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Original Research

Adsorption and Degradation of Cyanazine in Chinese Soils under Different Environmental Conditions

Wangcang Su, Yujia Niu, Fei Xue, Lanlan Sun, Hongle Xu, Renhai Wu°*

Institute of Plant Protection, Henan Academy of Agricultural Sciences; Zhengzhou 450002, People's Republic of China

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Abstract

Cyanazine is widely used for weed control, but its residues may contaminate the soil environment. To reduce the harm of these residues, we investigated cyanazine adsorption and degradation in four typical Chinese soils. We also examined cyanazine degradation in relation to moisture, temperature, pH, organic matter, biochar, biogas slurry, biological bacterial fertilizer, microorganisms, and initial concentration. The degradation rates of cyanazine in the four soil types were as follows: yellow cinnamon > Phaeozem > Inceptisol > sandy loam. Additionally, the adsorption ability of the soils followed this order: Phaeozem > yellow cinnamon > Inceptisol > sandy loam. The degradation rate of cyanazine increased with higher temperatures (15–35ºC), soil moisture (15-80%), and decreasing soil pH. The half-life of cyanazine was approximately six times longer in sterilized compared to unsterilized soil (61.72 vs. 9.84 d). Adding a small amount of organic matter, biological bacterial fertilizer, biochar, or biogas slurry to the soil increased the cyanazine degradation rates. These results provide guidance for risk prevention with the use of cyanazine. These findings indicate that soil physicochemical parameters, especially pH, organic matter content, and temperature, should be considered in combination with the cyanazine application rate for achieving satisfactory weed control and reducing environmental risk associated with using cyanazine in different crops.

Keywords: cyanazine, soil degradation, adsorption, residue, half-life

Introduction

Cyanazine (2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropiononitrile, Fig. 1), a triazine herbicide, primarily controls various annual gramineous weeds and broad-leaved weeds in corn and sugarcane fields by inhibiting photosynthesis [1, 2]. Notably, cyanazine is safe for wheat and can be effectively mixed with herbicides such as pyroxasulfone for weed control in wheat fields [3]. With the increasing resistance of maize field weeds to ALS-inhibiting herbicides (e.g., nicosulfuron) [4] and HPPD inhibitors (e.g., mesotrione) [5], resulting in decreased weed control efficacy, increased herbicide dosage is required. In contrast, resistance to photosynthesis-inhibiting herbicides such as cyanazine remains rarely reported. Concurrently, Chinese pesticide registration data (Pesticide Assistant Database: http://www.ny188.cn/Index.html) reveal

*e-mail: renhai.wu@163.com
Tel.:18037308799
°ORCID iD: 0000-0001-9319-0269

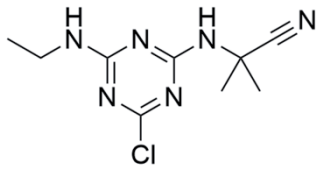

Fig. 1. The chemical structure of cyanazine.

a 52% increase in cyanazine-containing product registrations over the past decade, accompanied by expanding application areas and dosage volumes.

As a highly active herbicide, cyanazine demonstrates significant mobility and leaching potential [6]. Its residual detected in shallow groundwater (USA), paddy water, and paddy substrate (China) frequently exceeds ecological risk (MRQ value >1), posing an environmental risk to aquatic plants and microorganisms [7, 8]. For instance, cyanazine causes growth inhibition and development retardation in tadpoles [9]. Moreover, cyanazine inhibited the respiration of microbes in soil at a dose of 100 μg/g administered [10] and inhibited the activities of soil catalase and polyphenol oxidase [11]. Long-term exposure can cause adverse effects in humans, including endocrine dysfunction [12] and the danger of birth defects [13]. The US Environmental Protection Agency categorizes cyanazine as a hazardous and dangerous compound in agricultural production [14]. Field studies demonstrate its prolonged residual efficacy (>80% control of *Amaranthus retroflexus* and *Capsella bursa-pastoris* 1-2 months post-application) [15]. The frequency of cultivated land use in Huang-Huai-Hai, South China, and other regions of China is high; there is no fallow period, and large amounts of cyanazine very easily result in residual pesticide damage to crops. Moreover, soil types, climatic environments, and farming practices in different regions of China have large differences, creating diverse degradation dynamics for cyanazine. These factors underscore the critical need for accelerated degradation research to mitigate residual impacts.

The degradation of herbicides in soil is significantly influenced by environmental factors such as temperature, soil pH, moisture, and texture, with soil adsorption also serving as a critical determinant [16]. Current research on accelerated degradation of cyanazine soil residues has achieved notable progress: microbial degradation dominates in neutral to slightly basic soils, whereas chemical processes prevail in moderately acidic soils [17], primarily through hydrolysis into cyanazine amide and cyanazine acid [18]. The initial degradation rate of cyanazine in red and brown soil was higher than in black soil of China, and its degradation could be accelerated by enriching and cultivating microorganisms [19]. Over 90% of the applied cyanazine was dissipated within 56 d in a heavy clay soil [20]. Notably, no-tillage and cover crops impeded cyanazine degradation, while increased organic matter enhanced soil adsorption of the herbicide [21]. Despite these advances, existing studies predominantly focus on single or dual environmental variables under short-term simulated conditions. Significant gaps persist in systematically understanding cyanazine degradation across multifactorial environmental scenarios, particularly in quantifying degradation half-life ($t_{1/2}$) and elucidating mechanistic pathways under varying conditions. To fill this gap, this study systematically evaluated cyanazine degradation in typical soils in China under different environmental conditions.

To mitigate environmental side effects caused by cyanazine residues, building upon previous studies, we hypothesized that the behavior (i.e., persistence) of cyanazine in soil is influenced by the interaction of multiple soil environmental factors. The objectives of this study are as follows: (1) to systematically investigate the relationship between cyanazine degradation in Chinese soils and soil types and critical environmental conditions (temperature, moisture, and pH), as well as the effects of organic matter, microorganisms, biological bacterial fertilizer, biochar, and biogas slurry as soil amendments and initial concentrations. Special emphasis was placed on elucidating the mechanistic relationships between key variables, such as degradation half-life, and (2) characterizing adsorption patterns across soil types to unravel how soil properties influence cyanazine adsorption. Studying the factors influencing cyanazine adsorption and degradation can help understand the behavior of cyanazine in soil and determine the conditions required to achieve optimal degradation. Ultimately, this work can help develop recommendations to improve the management and use of cyanazine, particularly in China.

Materials and Methods

Soils and Materials

The soils used in the study are the main soil types in China: Inceptisol, yellow cinnamon, Phaeozem, and sandy loam. Soil samples were taken from the 0-10 cm topsoil from farmland with no history of cyanazine application. The main characteristics of the four soils are shown in Table 1. The soil was air-dried and passed through a 2-mm sieve before use.

Table 2 shows the main characteristics of chicken manure, biogas slurry, and biochar. Chicken manure and biogas slurry are rich in organic matter and can be used as high-quality organic fertilizers for crops; the main raw material of biogas slurry is pig manure. Chicken manure and biogas slurry were collected from a chicken farm in Kaifeng (China) and a household biogas digester, respectively. Before use, chicken manure was air-dried, homogenized, and sieved through a 2-mm sieve, while the biogas slurry was screened through a 2-mm sieve. Biochar is a material rich in organic carbon, which can significantly improve soil physical and chemical properties. Biochar was acquired from Liaoning Jinhefu Agricultural Development Co., Ltd.

Table 1. Soil properties.

Soil type	pH	Sand (%)	Silt (%)	Clay (%)	Total N (%)	Organic matter (%)
Inceptisol (Yuanyang, Henan Province)	8.1	21.8	69.1	9.1	0.046	0.55
Yellow cinnamon (Suiping, Henan Province)	6.5	35.8	44.6	19.6	0.103	1.44
Phaeozem (Harbin, Heilongjiang Province)	5.6	40.6	43.3	16.1	0.318	4.79
Sandy loam (Yancheng, Jiangsu Province)	9.1	72.5	11.3	16.2	0.101	0.47

Table 2. Soil amendment characteristics.

Material	pH	Organic matter (%)
Chicken manure	7.1	21.5
Biogas slurry	7.0	20.1
Biochar	8.8	58.6

Bacillus subtilis plays a very important role in improving soil microbial community structure. The *B. subtilis* live bacterial preparation was purchased from Shandong Junde Biotechnology Co., Ltd.

Cyanazine standard (purity>95%) and HPLC-grade methanol were acquired from Macklin Biochemical Co., Ltd. (Shanghai, China) and Fisher Chemical Co., Ltd. (Pennsylvania, USA), respectively. Analytical grade sodium chloride, petroleum ether, ethyl acetate, acetonitrile, and chloroform were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Syringe filters (PTFE, 0.22 μm) were acquired from Supelco (Bellefonte, PA, USA). Cyanazine (1000 mg/L) was prepared in methanol as a stock standard solution in advance and then diluted as needed. The test consisted of two parts, and the flowchart is shown in Fig. 2.

Adsorption Experiments

For the adsorption kinetics tests, 0.0500 g of cyanazine was dissolved in methanol to prepare a standard stock solution of 1000 mg/L and stored at −20ºC. The cyanazine standard stock solution was diluted to 10 mg/L with 0.01 mol/L $CaCl_2$ solution.

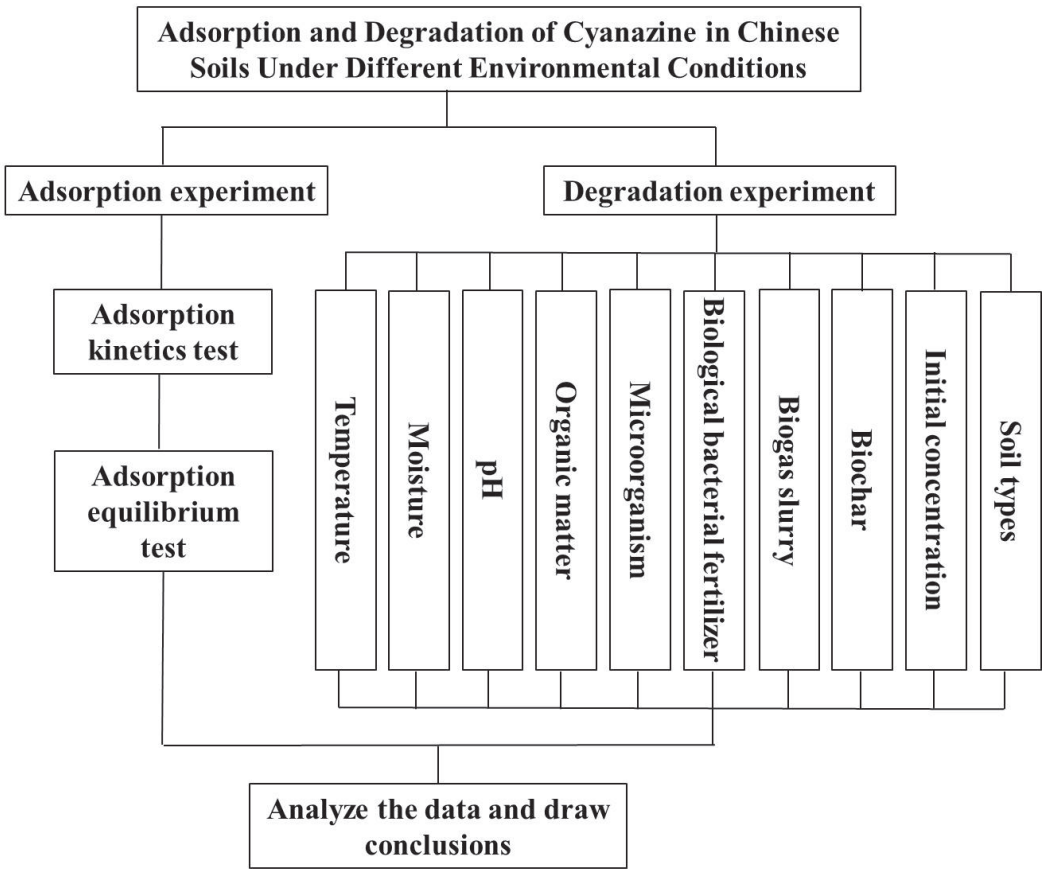

Fig. 2. Experimental flow chart.

After the soil was air-dried and passed through a 2-mm sieve, 5 g was weighed into a 150-mL stoppered shaking bottle, 10 mg/L cyanazine solution was added at a 2:1 water:soil ratio, and the bottle was sealed with a stopper. After shaking at 170 r/min at room temperature, 5 mL of supernatant was placed in an appropriate round-bottom flask for 2, 4, 8, 12, 16, 20, 24, and 32 h and purified by a Florisil-SPE column. The eluent was concentrated by rotary evaporation, and 2.0 mL of methanol-dissolved residue was obtained. The samples were filtered through 0.22-μm syringe filters and used for analysis.

For the adsorption equilibrium test, a series of 5.0 g of air-dried soil samples were placed in 150 mL plugged shaking bottles. Then, 10 mL of cyanazine solution was added at concentrations of 1, 5, 10, 15, 20, and 25 mg/L at a water:soil ratio of 2:1 at 25±1ºC. The mixture was shaken for 12 h at 170 rotations per minute (the adsorption kinetic test indicated that equilibrium was reached after 12 h of shaking for the cyanazine-water-soil system). Of the supernatant, 5 mL was placed in a suitable round-bottom flask, purified by a Florisil-SPE column, and dissolved in 2 mL of chromatographic methanol. The samples were filtered through a 0.22-μm filter before analysis.

The adsorption ratio (*A*) (%) and the cyanazine content adsorbed by the soil (*Cs*) (mg/kg) were calculated using the following equations:

$$A = \frac{M\text{-}Ce \times V_0}{M} \times 100 \qquad Cs = K_f \times (Ce)^{1/n}$$

where *Ce* is the concentration of cyanazine in the supernatant at the equilibration time, which is 2/5 of the concentration of the solution measured (g/mL); *M* (μg) and V_0 (mL) are the amount and volume of cyanazine, respectively; and K_f and 1/n represent Freundlich's adsorption coefficient and adsorption constant, respectively.

Degradation Experiment

Soil Treatment and Sampling

Of a 50 mg/L cyanazine solution, 20 mL was diluted in an appropriate amount of sterile distilled water and added to 1000 g of soil (dry weight equivalent) to obtain a 1 mg/kg cyanazine fortification level in Inceptisol soil. Then, the obtained Inceptisol was placed in a sterilization incubator (GXZ-300B, Jiangnan Instrument Manufacture, Ningbo, P. R. China) for subsequent experiments. The following test variables were set: five soil moisture contents (W water/W soil: 15%, 40%, 60%, 80%, and 90%), four temperatures (15, 25, 35, and 45ºC), five soil pH values (4.0, 6.0, 7.0, 8.0, and 10.0), four organic matter contents (0.55%, 1.0%, 2.5%, and 4.0%), four biochar contents (0%, 1.0%, 2.5%, and 5.0%), four biogas slurry contents (0%, 1.0%, 2.5%, and 4.0%), four biological bacterial fertilizer contents (0%, 1.0%, 2.5%, and 4.0%), microorganisms (sterilized and unsterilized), three initial concentrations (0.5, 1, and 3 mg/kg), and four soil types (Inceptisol, yellow cinnamon, Phaeozem, and sandy loam soils). The control soil samples were Inceptisol, with an organic matter content of 0.55%. To obtain soil with organic matter contents of 1.0%, 2.5%, and 4.0%, chicken manure was added to 1000 g of dry soil at levels of 21.0, 90.7, and 160.5 g, respectively. The biochar content was set at 0%, 1.0%, 2.5%, and 5.0% of soil weight, and the biogas slurry and biological bacterial fertilizer contents were set at 0%, 1.0%, 2.5%, and 4.0% of soil weight. The soil was autoclaved at 121ºC for 1 h for 3 consecutive days to obtain sterile soil. Experiments involving aseptic soil required an aseptic operation followed by cultivation in an aseptic incubator. The initial concentrations included 0.5, 1, and 3 mg/kg in Inceptisol, and cyanazine concentrations in other treatments were 1 mg/kg. The effect of soil type on cyanazine degradation was studied in Inceptisol, yellow cinnamon, Phaeozem, and sandy loam, and all other treatments were in Inceptisol. Except for experiments involving temperature and soil water content, all treatments were cultured at 25ºC with 60% soil moisture content in darkness, and each treatment was performed in three replicates. During the experiment, to control soil moisture content, each sample was weighed, and distilled water was added regularly to maintain the soil moisture content in the later period.

Three soil samples (each 20 g, dry weight equivalent) were taken from each treatment at 0, 1, 3, 7, 14, 21, 30, 45, 60, 90, and 120 d and used for subsequent analysis. Soil samples were stored at −18ºC before analysis.

Sample Extraction

Ten milliliters of water and 50 mL of acetonitrile were added to each sample in a 100-mL conical flask, followed by 1 h of shaking extraction. The resulting extraction solution was obtained after vacuum filtration. This solution was then transferred into a stoppered measuring cylinder containing a specific amount of sodium chloride, shaken thoroughly, and allowed to stand for 20 min. Next, 30 mL of the supernatant liquid was concentrated at 40ºC in a 100-mL flat-bottomed flask using a rotary evaporator.

Sample Purification

The residue was dissolved in 2 mL of petroleum ether and ethyl acetate solution (v/v = 95:5) and subjected to purification using a Florisil-SPE column (500 mg/6 mL). Prior to sample loading, the Florisil-SPE column was activated with 5 mL of petroleum ether and ethyl acetate solution (v/v = 95:5). After rinsing with 10 mL of petroleum ether:ethyl acetate solution (v/v = 95:5), the eluent was discarded. Subsequently, the column was rinsed with 20 mL of petroleum ether:ethyl acetate (v/v = 80:20), from which the eluent

was collected. The eluent was concentrated by rotary evaporation, and 2.0 mL of methanol was used to dissolve the residue. The samples were filtered through 0.22-μm syringe filters and used for analysis.

Analytical Method

The cyanazine content was determined by Agilent 6890N gas chromatography. The chromatographic column was an Agilent DB-17 capillary column (0.25 μm, 30 mm × 0.32 mm), using no-flow sampling mode, an injection volume of 1 μL, an inlet temperature of 250ºC, and constant current mode. The heating program was as follows: maintained at 60ºC for 2 min, increased to 260ºC at 25ºC/min over 8 min, and maintained for 10 min. The detector used was a nitrogen phosphorus detector at 330ºC; the carrier gas was high-purity nitrogen at a constant flow rate of 10 mL/min; and the combustion gas was hydrogen (3.5 mL/min) and air (60 mL/min).

Linear Regression Equation

The standard cyanazine solution was diluted with methanol to prepare 0.111, 0.556, 1.112, 5.561, and 11.121 mg/L standard solutions. Linear regression was performed using the cyanazine standard concentration (x, mg/L) as the abscissa and the chromatographic peak area (y) of the target peak as the ordinate. The linear equation obtained was $y = 44.135x + 3.8784$, $R^2 = 0.9996$.

Accuracy of the Method

A series of 20-g dry soil samples were taken, and the standard recovery test was carried out with three addition levels, which included five parallel additions. The cyanazine addition levels were 0.02, 0.1, and 0.5 mg/kg. Based on the aforementioned pretreatment techniques and instrument parameters, the recovery rate and relative standard deviation (RSD) of the amendments were calculated. The cyanazine recovery rate in the soil ranged within 95.13-103.27% with an RSD of 2.47-5.10%, satisfying the requirements for residue analysis. The limit of quantitation for cyanazine in soil is 0.005 mg/kg. These results substantiate the suitability of this method in detecting cyanazine residues in soil.

Data Analysis

Cyanazine degradation in soil followed first-order kinetics. The half-life can be determined by fitting the first-order equation $Ct = Coe^{-kt}$ to the degradation model, where Ct represents the concentration (mg/kg) of cyanazine at time t (d), Co is the initial concentration of cyanazine in soil (mg/kg), and k is the first-order rate constant (d^{-1}). The $t_{1/2}$ value can be calculated using $\ln 2/k$. All experiments were performed in parallel three times, and the results were reported as the mean and standard deviation (SD). Statistical analysis was conducted using Microsoft Excel 2010 and GraphPad Prism 9 at $P \leq 0.05$. There was no significant difference among repeated experiments ($P \leq 0.05$).

Results and Discussion

Variations in Cyanazine Absorption among Four Soils

Soil properties are presented in Table 1. Soil pH levels ranged from moderately acidic 5.6 to slightly basic 9.1, and soil organic content ranged from 0.47-4.79%. The adsorption rate of cyanazine in the four soils was initially fast and then slowed. After shaking for 2 h, the adsorption rate in Phaeozem was 20.8%, compared to 16.5% in sandy loam (Fig. 3a)). After shaking for 12 h, adsorption of cyanazine in the four soils basically reached equilibrium, and the adsorption rate peaked. The order of adsorption rate of the four soils follows: Phaeozem (38.3%) > yellow cinnamon (33.6%) > Inceptisol (30.7%) > sandy loam (28.6%). Soil colloids contain a large number of active functional groups,

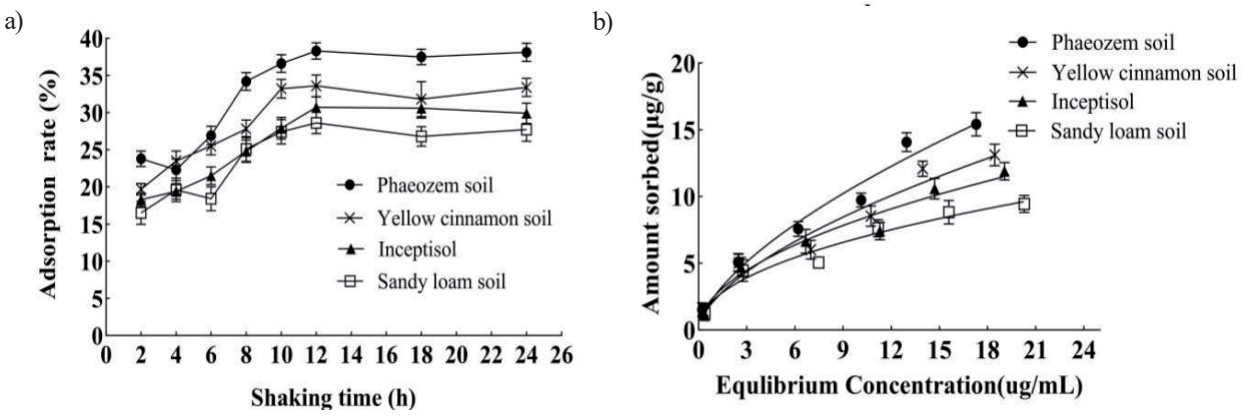

Fig. 3. a) Cyanazine adsorption ratio in different soil types for different shaking times. b) Adsorption isotherms of cyanazine. Each data point is the mean of three replicates. Error bars represent the SD of the mean.

and pesticide adsorption can be achieved by van der Waals' forces, hydrogen bonds, covalent bonds, hydrophobic bonds, protonation, and charge dipole–dipole bonds [22]. In addition to the physicochemical properties of organic pollutants, adsorption of pesticides by soil is also affected by factors such as soil organic matter, pH, soil solution composition, and external temperature [23]. Weakly basic triazine herbicides can be strongly protonated in acidic soil environments, resulting in increased and possibly irreversible adsorption [24]. In addition, the higher the organic matter content, the stronger the adsorption of cyanazine [25]. In this study, the Phaeozem soil was acidic and had the highest organic matter content and a higher adsorption rate for cyanazine than the other three soils, especially the sandy loam, which had the lowest organic matter content and a slightly basic pH.

Fitting of the Freundlich isotherm model to the adsorption isotherms of cyanazine in the four soils (Fig. 3b)) showed a good fit of the cyanazine adsorption process in the four soils. The initial slope did not increase with increasing cyanazine concentration in soil (0-3 μg/mL); after that, the slope gradually decreased with increasing concentration. The fitted parameters of the Freundlich isothermal adsorption model for cyanazine in the four soils (Table 3) showed that correlation coefficients of the model were R^2>0.970, adsorption constants (K_f) ranged within 2.146-3.213 $mg^{1-1/n} \cdot mL^{1/n}$ /kg, and empirical constants (1/n) were less than 1 (range 0.469-0.529). The adsorption kinetics and equilibrium results reflected that the adsorption capacity for cyanazine in the four soils was in the following order: Phaeozem > yellow cinnamon > Inceptisol > sandy loam.

The constant 1/n indicates the degree of nonlinearity between solution concentration and adsorption. An empirical constant of 1/n<1 corresponds to the L-type isotherm [26]. The study's results showed that the adsorption isotherms of cyanazine in the four soils conformed to the L-type. This is the same as the adsorption process of atrazine and its metabolites in sandy loam soil [23]. The adsorption constant reflects the adsorption capacity of soil for organic matter [27]. The larger the K_f value is, the stronger the adsorption capacity. Studies have shown that using pesticides with water solubility >30 mg/L and K_f<5 can easily lead to groundwater pollution [28]. At 25ºC, the solubility of cyanazine was 171 mg/L, much greater than 30 mg/L, and its K_f in the four soils was less than 3.3. Therefore, cyanazine is prone to migration and causes groundwater pollution, especially in sandy loam.

Table 3. Freundlich sorption parameters for cyanazine in four soils.

Soil type	$q_e = K_f C_e^{1/n}$		
	K_f	1/n	R^2
Inceptisol	2.657	0.529	0.972
Yellow cinnamon	2.802	0.469	0.985
Phaeozem	3.213	0.526	0.987
Sandy loam	2.146	0.506	0.971

Degradation Experiment

Effect of Temperature on Cyanazine Degradation

Soil temperature is one of the key environmental variables governing the degradation of pesticides. This study examined cyanazine degradation in soil at four temperatures (15, 25, 35, and 45ºC) while maintaining the same soil moisture content (60%). The cyanazine degradation data showed a good fit (R^2 = 0.910-0.979) to first-order kinetics (Fig. 4a) and Table 4). Temperature had a significant impact on the cyanazine degradation rate in soil. Both low and high temperatures can slow cyanazine degradation to some extent. The degradation rates in the soil significantly differed at different temperatures in the same period. Cyanazine could be completely degraded within 21 d at 35ºC, whereas the degradation rates were 41.4%, 74.4%, and 62.3% at 15, 25, and 45ºC, respectively, during the same period. The cyanazine degradation rate was higher at 35ºC than at 15, 25, and 45ºC; the corresponding half-lives were 5.87, 38.50, 10.66, and 23.90 d. The half-life of cyanazine at 35ºC was about 1/7 that at 15ºC.

Temperature controls the process of most chemical and microbial reactions. In general, the rate of degradation of herbicides increases with increasing soil temperature [29]. This is because equilibrium adsorption of most organic compounds generally decreases with increasing temperature [30], resulting in an increase in pesticide degradation as adsorption capacity decreases. Previous research demonstrated that when the temperature was raised by 30ºC, the atrazine degradation rate increased by 43 times [31]. Moreover, the loss of cyanazine toxicity in soil seems mainly due to abiotic degradation or the combination of biological and abiotic degradation, wherein the number and activity of microorganisms play a vital role [32]. Faster dissipation at higher temperatures, within the range suitable for microbial growth, is attributed to the higher levels of microbial activity resulting from increased temperature [33]. The cyanazine degradation order was 20ºC = 35ºC = 50ºC > 5ºC [34]. The fact that 35ºC appears to be the optimum temperature for cyanazine dissipation is consistent with our findings and corroborates research indicating that cyanazine degradation is microbially dependent.

Effect of Soil Moisture on Cyanazine Degradation

This study investigated the degradation of cyanazine under varying soil moisture conditions (15%, 40%, 80%, and 90%) at a constant soil temperature of 25ºC. The cyanazine degradation data showed a good fit

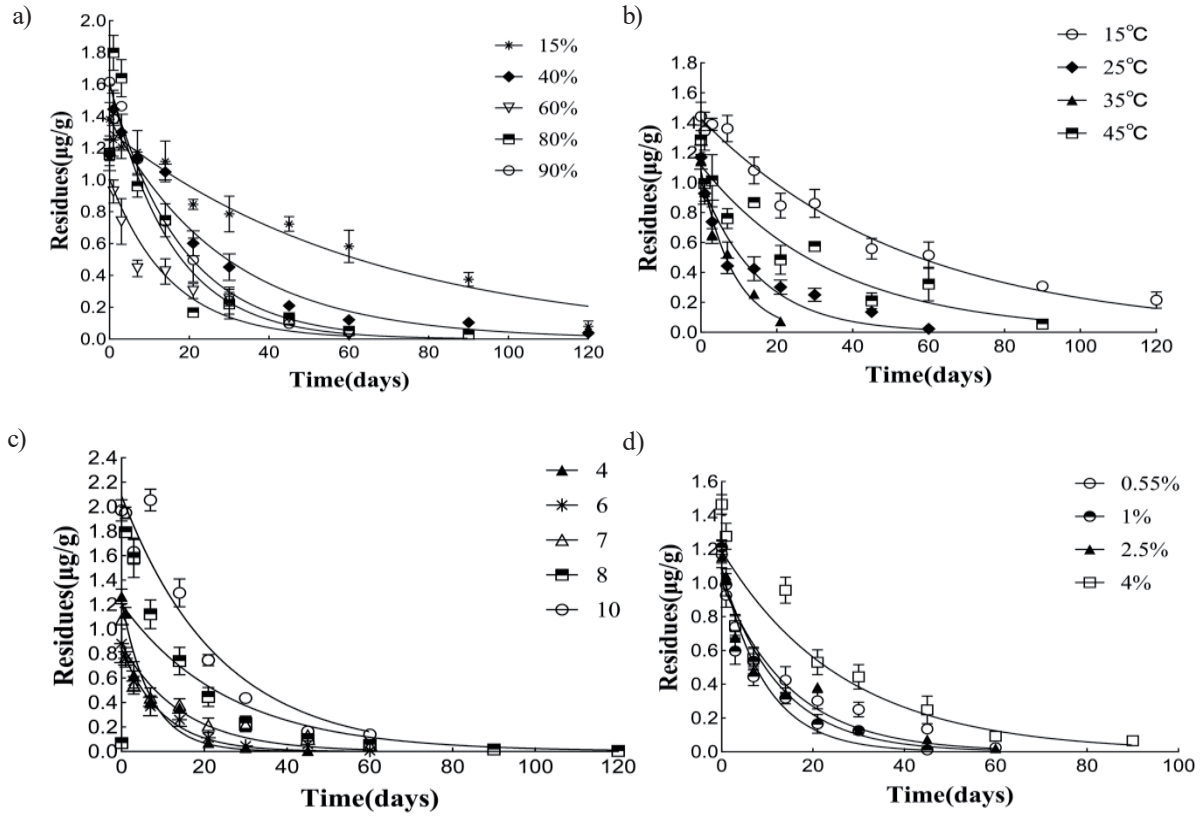

Fig. 4. Cyanazine degradation dynamics in soil as influenced by a) moisture content, b) temperature, c) pH, and d) organic matter content. Each data point is the mean of three replicates. Error bars represent the SD of the mean.

(R^2 = 0.915–0.996) to first-order kinetics (Fig. 4b) and Table 4). The degradation rate of cyanazine in soil increases as the soil moisture content increases (range 15-80%). Under different soil moisture conditions, the half-lives of cyanazine were 46.2 d (15%), 20.38 d (40%), 10.66 d (60%), and 10.50 d (80%). When the soil water content reached 90%, the cyanazine half-life was 11.18 d, which was higher than that at 60% and 80%.

The effect of soil moisture content on herbicide degradation has been well documented [31, 35]. An increase in moisture content increases the soil's pore size, increases the herbicide's concentration in the aqueous phase, and facilitates its distribution through the soil. Pesticides dissolved in water are more accessible to soil microbes [36, 37]. Zhu showed that elevated soil moisture content promotes the hydrolysis reaction at the atrazine C-2 position and thus also enhances the atrazine degradation rate in soil [38]. Therefore, it can be deduced that in soils with higher water content, atrazine easily combines with water molecules to form intermediates, encouraging hydrolysis at the C-2 position of cyanazine. Furthermore, an increase in soil water content within the range suitable for microbial growth can also stimulate microbial propagation and activity [39]. However, when the soil water content reaches saturation, soil permeability may be reduced, negatively impacting microorganisms' aerobic respiration and directly affecting the biodegradation rate [40]. In our research, when the soil water content reached water saturation (at about 90%), the cyanazine degradation rate was lower than at 60% and 80% water contents. In contrast, when the soil water content was very low (15%), the half-life of cyanazine was more than four times that at 80% water content. This may be due to the inhibition of microbial activity in dry soil, which affects microbial degradation [41]. It is evident that a higher water content is closely linked to both the chemical hydrolysis and microbial activity involved in cyanazine degradation.

Effect of Soil pH on Cyanazine Degradation

The pH value is a key factor affecting microbial activity in soil and cyanazine hydrolysis. The effect of soil pH on cyanazine degradation was studied for various pH levels (4.0, 6.0, 7.0, 8.0, and 10.0). The cyanazine degradation data showed a good fit (R^2 = 0.928-0.986) to first-order kinetics for all pH values applied to soil (Table 4), and the cyanazine degradation rate decreased with increasing soil pH (Fig. 4c)). When the soil was acidic (pH 4 and 6), cyanazine was degraded faster in the soil, with half-lives of 4.85 and 6.79 d, respectively; when the soil was neutral or alkaline, the half-lives were 10.19 d (pH 7), 11.36 d (pH 8), and 16.11 d (pH 10). Thus, acidic soil conditions favored cyanazine degradation.

The half-life of the triazine herbicides atrazine and simazine has been reported to decrease when the soil pH becomes acidic [32, 42]. Cyanazine degradation is similarly affected. The results of this study indicate

that the cyanazine degradation rate decreased under basic soil conditions. However, under weakly acidic conditions, the degradation is accelerated due to the promotion of cyanazine hydrolysis facilitated by the acidic environment [43]. Cyanazine degradation was dominated by chemical processes in both a moderately acidic and a neutral pH soil but showed a significant microbial involvement in a basic soil [17]. Therefore, after application of cyanazine in neutral or weakly alkaline soil, acid fertilizers could be appropriately applied to ensure soil vitality and accelerate cyanazine degradation.

Effect of Soil Organic Matter Content on Cyanazine Degradation

Soil organic matter content affects microbial activity and soil adsorption. The experiment investigated the effect of varying soil organic matter contents (0.55%, 1%, 2.5%, and 4%) on cyanazine degradation. The cyanazine degradation data showed a good fit (R^2 = 0.906-0.947) to first-order kinetics for all of the organic matter doses in soil (Fig. 4d) and Table 4), and the corresponding half-lives of cyanazine were 10.66, 6.66, 8.88, and 18.24 d. When the organic matter content was 1%, the cyanazine degradation rate was the fastest; however, when the organic matter content was 4.0%, the degradation rate decreased significantly. This indicated that the cyanazine degradation rate was faster in lower soils than in higher organic content.

The influence of soil organic matter content on cyanazine degradation was the combined result of its effects on microorganisms and soil adsorption [44]. Chicken litter used as an organic amendment can promote the growth of microorganisms and accelerate cyanazine degradation [19]. In addition, organic matter is also a crucial factor influencing the soil adsorption of pesticides, with soils of higher organic content having higher pesticide adsorption capacity, generally decreasing microbial degradation [45]. In our research, the higher the organic matter content, the weaker the degradation capacity of cyanazine, while low organic matter content, on the contrary, increased the cyanazine biodegradation capacity. Therefore, avoiding excessive application of organic fertilizers in areas prone to cyanazine residual hazards is important.

Cyanazine Degradation in Sterilized and Unsterilized Soil

The effect of microorganisms on the cyanazine degradation rate was evaluated by testing cyanazine degradation dynamics in sterilized and unsterilized soils. The cyanazine degradation data showed a good fit (mostly R^2>0.915) to first-order kinetics in sterilized and unsterilized soil (Fig. 5a) and Table 4). Sterilizing the soil significantly decreased the cyanazine degradation rate, and the amount of cyanazine was significantly greater than that in unsterilized soil. The residue found was 2.05% of the initial cyanazine concentration in the unsterilized soil compared to 59.89% in the sterilized soil after 60 d. The cyanazine half-life in sterilized soil was 61.72 d, which was approximately six times that in unsterilized soil (9.84 d).

The study results showed that both biological and chemical mechanisms contributed to cyanazine degradation, but microbial degradation was probably the most important pathway. In the microbial degradation process, microbial biomass and activity significantly affected the cyanazine degradation process. After soil sterilization, the number and activity of microorganisms decreased, significantly prolonging the cyanazine half-life. A similar trend has been reported for other herbicides, including florasulam, mesotrione, imazapic, and atrazine, with their degradation rates significantly lower in sterilized compared to unsterilized soils [39, 46-48].

Effect of Biological Bacterial Fertilizer on Cyanazine Degradation

To investigate the effect of using biological bacterial fertilizer on the residual activity of cyanazine in soil, different amounts of bacterial fertilizer (0%, 1%, 2.5%, and 4%) were added to the soil to assess their impact on the cyanazine degradation rate. The cyanazine degradation data showed a good fit (R^2 = 0.887-0.955) to first-order kinetics when biological bacterial fertilizer doses of 0%, 1%, 2.5%, and 4% were applied to the Inceptisol (Fig. 5b) and Table 4). Cyanazine residues were 21.37%, 18.90%, 12.55%, and 19.65% of the initial concentration under the biological fertilizer contents of 0%, 1%, 2.5%, and 4% after 30 d, respectively. The half-lives showed that degradation was most rapid following the addition of 2.5% biological fertilizer ($t_{1/2}$ = 10.50 d) and slowest following the addition of 4% biological fertilizer ($t_{1/2}$ = 11.95 d). The results showed that adding a specific amount of bacterial fertilizer helps accelerate cyanazine degradation in soil, but excessive use of biological fertilizer would inhibit cyanazine degradation to some extent.

Biological bacterial fertilizer is an efficient organic fertilizer created through the advanced fermentation method by combining certain microbial strains with organic matter as the carrier and the mineral nutrients required by plants, which helps to improve the physical properties and fertility of soil [49, 50], as well as increase the number and activity of beneficial microorganisms in the soil and promote microbial metabolic activities [51]. Biological bacterial fertilizer can increase the activity of soil enzymes, such as cellulase, sucrase, and catalase [52]. However, only a few bacteria in the soil can perform the degradation process, and the interplay among various microorganisms in complex environments affects their degradation efficacy. Additionally, the environmental adaptability of degrading bacteria to survive and degrade is significantly impacted by environmental factors, and other soil microorganisms

Table 4. Half-lives and best-fit equations describing cyanazine degradation in soil in response to different factors.

Factor		Degradation equation	R^2	Half-life, $t_{1/2}$ (d)
Soil moisture content (25ºC)	15%	$C = 1.3091e^{-0.015t}$	0.970	46.20
	40%	$C = 1.3874e^{-0.034t}$	0.957	20.38
	60%	$C = 1.0067e^{-0.065t}$	0.915	10.66
	80%	$C = 1.6143e^{-0.066t}$	0.920	10.50
	90%	$C = 1.6055e^{-0.056t}$	0.996	11.18
Temperature (60%)	15ºC	$C = 1.4278e^{-0.018t}$	0.979	38.5
	25ºC	$C = 1.0067e^{-0.065t}$	0.915	10.66
	35ºC	$C = 1.0821e^{-0.118t}$	0.974	5.87
	45ºC	$C = 1.1166e^{-0.029t}$	0.910	23.90
Soil pH	4	$C = 1.2276e^{-0.143t}$	0.956	4.85
	6	$C = 0.8423e^{-0.102t}$	0.986	6.79
	7	$C = 0.8722e^{-0.068t}$	0.948	10.19
	8	$C = 1.2041e^{-0.061t}$	0.931	11.36
	10	$C = 2.0894e^{-0.043t}$	0.928	16.11
Organic matter content (25ºC, 60%)	0.55%	$C = 1.0067e^{-0.065t}$	0.915	10.66
	1%	$C = 1.0943e^{-0.104t}$	0.947	6.66
	2.5%	$C = 1.057e^{-0.078t}$	0.932	8.88
	4%	$C = 1.1928e^{-0.038t}$	0.906	18.24
Biochar (25ºC, 60%)	0%	$C = 1.0067e^{-0.065t}$	0.915	10.66
	1%	$C = 1.0021e^{-0.094t}$	0.941	7.37
	2.5%	$C = 1.0854e^{-0.119t}$	0.921	5.82
	5%	$C = 0.9207e^{-0.073t}$	0925	9.49
Biogas slurry (25ºC, 60%)	0%	$C = 1.0067e^{-0.065t}$	0.915	10.66
	1%	$C = 0.9589e^{-0.081t}$	0.935	8.56
	2.5%	$C = 0.9609e^{-0.106t}$	0.889	6.54
	4%	$C = 0.9931e^{-0.107t}$	0.857	6.48
Biological bacterial fertilizer (25ºC, 60%)	0%	$C = 1.0067e^{-0.065t}$	0.915	10.66
	1%	$C = 1.6143e^{-0.064t}$	0.887	10.83
	2.5%	$C = 1.3917e^{-0.066t}$	0.986	10.50
	4%	$C = 1.2432e^{-0.058t}$	0.955	11.95
Microorganisms (25ºC, 60%)	Unsterilized	$C = 1.0067e^{-0.065t}$	0.915	10.66
	Sterilized	$C = 1.1445e^{-0.010t}$	0.966	69.30
Initial concentration (25ºC, 60%)	0.5 mg/kg	$C = 0.5597e^{-0.057t}$	0.956	12.16
	1 mg/kg	$C = 1.0067e^{-0.065t}$	0.915	10.66
	3 mg/kg	$C = 2.8071e^{-0.049t}$	0.975	14.14
Soil type (25ºC, 60%)	Inceptisol	$C = 1.0067e^{-0.065t}$	0.915	10.66
	Yellow cinnamon	$C = 0.8094e^{-0.086t}$	0.991	8.06
	Phaeozem	$C = 0.8269e^{-0.081t}$	0.951	8.56
	Sandy loam	$C = 1.3375e^{-0.031t}$	0.940	22.35

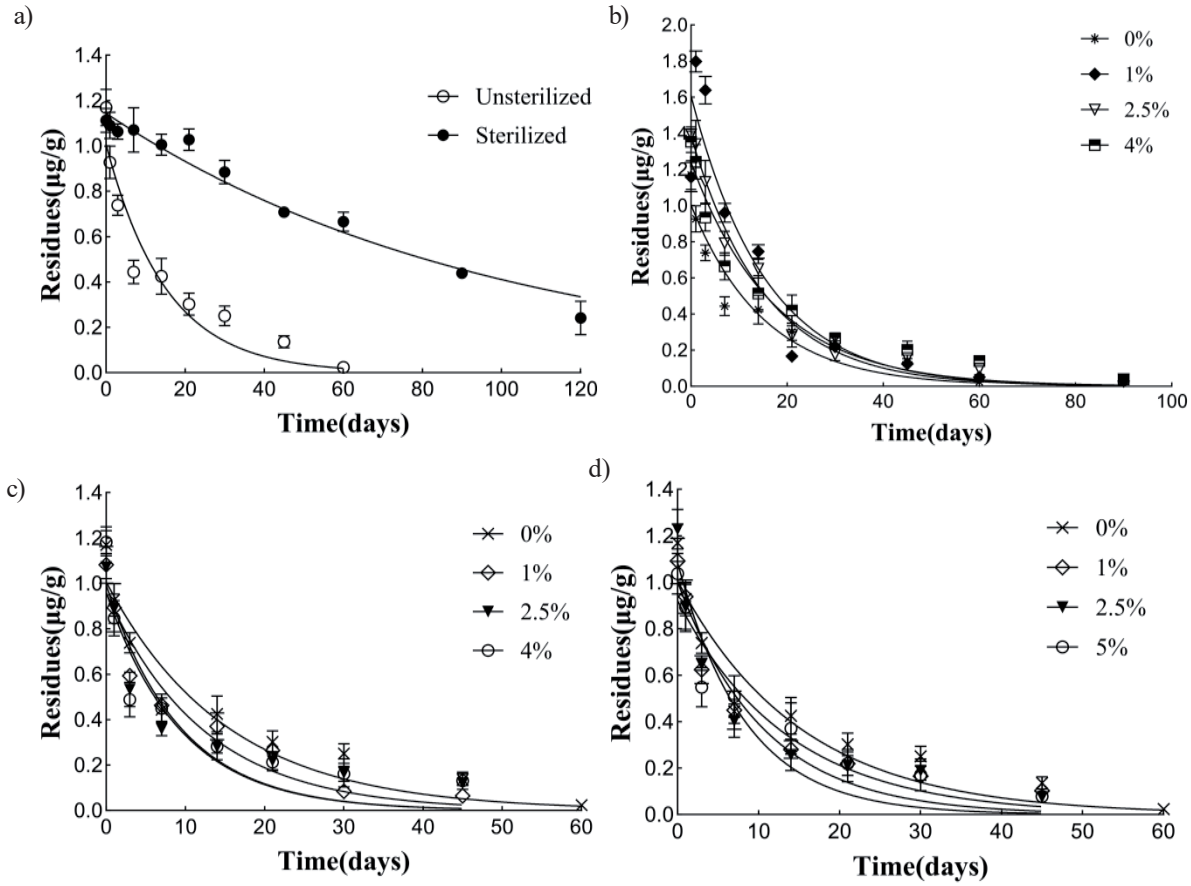

Fig. 5. Cyanazine degradation dynamics in soil as influenced by a) biochar, b) biogas slurry, c) biological bacterial fertilizer, and d) microorganisms. Each data point is the mean of three replicates. Error bars represent the SD of the mean.

compete with them for nutrients. It has been reported that the degradation of 50 mg/L bensulfuron by adding *Hansschlegelia zhihuaiae* S113 microbial agents was 94.25% [53]. Bensulfuron-degrading strain *Hansschlegelia zhihuaiae* S113 microbial agents degradation rates of 6 μg/kg chlorimuron-ethyl by Nongda bio-agent, Shilu bio-fertilizer, and Nongda bio-fertilizer were 61.5%, 58.3%, and 62.7%, respectively, 17.8%, 14.6%, and 19.0% higher than those under natural conditions [54]. Thus, using bacterial biological fertilizers necessitates understanding their inoculation volumes and nutrient requirements for optimal function [55, 56].

Effect of Biogas Slurry on Cyanazine Degradation

The study examined the cyanazine degradation process in response to different biogas slurry contents of soils (1%, 2.5%, and 4%). The cyanazine degradation data showed a good fit (R^2 = 0.857-0.915) to first-order kinetics for biochar doses of 0%, 1%, 2.5%, and 4% applied to the Inceptisol (Fig. 5c) and Table 4). The results demonstrated that adding biogas slurry accelerated cyanazine degradation, and the half-life of cyanazine in soil decreased with increasing biogas slurry addition. Specifically, the half-lives for 0%, 1%, 2.5%, and 4% biogas slurry added were 10.66, 8.56, 6.54, and 6.48 d, respectively.

Biogas slurry contains a variety of nutrients, trace elements, and organic substances that enrich the soil. As a soil modifier, it not only regulates crop growth and metabolism, providing essential nutrients for plants, but also stimulates the growth of microorganisms [57]. Because cyanazine degradation is predominantly a microbial process [17], adding biogas slurry to soil could increase the amount of microorganisms and their activity, resulting in accelerated degradation of herbicides in soil. Previous research has shown that applying biogas slurry significantly promotes the biodegradation of herbicides such as atrazine and florasulam in soil [39]. This study confirmed that adding biogas slurry to soil can expedite cyanazine degradation, indicating a vital role of biodegradation mediated by microorganisms. Therefore, applying biogas slurry may be a feasible solution to cyanazine contamination.

Effect of Biochar on Cyanazine Degradation

To investigate the impact of biochar on cyanazine residual activity, we studied the effects of varying biochar amounts (0%, 1%, 2.5%, and 4%) on the

cyanazine degradation rate. The cyanazine degradation data showed a good fit (R^2 = 0.915-0.975) to first-order kinetics when biochar doses of 0%, 1%, 2.5%, and 4% were applied to the Inceptisol. Under specific amounts of biochar addition, cyanazine degradation was accelerated (Fig. 5d) and Table 4). Notably, biochar significantly affected the soil degradation rate at 2.5%, with a half-life of 5.82 d, approximately one-half of that without additional biochar (10.66 d).

As a soil modifier with high organic matter content, a large specific surface area, and a multi-microporous structure, biochar can improve soil physical and chemical properties, enhance microbial biomass and activity, and thus reduce residual pesticide activity in soil [58, 59]. The addition of biochar was reported to significantly promote degradation of pesticides in soil [60]; compared to without biochar, the degradation rate of atrazine increased by 13.88% in the treatment adding 5% biochar to soil, and urease activity also increased by 9.14% [61]. In addition, biochar can significantly reduce the residual atrazine activity in soil by increasing the soil organic matter content, water-holding capacity, and microbial biomass and activity [62-64]. In our study, the organic matter content of the biochar used was 58.6%, which can promote microbial activity and accelerate pesticide degradation. In summary, biochar addition can contribute to the accelerated degradation of cyanazine in soil.

Effect of Initial Concentration on Cyanazine Degradation

The effect of the initial cyanazine concentration on cyanazine degradation was evaluated using initial concentrations of 0.5, 1, and 3 mg/kg. The cyanazine degradation data showed a good fit (R^2 = 0.915-0.975) to first-order kinetics for all cyanazine doses applied to the Inceptisol (Table 4). No residues were detected in soil spiked with 0.5 mg/kg cyanazine after 42 d, no residues were detected in soil spiked with 1 mg/kg cyanazine after 60 d, but residues were detected at 90 d when the initial cyanazine concentration was 3 mg/kg (Fig. 6a)). In addition, the half-lives of cyanazine in soil were longer as the dose increased. Specifically, the half-lives of cyanazine were $t_{1/2}$ (1 mg/kg) < $t_{1/2}$ (0.5 mg/kg) < $t_{1/2}$ (3 mg/kg), indicating that the cyanazine degradation was affected by the application rate.

High application rates may inhibit microbial biomass and activity. It was reported that application of imazethapyr at a low rate had a non-significant effect on dehydrogenase and alkaline phosphatase activities, whereas short and momentary toxic effects were observed at 0.8 and 1.5 μg/kg [65]. The effect of a low cyanazine concentration on soil microbial respiration was not significant, but a high concentration (100 μg/g) significantly inhibited soil microbial respiration [10]. Therefore, a high application rate, such as 3 mg/kg, may inhibit the activity and diversity of cyanazine-degrading bacteria. However, the relatively long half-life at low concentrations may be due to the formation of condensate after cyanazine is adsorbed by the soil, with a low degree of desorption, which makes it difficult for the residue to be degraded by microorganisms [25]. In conclusion, increasing the cyanazine concentration over a threshold favors cyanazine degradation.

Effect of Soil Types on Cyanazine Degradation

Inceptisol, yellow cinnamon, Phaeozem, and sandy loam soils were used in this study to investigate cyanazine degradation. The R^2 of different soil types ranged within 0.915-0.991, indicating that first-order kinetics models fit the cyanazine degradation data well. The order of cyanazine degradation rates in the four soil types was yellow cinnamon > Phaeozem > Inceptisol > sandy loam, with corresponding half-lives of 8.06, 8.56, 10.66, and 22.35 d (Fig. 6b) and Table 4), indicating that cyanazine degradation rate was affected by soil type.

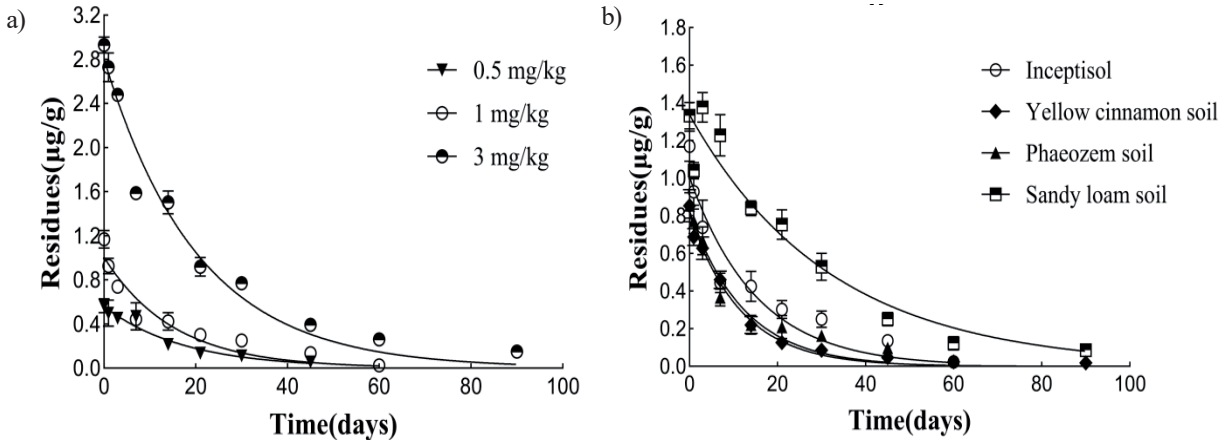

Fig. 6. Cyanazine degradation dynamics in soil as influenced by a) initial concentration and b) soil type. Each data point is the mean of three replicates. Error bars represent the SD of the mean.

The degradation of cyanazine in soil is a complex process that involves the interaction of various components. The following inferences can be drawn by comparing the soil's physical and chemical properties. First, the higher degradation rate of yellow cinnamon soil may be attributed to weak soil acidity promoting cyanazine hydrolysis and a higher organic matter content, which is suitable for microbial survival, which offsets the soil adsorption of cyanazine to some extent. Second, the faster rate of degradation in Phaeozem than in Inceptisol may be due to the weakly acidic pH of Phaeozem, which accelerates the hydrolysis of cyanazine. Finally, cyanazine had the longest half-life in sandy loam because cyanazine degradation in alkaline soil might be mainly caused by microorganisms, and the low organic matter content in the alkaline environment in sandy loam soil would affect the vitality of microorganisms [23, 44]. Consequently, our comprehensive analysis of degradation rates of cyanazine in four soil types showed that cyanazine degradation was affected by many different physical and chemical properties and microbial activity in soil that collectively contributed to its degradation.

Conclusions

The effect of different soils on cyanazine adsorption was investigated by analyzing the relationships between various physicochemical indicators of soil and adsorption rate, which showed that Phaeozem soil had the strongest cyanazine adsorption capacity. The effect of different soil environments on cyanazine degradation was studied using Inceptisol soil, which has the largest area in northern China. The results showed that microbial degradation was the primary mechanism of cyanazine degradation. The cyanazine degradation rate increased with lower pH. In addition, adding 1% organic matter to the soil favored cyanazine degradation. Soil moisture content is an important environmental factor affecting cyanazine degradation, and the cyanazine half-lives decreased with increasing water content. Another important environmental factor is the soil culture temperature; cyanazine degradation rates generally increased with rising temperatures. Consequently, high temperature and high humidity have driving effects on cyanazine degradation. Our research results will aid agricultural managers in altering soil conditions to shorten residual periods based on specific requirements and degradation data while also providing theoretical support for the degradation of other triazine herbicides in soil.

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Conflict of Interest

The authors declare no competing interests.

Data availability

The datasets are available on reasonable request.

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