at 3000 r/min for 5 min. About 10-mL upper layer was removed into 50-mL bottle for cleanup process. After pre-elution with 10-mL acetonitrile, upper layer was removed into HC-C_{18} column and eluted with 15-mL acetonitrile. All effluents were collected and concentrated to about 1 mL with rotary evaporation for further cleanup. About 2 cm anhydrous sodium sulfate was added on the top of active carbon column, and the column was connected to the top of amino column and pre-eluted with 4-mL acetonitrile/methylbenzene (3:1, *v:v*). The sample bottles were washed three times with 2-mL solution each time, then eluted with 25-mL acetonitrile/

Table 1 Detailed field conditions for atrazine residue detection

	Final residue			Dynamic dissipation		
	Application rates (g ai./ha)	Spray times	Location	Application rates (g ai./ha)	Spray times	Location
Apple	1875–2812.5	1	Beijing, Anhui, Shandong, Henan, Ningxia, Liaoning	2812.5	1	Beijing, Anhui
Grape	3000–4500	1	Beijing, Anhui, Shandong, Henan, Zhejiang, Shanxi	4500	1	Beijing, Anhui
Tea	2250–3375	1	Anhui, Guangdong, Hubei, Hunan, Zhejiang, Fujian	3375	1	Anhui, Guangdong

methylbenzene (3:1,*v:v*). All effluents were collected and condensed to about 0.5 mL by rotary evaporation. Five milliliters of heavily steamed petroleum ether was added twice and diluted to 1 mL with the solution. Forty-microliter internal standard solution was added and mixed up for GC-MS analyzing.

For soil samples, 10-g sample was weighed in 50-mL centrifuge tube and 20-mL acetonitrile was added, shaken with hands for 1 min and extracted with supersonic wave for 15 min. Six-gram NaCl was added for each sample, which was shaken again for another 1 min, and centrifuged at 3000 r/min for 3 min. Ten-milliliter upper layer was removed in 100-mL bottle for rotary evaporation. The acetone/petroleum ether (2:8, *v:v*) was added to a constant volume of 2.5 mL for detection by GC-NPD.

Chromatography conditions

Instrumental conditions were carefully selected to provide best results between sensitivity, selectivity, and structural information for further detection. A GC-MS equipped with EI source (Agilent5977A) was used. A DB-1701 (30 m × 0.25 mm × 0.25 μm) column was used for chromatographic separation with helium (≥99.999% purity) as carrier gas (0.738 mL/min). The program of column temperature was as follows: initially kept at 130 °C for 1 min, gradually increased to 270 °C at the rate of 10 °C/ min, and kept for 5 min. The injector temperature was set as 290 °C and a volume of 1 μL solution was injected with splitless mode. Electron ionization was set at 70 eV and the GC-MS connector temperature was set at 230 °C. 353 m/z and 200 m/z were chosen as quantitation ions for heptachlor epoxide and atrazine separately, and 215 m/z and 173 m/z were chosen as identification ions for atrazine. And 355 m/z and 351 m/z were chosen as identification ions for heptachlor epoxide. Retention time of atrazine was 11.1 min. And retention time of heptachlor epoxide was 13.4 min.

A GC-NPD (Agilent7890A) was used; HP-5 column (30 m×320 μm×0.25 μm) was used with helium (≥99.999% purity) as carrier gas (2 mL/min). The program of column temperature was set as follows: initially kept at 120 °C for 4 min, gradually increased to 280 °C at the rate of 35 °C/min, and kept for 5 min. The injector temperature was as 280 °C and a volume of 2 μL solution was injected with splitless mode. The detection temperature was 340 °C; flow rate of hydrogen, air, and nitrogen gas were 2 mL/min, 60 mL/min, and 4.972 mL/min separately. Retention time was 7.4 min.

Dietary risk assessment calculations

The risk quotient (RQ) was used to evaluate whether the atrazine residues in the agricultural product pose a significant threat to the health of consumers. RQ was the ratio of national estimated daily intake (NEDI) to acceptable daily intake (ADI). When its value exceeded 100%, that is, NEDI was greater than ADI, it meant that the dietary risk was too high to be acceptable (Chen et al. 2020).

The calculation formula of NEDI and RQ was as follows:

$$\mathrm{NEDI} = \sum \mathrm{STMR}_i \times F_i \quad (1)$$

$$\mathrm{RQ} = \mathrm{NEDI}/(\mathrm{ADI} \times bw) \times 100\% \quad (2)$$

where $\mathrm{STMR_i}$ (mg/kg) was the supervised trials median residue of atrazine in apple, grape, or tea in China. If there was no suitable $\mathrm{STMR_i}$, the corresponding maximum residue limits (MRLs) could be used instead of calculating the NEDI value. F_i (kg) was the average daily intake of a certain food in China; bw was the average weight of Chinese adults (63 kg).

Ecological risk assessment calculations

The SSD model was used to estimate the impact of the corresponding pollutant concentration on the biological population and then to evaluate its ecological risk.

The ecological risk assessment was based on the pesticides' ecological risk assessment soft platform of Species Sensitivity Distribution based on Bayesian Inference (BITSSD) (Web URL, http://139.199.128.164/pesrisk/download.html; Download URL, http://139.199.128.164/pesrisk/BITSSD%

20v1.0.rar). However, it should be mentioned that this software is developed with interface language of Chinese. The English interface will be developed and might be uploaded to the Github or Gitee in the near future. This software has a previous version with name of BMCSSD with English interface. It could be downloaded by the website (http://139.199.128.164/bmcssd2/index_en.html). The first version has been applied in several cases of the previous researches (He et al. 2014a, b, 2019). The toxicity data were collected from ECOTOX (https://cfpub.epa.gov/ecotox/). The preliminary screen criteria followed species in terrestrial; endpoints of NOEC, NOEL, LOEL, and LOEC; test locations of lab and field; and exposure media of mineral soil, soil mixture, natural soil, and unspecified soil. Then, we exclude the data whose unit could not be converted into mg/kg. The species were also checked to guarantee their living in China. Finally, the geometric mean of multiple data values for the same species was calculated as shown in Table S1. To optimize the best mode, previous literatures have recommended Akaike information criterion (AIC), Bayesian information criterion (BIC), and deviance information criterion (DIC) as the goodness of fit (He et al. 2019; Spiegelhalter et al. 2002). BITSSD employed average value of all three criteria to check the goodness of fit. Typically, lower values indicate better fit.

BITSSD will use posterior parameters to directly estimate the relevant parameters for evaluating ecological risks, such as hazard threshold HCx and PAF. PAF is an important data reflecting the results of ecological risk assessment, and its value directly reflects the level of ecological risk. HC_5 is the concentration of pollutants that 5% of the biological population in the environment is significantly affected, which is generally used as the hazard threshold. If the environmental concentration exceeds this value, it is considered as a potential risk. Therefore, the HC_5 value is also an important parameter to judge the ecological toxicity of pesticides. It was worth noting that HC_5 calculated by SSD could give the hazardous threshed concentration for the most sensitive species. Thus, the species with low toxicity would affect the HC_5. In other words, all the species were safe if the concentration of atrazine in the soil was lower than the tolerance of the most sensitive species. To reduce the effect of the low value, we collected more toxicity data from ECOTOX as shown in Table S1 and Figure S1.

Results and discussion

Linearity, recovery, and limit of quantification

Different concentrations of atrazine standard solutions (0.05, 0.1, 0.2, 0.5, 1, 2, 5 mg/L) were prepared by diluting the stock solution in different matrixes blank solution. All solutions were analyzed and determined under chromatographic conditions as described above. All calibration curves, as shown in Table 2, were obtained by the absolute amounts of atrazine against peak areas.

Table 2 Calibration curves of atrazine in different matrixes

Matrix	Calibration curve	R^2
Apple	$y = 0.9853x - 0.0036$	0.9997
Grape	$y = 1.564x - 0.0218$	0.9971
Tea	$y = 1.1052x + 0.028$	0.9997
Soil	$y = 164.12x - 3.4439$	0.9996

The recoveries of atrazine in different samples obtained with this method are listed in Table 3. Five samples were extracted, purified, and analyzed at fortified level of 0.01, 0.1, and 1 mg/kg. The typical GC-MS and GC-NPD chromatograms of atrazine are shown in Fig. 1. For all matrixes, the recoveries from all fortified samples were in the range of 75.6–105.4%. The relative standard deviation (RSD) ranged from 1.0 to 8.9% and suggested that extraction and clean-up procedure could be considered suitable for routine analysis of atrazine in experimental matrices. The LOQ was defined as the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions of test (Li et al. 2017, 2021). According to this definition, the LOQ was 0.01 mg/kg for all matrices of apples, grapes, tea, and soil, which were determined as the lowest spiked level performed in the experiment.

Dissipation of atrazine

The method was applied to detect atrazine residues in apple, grape, and tea at different experiment sites. Dissipation curves of atrazine followed the first-order rate equation: $C_t = C_0 e^{-kt}$, where C_t represents the concentration of atrazine at the specific time of t and C_0 refers to the initial concentration after application, while k is the dissipation degradation rate constant. Half-life ($t_{1/2}$) was obtained from the equation of $t_{1/2} = ln\,2/k$.

Dynamic dissipation experiments on apples were carried out in Beijing and Anhui. No atrazine residue was detected on apple samples in both places; half-lives of atrazine residue in apple soil from Beijing and Anhui were 9.1 days and 2.4 days with dissipation equations of $C = 2.2e^{-0.076t}$ and $C = 4.1e^{-0.29t}$, separately. Dissipation experiments on grapes were also conducted in Beijing and Anhui. No atrazine residue was detected on grape samples in both places; atrazine residue equations for grape soil were $C = 9.9e^{-0.1t}$ with $t_{1/2} = 6.9$ days in Beijing and $C = 6.1e^{-0.34t}$ with $t_{1/2} = 2.0$ days in Anhui. For tea soil samples in Anhui and Guangdong Province, the half-lives of atrazine in tea soil samples of Anhui and Guangdong were 5.3 days and 3.9 days with corresponding equations of $C = 5.9e^{-0.13t}$ and $C = 5.1e^{-0.18t}$. Dissipation curves of soil can be seen in Fig. 2. It has been reported that variations in soil properties with depth strongly could influence the degradation

Table 3 Recovery of atrazine in different samples *(n=5)*

Matrix	0.01 mg/kg		0.1 mg/kg		1 mg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Apple	85.0	5.2	82.0	1.0	86.0	4.1
Grape	94.4	4.5	98.4	2.3	95.6	8.9
Tea	105.4	3.6	93.0	2.3	102.4	2.0
Soil	75.6	6.0	85.6	1.3	84.6	2.0

of atrazine, and the corresponding dissipation half-lives values could increase with soil depth (Bedmar et al. 2017). The results of atrazine half-lives in apple, grape, and tea soil for a depth of 10 cm of soil were 2.0–9.1 days, which were similar with the results with the similar soil depth in previous works (Bedmar et al. 2017).

Different dissipation rates may be caused by the climate type and soil type at different sites. The soil type was established according to the United States Department of Agriculture (USDA) soil textural triangle classification (Groenendyk et al. 2015). For example, the Beijing test area has a continental monsoon climate with obvious monsoons, four distinct seasons, and concentrated rainfall. The annual average temperature is 12 °C, and the annual average rainfall is 644 mm. The soil type of the test site is loam (sand 47.2%, silt 35.7%, clay 17.1%), with a pH of 7.1 and an organic

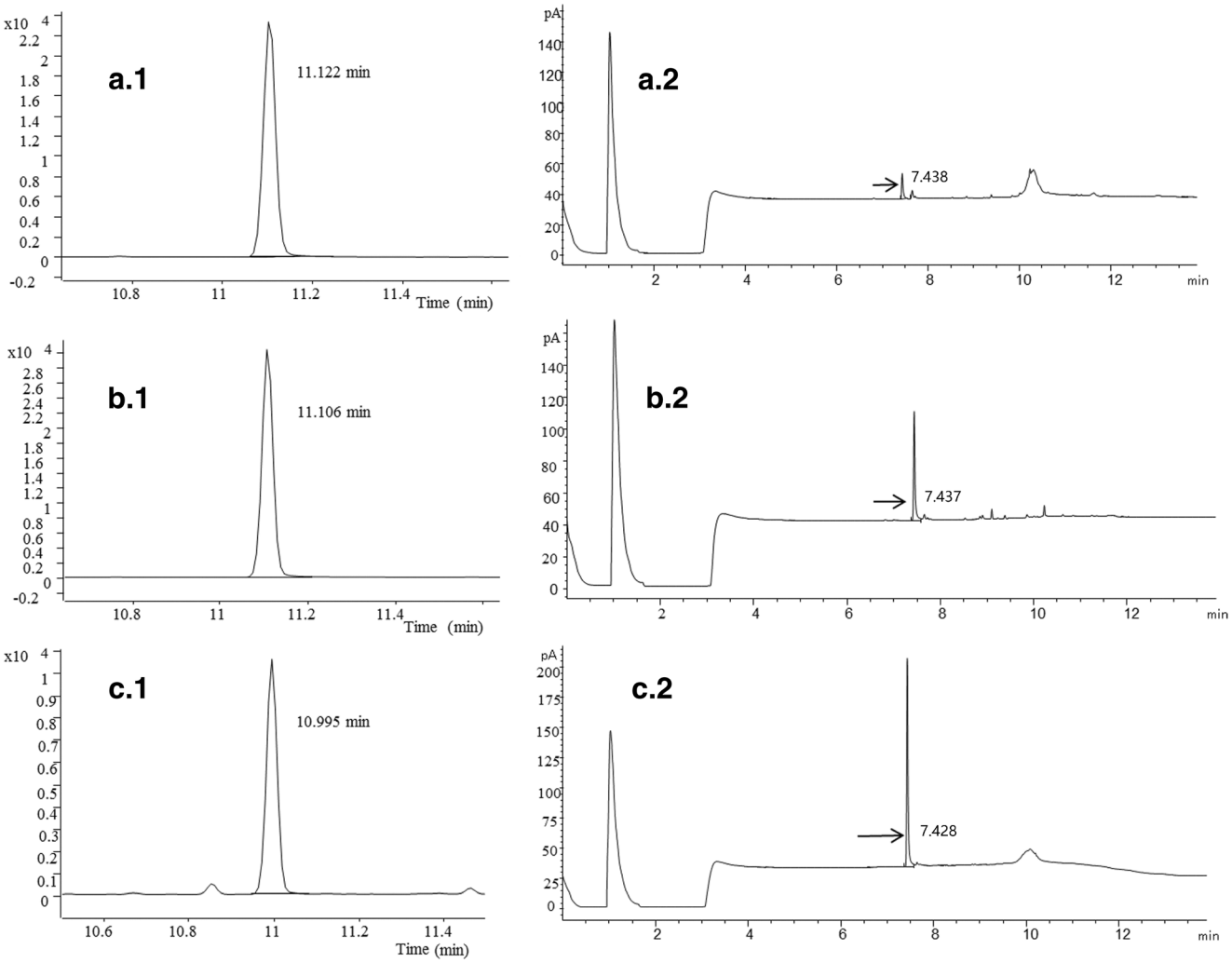

Fig. 1 Typical chromatograms of atrazine in different matrixes. **A.1** Atrazine residue in apple. **A.2** Atrazine residue in apple soil. **B.1** Atrazine residue in grape. **B.2** Atrazine residue in grape soil. **C.1** Atrazine residue in tea. **C.2** Atrazine residue in tea soil

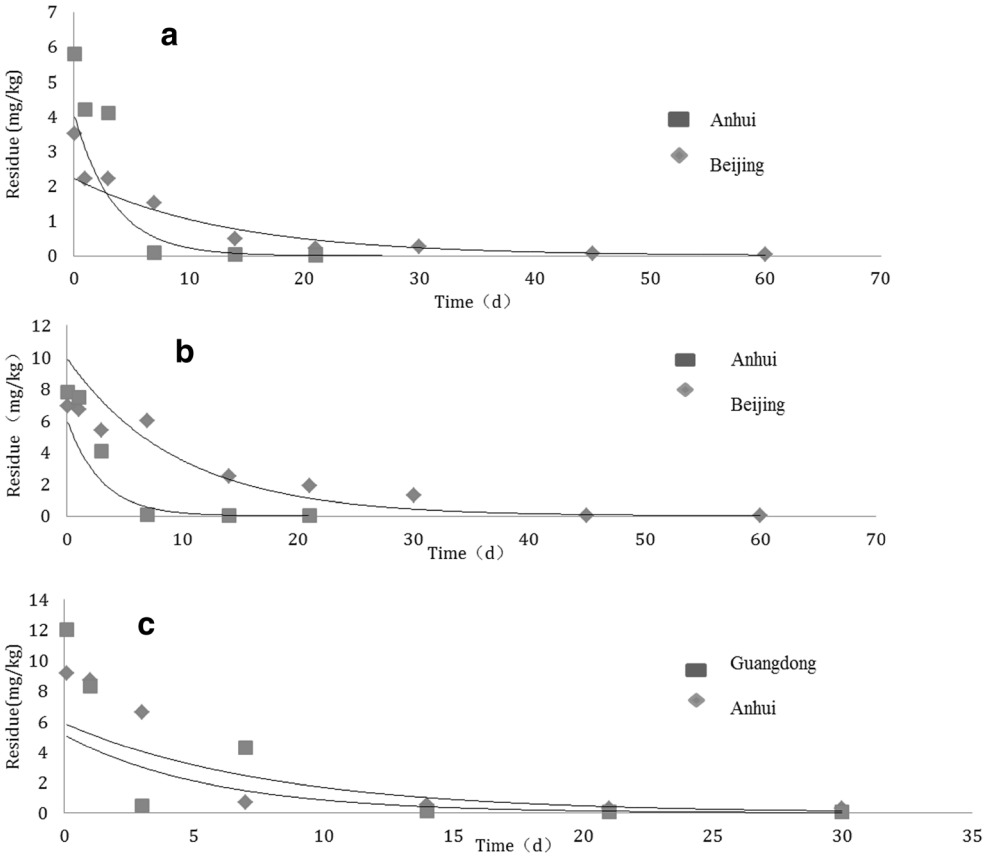

Fig. 2 Dissipation curves of atrazine in soil matrix. **a** Apple soil. **b** Grape soil. **c** Tea soil

matter content of 3.1%. However, the Anhui test area has a warm temperate semi-humid monsoon climate with four distinct seasons, sufficient sunlight, moderate rainfall, and simultaneous rain and heat. The annual average temperature is 14 °C, the annual average rainfall is 811 mm, and the rainfall is concentrated in June to August. The soil type of the test site was sandy loam (sand 58.8%, silt 26.4%, clay 14.8%), with a pH value of 7.4 and an organic matter content of 1.14%. And the Guangdong test area has a subtropical monsoon climate type. The summer is the longest in a year, and the spring, autumn, and winter are shorter. The annual average temperature is 20 °C, and the annual average rainfall is 1890 mm. The soil type of the test site was loam (sand 35.3%, silt 39.1%, clay 25.6%), with a pH value of 5.0 and an organic matter content of 1.5%. Bedmar et al. (2017) reported that the half-life values of atrazine were negatively correlated with the organic matter content and were positively correlated with pH. Thereby, it is reasonable that the half-life values of atrazine results in tea soil of Anhui and Guangdong are negatively correlated with the organic matter content, and the half-life values of atrazine results in apple and grape soil of Anhui and Beijing are positively correlated with pH. Besides, the results in Beijing, Anhui, and Guangdong also showed that for the same test agricultural product, the more south of the test site latitude is (the higher annual average temperature and annual average rainfall), the faster the dissipation rate of atrazine in the soil. It suggested that the difference in comprehensive environmental factors at different locations could lead to the difference in dissipation rate of atrazine.

Final residue of atrazine

Results of the final residue experiment under GAP application on apple (Table S2), grape (Table S3), tea (Table S4), and their soil are listed in supplementary material. The typical chromatograms of atrazine in the matrix standard, real samples in the actual application, and blank sample of apple soil, grape soil, and tea soil are documented in Figure S2. Final residues of atrazine in apples, grapes, and tea were all <0.01 mg/kg. No significant difference was observed in the residue at each spot, confirming the fact that the frequency of use were followed the label directions. Final residues of apple soil, grape soil, and tea soil were about proportional to the rate of application, within the range of <0.01–9.2 mg/kg. It can be seen from the field test results that in the two experiments with different rate of application in the same area, the final residues of atrazine in the soil are significantly different. The residues of a few groups under high application doses are lower than the low ones; these should be caused by the differences in haphazard sampling and local environment conditions of the independent experiments.

Dietary risk assessment

According to the above method (Li et al. 2019), the corresponding NEDI was calculated by the STMR or MRL of atrazine and then compared with ADI, the reasonable risk probability, namely RQ value, was obtained. The dietary risk assessment results are shown in Table 4. The ADI of atrazine was 0.02 mg/kg (bw) based on the National Food Safety Standard of China (GB2763-2019). The field trials showed that the STMR of atrazine in apple and grape (food classification is fruits) and tea (food classification is salt) were 0.01 mg/kg. From this, combined with other reference residue limits, the total NEDI value can be calculated to be 0.002412 mg. Finally, it was calculated that the RQ of atrazine for Chinese consumers was 0.2%, indicating that the atrazine residues in the current study will not cause significant health risks to consumers.

In addition, the dietary risk of atrazine to consumers can be evaluated by comparing the residues and MRLs of atrazine in apple, grape, and tea. It is known to all that MRLs are useful and reliable tools to monitor and guide scientific use of various herbicides (Huan et al. 2013) and to keep consumers from possible adverse effects (Juan-Borrás et al. 2016; Liu et al. 2014). MRLs in apples and grapes for atrazine in China are all established as 0.05 mg/kg while MRLs for tea is established as 0.1 mg/kg. Final residues of atrazine in plant samples were all lower than these MRLs. It was showed that under GAP conditions, residues of atrazine in apples, grapes, and tea present de minimis risk.

Ecological risk assessment

Based on the above method, the SSD curve of atrazine was calculated, as shown in Figure S1. According to the fitting results of BITSSD, the logical normal model was finally selected as the reasonable SSD model for ecological risk assessment in this study. The results of the study show that under the test conditions, the PAF of atrazine on organisms in soil samples is between 0.01 and 65.8% (Table S2-S4). The residual amount of atrazine in all soil samples was between <0.01 and 9.2 mg/kg. Atrazine residues in 43.1% soil samples were higher than 0.11 mg/kg, which was the HC_5 of atrazine in soil, which shows that in the use of pesticides under GAP conditions, the residue of atrazine in soil will bring significant risks to the ecological environment.

Table 4 Dietary risk assessment of atrazine in apple, grape, and tea

Food classification	Fi (kg)	Reference residue limits (mg kg^{-1})	Sources	NEDI (mg)	ADI (mg)	Risk probability (%)
Rice and its products	0.2399					
Flour and its products	0.1385					
Other cereals	0.0233	0.05	China	0.001165		
Tubers	0.0495					
Dried beans and their products	0.016					
Dark vegetables	0.0915					
Light vegetable	0.1837					
Pickles	0.0103					
Fruits	0.0457	0.01	STMR	0.000457		
Nuts	0.0039				0.02×63	
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327					
Animal oil	0.0087					
Sugar, starch	0.0044	0.05	China	0.00022		
Salt	0.012	0.01	STMR	0.00012		
Soy sauce	0.009	0.05	China	0.00045		
Total	1.0286			0.002412	1.26	0.2

Conclusions

In this study, a sensitive and effective GC-MS method to detect atrazine residue in apples, grapes, tea, and GC-NPD determination method for their soil has been established. The recoveries of atrazine were 82.0~86.0% with RSD of 1.0~5.2% for apple, 94.4~98.4% with RSD of 2.3–8.9% for grape, 93.0~105.4% with RSD of 2.0~3.6% for tea, and 75.6~85.6% with RSD of 1.3~6.0% for soil. Half-lives of atrazine residue were 9.1 days and 2.4 days in apple soil of Beijing and Anhui, 6.9 days and 2.0 days in Beijing and Anhui in grape soil, and 5.3 days and 3.9 days in tea soil samples of Anhui and Guangdong, separately. At harvest time, final residues of atrazine in apples, grapes, and tea were lower than LOQ of 0.01 mg/kg. However, the final residual amount of atrazine measured in all soil samples was <0.01–9.2 mg/kg and the atrazine residues in 43.1% soil samples were higher than the atrazine HC_5 value of 0.11 mg/kg. The PAF of atrazine in soil samples ranged from 0.01 to 65.8%. The risk assessment results showed that the residue of atrazine in apples, grapes, and tea could not have a significant impact on the health of consumers under the recommended frequency and dosage GAP conditions. However, the residue of atrazine in apples, grapes, and tea garden soil could lead to a high ecological risk even under the same GAP conditions. This study could provide guidance for comprehensive risk assessment of atrazine proper used.

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Data and materials availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request. The raw data of atrazine in soil, the SSD risk assessment data of ReWeibull, and the toxicity data of atrazine have been provided as the supplementary material.

Author contribution LY: Experimental design and writing.
YC: Data analysis and software.
CL: Method development validation and writing.
RL: Manuscript reviewing and language editing.
ZC: Manuscript reviewing and language editing.
LL: Field experiment and sample preparation.
WL: Field experiment and sample preparation.
YH: Experimental supervision and manuscript reviewing.
All authors read and approved the final manuscript.

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Declarations

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