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Residual Characteristics of Atrazine and Its Metabolites in the Liaoning Province of China

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Abstract: The simultaneous determination of atrazine residue and its metabolites was developed using liquid chromatography-tandem mass spectrometry in Liaoning Province, China. To ensure agricultural production and environmental safety, their contamination level was assessed. A total of 2142 samples were collected between 2014 and 2020, including 1213 soil samples, 190 surface water samples, and 739 groundwater samples. The overall pollution level and detectable level of the herbicides in Liaoning Province was found to be the highest in soil followed by surface water and groundwater. The residual level of the analytes in the collected samples decreased in the following order: atrazine > hydroxyatrazine > desethylatrazine > desisopropylatrazine. From 2014 to 2020, atrazine was detected in soil and surface water, whereas hydroxyatrazine was found in soil without the selected analytes detected in groundwater. The pollution of atrazine in soil was higher than that of hydroxyatrazine, desethylatrazine, and desisopropylatrazine. To maintain sustainable agricultural development, it is critical to pay attention to the residual determination of atrazine in the environment.

Keywords: atrazine; residual characteristics; environmental safety; triazine herbicide

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1. Introduction

Triazine herbicides have been widely used to control broadleaf and grassy weeds in agricultural production. However, due to their widespread use, herbicides pose a major threat to the environment and food safety. As a result, the potential hazards of herbicide residues in cultivated crops, water, and soil have received much attention [1,2].

Atrazine (ATZ) is the most frequently utilized triazine herbicide, which poses a severe threat to the environment and humans because of its carcinogenic and endocrine disruptor qualities [3]. ATZ has more than 15 metabolites, and among them, the four major metabolites are desethylatrazine (DEA), desisopropylatrazine (DIA), didealkylatrazine (DDA), and hydroxyatrazine (HYA) (Figure 1) [4]. ATZ has a relatively high environmental persistence in soil (half-life of more than 100 days), whereas its half-life in surface water and sediments is 85 days and 14.30 days, respectively [5,6]. Therefore, its long half-life and low absorption capacity results in the contamination of farmland. The application of ATZ also alters the structure of bacterial community in soil. Although bacteria degrade ATZ in soil after its application, its residual concentration is still approximately 100 times higher than its allowable concentration in soil, which has received considerable attention [7]. In addition, it is reported that ATZ could be detected in soil after 22 years of environmental exposure, indicating the potential long-term risks of ATZ to soil and groundwater [8].

The residual dynamics of ATZ in sewage irrigated fields in the Mezquital Valley in central Mexico were determined. The persistence and migration of ATZ and its main metabolites (DEA and HYA) along the planting cycle in sewage-irrigated cornfields were also explored. The study showed that herbicides should be applied a few days after irrigation to reduce their pollution of soil and groundwater [9]. ATZ residue and its

metabolites in three soils with different clay and organic carbon contents were determined using a HPLC with a Diode Array Detector (HPLC-DAD). Diaminoatrazine was detected in several places, whereas DEA and DIA were determined in most areas of the soil profile [10].

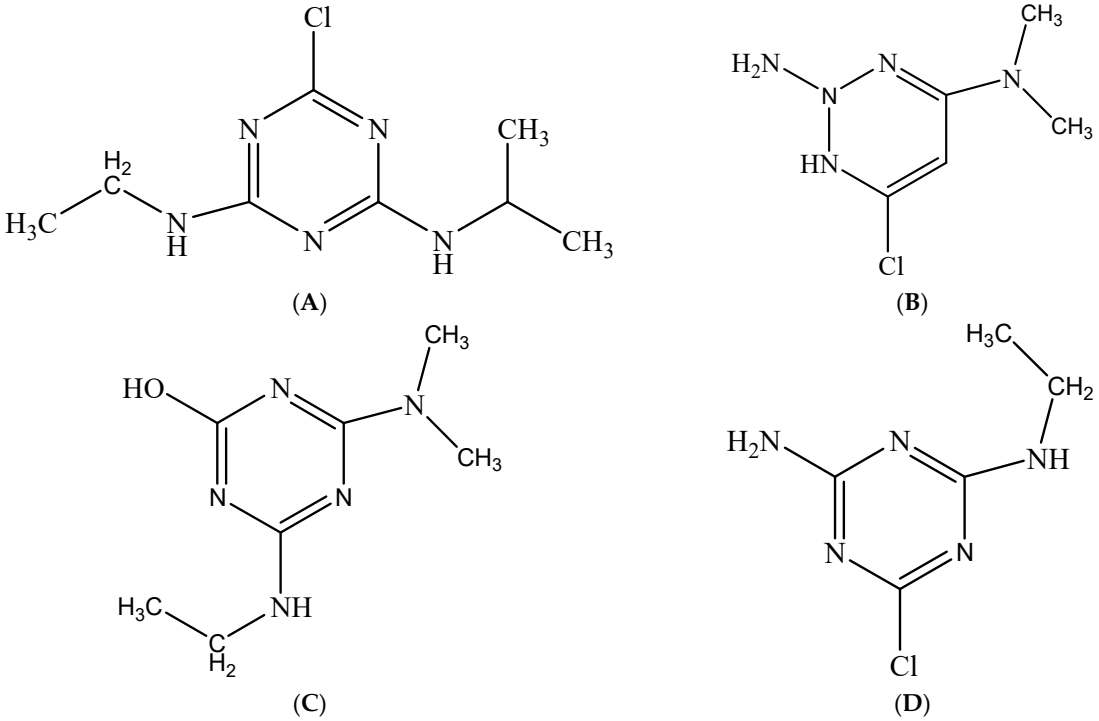

Figure 1. The chemical structure of atrazine and its metabolites: (**A**) atrazine (ATZ); (**B**) Desethylatrazine (DEA); (**C**) Hydroxyatrazine (HYA); (**D**) Desisopropylatrazine (DIA).

The contamination of ATZ and its metabolites to aquatic environments is also an issue of popular concern because of their high persistence and mobility. Liu et al. reported that ATZ and its chlorometabolites had toxic effects on zebrafish because of the high concentrations of ATZ in surface water (even more than 300 μg/L) [11]. Diaminochlorotriazine (DACT), DEA, and DIA, which are the primary metabolites of ATZ, are commonly detected in natural water and even drinking water [12–14]. Higher concentrations of ATZ and its metabolites were detected in tap water than in groundwater by liquid chromatography-tandem mass spectrometry (LC-MS/MS), with significant spatial differences in some regions of China [12]. Most metabolites of ATZ have similar or even higher toxicity than ATZ. For instance, the toxicity of DACT was reported to be significantly higher than that of ATZ, posing a serious hazard to the aquatic system [11,15]. Xue et al. investigated the presence, migration, and transformation of ATZ and its three metabolites DEA, DIA, and DDA in surface seawater, sediments, and aquatic organisms in Xiangshan Harbor using gas chromatography-tandem mass spectrometry (GC-MS/MS). DIA and DDA were only found in aquatic and marine samples, whereas ATZ was found in all the samples. ATZ was shown to be more toxic to algae than fish and invertebrates in their study [16]. Triassi et al. detected ATZ and its five metabolites in superficial water in southern Italy for the first time by LC-MS/MS. The concentration of ATZ, DIA, DEA, HYA, desethylhydroxyatrazine (DEHA), and desisopropylhydroxyatrazine (DIHA) in water was higher than that in sediment due to the high solubility of ATZ in water, high persistence in the environment, and low adsorption capacity to sediment [17].

Since the pollution of ATZ and its metabolites to farmland and aquatic environments should not be ignored, it is very important to determine their residues in soil, surface water, and groundwater [18].

A variety of methods have been used to analyze ATZ residues and its metabolites in soil and water. The QuEChERS method was applied to determine ATZ, DIA, and DEA in surface water. The optimized method showed good linearity ($r^2 > 0.99$), high precision (RSD < 11%), and accuracy (83% to 105%), with their limits of quantitation (LOQ) close to 0.2 μ g/L in surface water [19]. Min et al. simultaneously determined ATZ, DIA, and DEA in soil and water samples by gas chromatography-mass spectrometry (GC-MS) using multi-walled carbon nanotubes as solid-phase extraction (SPE) adsorbent. The limits of detection (LOD) (S/N = 3) of ATZ, DIA, and DEA in water and soil ranged from 0.02 μg/kg to 1.0 μg/kg, with average recoveries of 72.27–109.68% [20]. Zumpano et al. developed a label-free electrochemical immunosensor for quick determination of ATZ in drinking water with its LOD of 0.011 ng/mL [21]. A white light reflectance spectroscopy biosensor was also applied for simultaneous determination of ATZ and paraquat in water samples. The biosensor presented high sensitivity with LOD of 50 pg/mL for ATZ [22]. Buarque et al. extracted and purified ATZ in real water samples using aqueous biphasic system (ABS) based on tetrahydrofuran and glycerol. The target was determined by ultra-fast liquid chromatography coupled with TOF mass spectrometer (UFLC-MS), and high detection sensitivity was achieved with its LOD of 50 ng/L [23]. The method provided the advantages of fast speed, simple operation, and high enrichment factor of up to 250. A direct competitive enzyme-linked immunosorbent assay (ELISA) and a colloidal gold-based immunochromatographic (ICG) strip was developed for rapid analysis of ATZ in water samples. Both the ELISA and ICG strip assay presented high specificity, sensitivity, and fast speed with its LOD of 0.01 ng/mL and 2 ng/mL, respectively [24]. Cao et al. developed an UPLC-TOF-MS/MS method to investigate the metabolic pathway of ATZ by a high-efficient bacterial strain, *Arthrobacter* sp. C2 isolated from soil. ATZ was firstly dechlorinated to HYA, then dealkylated to isopropylamide, and the final product was cyanuric acid. The introduction of the isolate C2 into soil could promote the degradation of ATZ and eliminate the toxic effect of the herbicide on wheat growth [25]. Hernandes et al. used the sawdust of the wood forest species *Cedrella fissilis* as the raw material for preparing biochar. They evaluated the adsorption performance of the material on the river water polluted by ATZ. The adsorbent presented high efficiency for the removal of ATZ from real water samples, with a removal rate above 71.0% [26].

In the study, in order to investigate the residues of ATZ and its metabolites in the Liaoning province of China, the samples from soil, surface water, and groundwater were collected from 2014 to 2020. The residual behavior of ATZ and its metabolites was studied by LC-MS/MS to evaluate its risk to environmental safety, and to ensure the development of sustainable agricultural production.

2. Materials and Methods

2.1. Reagents

Acetonitrile (HPLC grade) was purchased from Fisher company (Schwerte, Germany). The water used in the study was prepared by the Millipore water purification system (Bedford, MA, USA). All analytical grade reagents were provided by Sinopharm Chemical Reagent Company (Beijing, China). The standards of atrazine and its metabolites (desethylatrazine, desisopropylatrazine, and hydroxyatrazine) (purity $\geq$ 95%) were purchased from the Institute for the Control of Agrochemicals (The structure of the analytes are presented in Figure 1).

Stock standard solutions (1.0 mg/mL) of ATZ and its metabolites were prepared in acetonitrile. An intermediate mixture solution of 100 μg/mL was prepared from individual stock solutions. Matrix-matched calibration solutions were prepared by serial dilution with a blank extract of soil, groundwater, or surface water for the calibration curve.

2.2. Sample Collection and Preparation

To explore the residual characteristics of the selected herbicides, residues of ATZ and its three metabolites (DEA, DIA, and HYA) were evaluated in the water and soil of farmland

in Liaoning Province, China. A total of 2142 samples were detected, including 1213 soil samples, 190 surface water samples, and 739 groundwater samples.

The soil sample (10 g) was accurately weighed, and then 20 mL acetonitrile was added with shaking extraction for 1 h. The supernatant was collected, and then 20 mL acetonitrile was added into the remnant with extraction for a further 1 h. The supernatants were combined, 7 g NaCl was added, and then they were centrifuged at 4000 rpm for 5 min. In total, 20 mL supernatant was collected, evaporated to almost dryness, and then redissolved by 5.0 mL acetone/ethyl acetate (2:98, v/v). Moreover, 2 mL solution was collected, evaporated to almost dryness by nitrogen, and redissolved by 1.0 mL methanol. The solution was filtered through a 0.22 μm filter membrane for LC-MS/MS analysis.

A total of 60 mL solution of acetone/dichloromethane (50:50, v/v) was added to a 20 mL water sample, shaken violently for 10 min, and then kept at a standstill for 20 min to achieve phase separation. The lower phase was then collected, and the upper phase was repeatedly extracted. The lower phases were combined, evaporated to almost dryness, and redissolved by 2.00 mL acetone/hexane (50:50, v/v). In total, 1.0 mL of the solution was evaporated by nitrogen to near dryness and redissolved with 1.0 mL acetonitrile/water (50:50, v/v). The solution was filtered with a 0.22 μm filter membrane for LC-MS/MS analysis.

2.3. Analytical Conditions

An Agilent 1290 infinity II-6460 Triple Quad LC-MS/MS (Agilent Technologies, Santa Clara, CA, USA) was used to determine the analytes.

LC–MS/MS separations were carried out on an Eclipse Plus C_{18} column, 2.1 mm × 100 mm (1.8 μm, Agilent Technologies Inc.). The column temperature was 30 °C. Gradient elution was performed with 5 mmol/L ammonium formate solution (A) and methanol (B) as mobile phase. The flow rate was 0.25 mL/min, and the injection volume was 5 μL.

The gradient elution conditions for the analytes: the analysis started with 30% (v/v) B, which was increased linearly up to 90% in 3.0 min, and then held for a further 1.5 min before being returned to 30% B in 1.0 min, followed by a re-equilibration time of 1.0 min.

MS/MS detection was performed in positive ionization mode. The MRM mode was used to determine the analytes (Table 1). Other conditions were set as: gas temperature 350 °C, capillary voltage 4000 V, sheath gas temperature 350 °C with flow rate 10.0 L/min.

Table 1. MRM conditions for determination of the analytes by LC-MS/MS.

Analyte	Retention Time min	Parent Ion *m/z*	Product Ion *m/z*	Dwell Time ms	Collision Energy eV
HYA	2.46	198.1	156 [a]	10	24
			86	10	29
DIA	2.56	173.8	95.9	10	25
			103.8 [a]	10	29
DEA	3.19	187.9	146 [a]	10	23
			104	10	32
ATZ	4.05	216	174 [a]	10	23
			104.1	10	39

[a]: Quantitative ion pairs.

3. Results and Discussion

3.1. Development and Evaluation of the Analytical Method

The LC-MS/MS method was evaluated with spiked soil or water samples. The developed method showed good linearity between the measured peak area and the concentration of the analytes (linear range 0.1~10.0 μg/kg) with correlation coefficients above 0.9950. The targets' limit of detection (LOD, S/N = 3) and limit of quantitation (LOQ, S/N = 10) were 0.04 μg/kg and 0.1 μg/kg, respectively. The average recoveries of the analytes at three spiked levels (0.1 μg/kg, 0.5 μg/kg, 1.0 μg/kg) were higher than 75%, with the relative

standard deviations (RSDs) in the range of 7.3% to 9.5% (Table 2). The intra-day precision was in the range of 7.8~9.7%, whereas inter-day precision was in the range of 8.5~10.5%. The results indicated that the proposed method achieved good accuracy and precision, which was applied to the determination of the analytes in the collected samples.

Table 2. Recoveries and precisions for the analytes spiked in soil and water samples.

Matrices	Analytes	Average Recoveries (%) [a]			Intra-Day Precision [b] (RSD, %)	Inter-Day Precision [b] (RSD, %)
		0.1 (μg/kg)	0.5 (μg/kg)	1.0 (μg/kg)		
Soil	ATZ	75 (9.1)	80 (8.0)	83 (8.5)	8.4	8.9
	DIA	82 (8.2)	90 (7.7)	86 (9.5)	8.6	9.1
	DEA	81 (7.3)	87 (8.7)	101 (9.2)	8.9	10.0
	HYA	75 (9.6)	80 (7.5)	84 (8.9)	9.7	10.5
Surface water	ATZ	82 (7.9)	78 (9.2)	91 (7.9)	9.3	10.4
	DIA	90 (9.0)	85 (8.6)	98 (8.1)	8.9	9.2
	DEA	90 (8.1)	78 (7.6)	89 (8.9)	9.0	9.5
	HYA	94 (8.0)	79 (9.4)	106 (9.0)	9.4	10.3
Groundwater	ATZ	77 (9.0)	85 (7.6)	90 (8.3)	8.7	9.2
	DIA	80 (8.2)	83 (8.0)	87 (7.8)	7.8	9.4
	DEA	81 (9.5)	80 (8.6)	84 (9.0)	8.3	8.5
	HYA	82 (9.4)	81 (7.6)	90 (7.9)	8.8	9.6

[a]: RSD values of repeatability are given in brackets (n = 5). [b]: RSD values obtained at 0.5 μg/kg (n = 5).

The comparison of the proposed method with other techniques for the analytes analysis is indicated in Table 3. The developed method presented advantages: simple operation, and relatively low LODs in the same range of the reported methods.

Table 3. Comparison of the method with other techniques for ATZ and its metabolites analysis.

Method	Instrument	Analytes	Sample	LOD	Recovery (%)	Reference
QuEChERS	HPLC-DAD	ATZ, DEA, DIA	Natural water	0.08 μg/L	83~105	[19]
SPE [a]	GC-MS	ATZ, DEA, DIA	Soil, water	0.02 μg/kg (water); 1.0 μg/kg (soil)	72.27~109.68	[20]
SPE	Label-free electrochemical immunosensor	ATZ	Drinking water	0.011 ng/mL	95.7~108.4	[21]
Without pretreatment	White light reflectance spectrocscopy	ATZ, paraquat	Water	50 pg/mL (ATZ); 40 pg/mL (paraquat)	90~110	[22]
ABS	UFLC-MS	ATZ	Water	50 ng/L	70.9~96.5	[23]
Without pretreatment	ELISA; ICG strip	ATZ	Water	0.01 ng/mL (ELISA); 2 ng/mL (ICG)	96.5	[24]
LLE [b]	UPLC-TOF-MS/MS	ATZ	Soil, bacterial strain	0.01 mg/kg	No report	[25]
LLE	LC-MS/MS	ATZ, DEA, DIA, HYA	Soil, water	0.04 μg/kg	≥75	This work

[a]: SPE, solid phase extraction. [b]: LLE, liquid–liquid extraction.

3.2. Detectable Rate of Pesticides in the Collected Samples

The detectable rate of herbicides found in soil, groundwater, and surface water from 2014 to 2020 is presented in Figure 2. ATZ and HYA were detected in soil samples with a high detectable rate, whereas ATZ and DEA were detected with high frequency in groundwater and surface water.

The results indicated that ATZ had a high detectable rate in soil, ground water, and surface water in Liaoning province for seven years in a row from 2014 to 2020. In contrast, DEA was found at a high rate in water samples. It was also reported that ATZ and DEA was detected in more than 90% of the ground water samples (n = 95, collected from private home wells) in China during 2019 [12]. Therefore, ATZ and DEA were most frequently detected in ground and surface water.

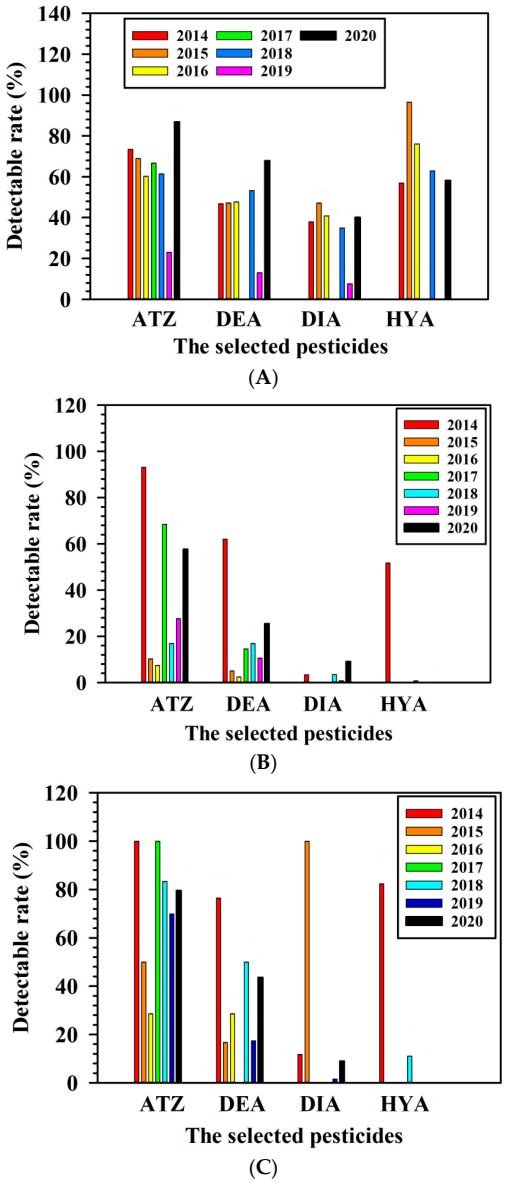

Figure 2. Detectable rate of the analytes in (**A**) soil samples; (**B**) groundwater samples; (**C**) surface water samples.

3.3. Detectable Level of Pesticides in the Collected Samples

The detectable levels of ATZ, DEA, DIA, and HYA in the collected samples from the Liaoning province of China from 2014 to 2020 are indicated in Figure 3. The average residual concentration (ARC) of analytes in soil was found to be higher than that in surface water and groundwater. The highest residual concentrations of ATZ, DEA, DIA, and HYA in soil reached 30.16 μg/kg in (2018), 4.44 μg/kg in (2014), 4.27 μg/kg in (2014), and 19.00 μg/kg in (2018), respectively.

The average residual concentrations of ATZ, DEA, DIA, and HYA in soil samples were 5.72 μg/kg, 1.32 μg/kg, 0.90 μg/kg, and 2.81 μg/kg, respectively, from 2014 to 2020. The average concentrations in surface water samples were 0.70 μg/L, 0.20 μg/L, 0.02 μg/L, and 0.02 μg/L, respectively. The average concentrations detected in groundwater samples were 0.16 μg/L, 0.10 μg/L, 0.03 μg/L, and 0.01 μg/L, respectively. As a result, the residual levels of the analytes in soil were greater than those in ground and surface water. The concentration of ATZ in the Liao-He River was reported to be 1.6 μg/L [27], higher than that of ATZ in water samples in the study. It was previously reported that the residual concentration of ATZs (the sum of ATZ and its metabolites) in groundwater varied from

0.04 ng/L to 2.38 μg/L in China. The maximum residual level of ATZs was detected in Northeastern China. The median concentration of ATZ, as the highest residual analyte in groundwater, was 0.76 ng/L, followed by DEA with 0.45 ng/L, DIA with 0.24 ng/L, and HYA with 0.13 ng/L [12], which was relatively lower than that of the analytes in the study. The high residual level of ATZs in Liaoning Province could be attributed to the high usage of ATZ on summer maize.

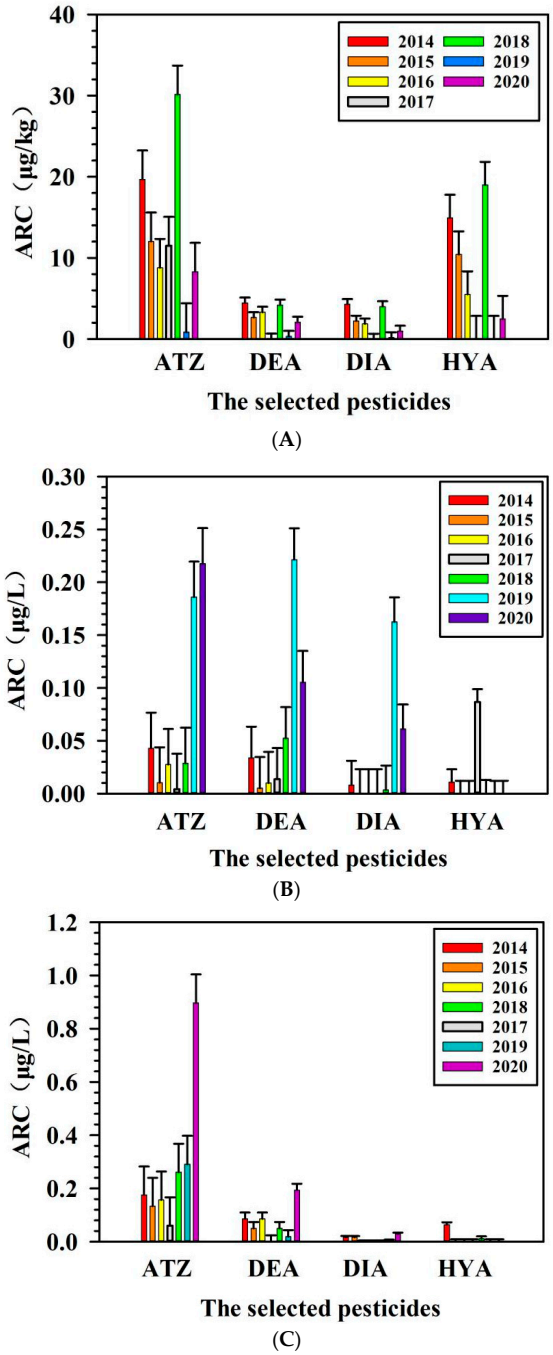

Figure 3. Average residual concentration of the analytes detected in (**A**) soil; (**B**) ground water; (**C**) surface water.

3.4. Residual Level of the Analytes in Different Regions of Liaoning in 2018

Soil and groundwater were collected to survey the average residual level (ARL) of the analytes in different regions of Liaoning in 2018 (Figure 4). The sampling regions are presented in Figure 5. It was found that the most serious soil pollution with the analytes in

Liaoning was from Fuxin, where the average residual concentration reached 292.38 μg/kg. In contrast, the pollution of Tieling, Anshan, Benxi, Liaoyang, and Qingyuan was relatively serious, with residual levels of 82.03 μg/kg, 75.94 μg/kg, 63.34 μg/kg, 77.53 μg/kg, and 66.52 μg/kg, respectively. The groundwater pollution in Tieling, Chaoyang, and Qingyuan was much more serious, and the residual levels were 0.26 μg/L, 0.33 μg/L, and 0.20 μg/L, respectively. Considering the relatively high residual level of the analytes in the selected areas, it is necessary to investigate the local agricultural activities and pesticides utilized or whether there is a pesticide factory near the sampling areas.

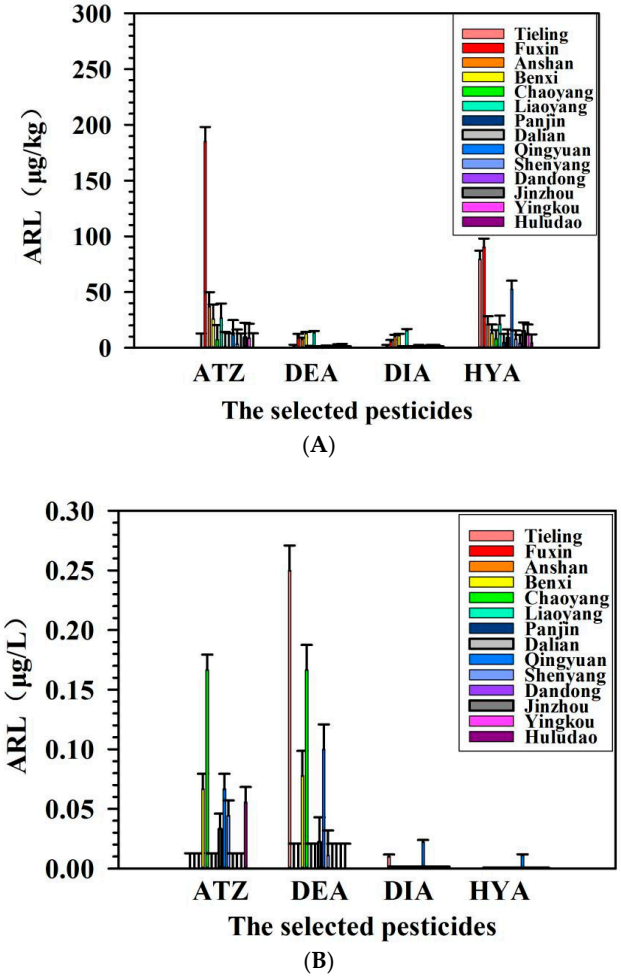

Figure 4. Average residual concentration of the analytes in the collected samples from different regions of Liaoning in 2018. (**A**) soil; (**B**) groundwater.

ATZ was found in soil and surface water from 2014 to 2020, whereas HYA was found in soil, but no pesticides were found in groundwater. The analytes' residue is related to the occurrence of plant diseases, pests, weeds, the physical and chemical properties of pesticides used, and the sampling time, place, and sample matrix.

In order to quantify the pesticides pollution in the agricultural environment of the selected area, it is necessary to continuously monitor the residual levels of the pesticides in water and soil. In addition, the sampling and detection of surface water should be strengthened. The analytical method for detecting pesticide residues should be improved in terms of sensitivity and selectivity. Soil pollution should not be neglected, except for the pollution of water sources. The technology of soil remediation presents a high potential to reduce the pollution level of the agricultural environment.

Figure 5. The sampling regions in Liaoning Province.

4. Conclusions

In conclusion, the overall pollution of farmland and the detectable level of the analytes in Liaoning Province was found highest in soil followed by surface water and groundwater. The detectable rate of the analytes: atrazine > hydroxyatrazine > desethylatrazine > desisopropylatrazine. In Liaoning Province, soil pollution was at the most serious levels, and atrazine was detected in the collected samples with the highest residual concentration. As a result, the presence of atrazine residue in soil should attract considerable attention.

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