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Atrazine and its degradation products in surface and ground waters in Zhangjiakou District, China

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Abstract A method using the solid phase extraction (SPE) and liquid chromatography-mass spectrometry (LC-MS) to analyse atrazine and its degradation products at levels of low nanograms per liter in water has been developed. The environmental water samples were filtered and then extracted by SPE with a new sulfonation of poly(divinylbenzene-co-N-vinylpyrrolidone) sorbents MCX. HPLC/APCIMS was used for the analysis of atrazine and its degradation products, desethylatrazine (DEA), deisopropylatrazine (DIA), didealkylatrazine (DEDIA), and hydroxyatrazine (HYA). The detection limits ranged from 10–50 ng/L in water samples. Samples were collected from deep wells and a reservoir near a plant that produced atrazine. Atrazine concentration levels

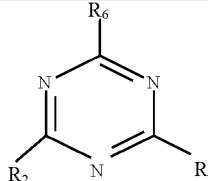
in most surface samples were above the limit of the China Surface Water Regulation (3 µg/L). In ground water, the levels of degradation product were more than 0.1 µg/L and 5–10 times greater than those of atrazine. The highest DEA concentration in the groundwater sample taken at the 130 m depth was 7.2 µg/L.

Keywords: atrazine, degradation chemicals, SPE, ground water, HPLC-MS.

Atrazine (ATR) is widely used as a herbicide in the world. Many studies on the impact of environmental ATR exposure have been reported^[1–3]. Stomach cancer incidence has been associated with ATR contamination levels ranging from 50 to 649 µg/L^[1]. A relationship between exposure responses and daphnia sex ratio was reported^[2]. At present, the maximum contaminant level (MCL) of ATR in drinking water is 3 µg/L in US, and 0.1 µg/L in EU. In 1998, China EPA set the MCL of 3 µg/L for ATR in surface water.

In the environment, ATR can be carried from runoff to surface water, percolated in ground water or retained in the soil. It can either remain chemically intact or further degrade. Four of the major degradation products (DPs) of ATR, desethylatrazine (DEA), deisopropylatrazine (DIA), didealkylatrazine (DEDIA), and hydroxyatrazine (HYA)

Table 1 Chemical structure of ATR and its DPs

Structure	Compound	R ₂	R ₄	R ₆	log <i>P</i> _{oct}	p <i>K</i> _a
	ATR	NHCH(CH ₃) ₂	NHC ₂ H ₅	Cl	2.7	1.7
	DEA	NHCH(CH ₃) ₂	NH ₂	Cl	1.6	1.3
	DIA	NH ₂	NHC ₂ H ₅	Cl	1.2	1.3
	HA	NHCH(CH ₃) ₂	NHC ₂ H ₅	OH	1.4	4.9
	DEDIA	NH ₂	NH ₂	Cl	0	1.5

are shown in table 1^[4]. The toxicity of DEA and DIA is similar to that of ATR, thus, they has been regulated by the National Pollution Survey (NPS) in the US and also routinely monitored in drinking water by some countries of EU.

Since ATR was used in China in the 1980s, its usage has increased. Currently, the total annual amount of ATR used in fields is up to 2000 t^[5]. Recently, several cases about the drop of corn yield were reported due to the ATR contamination in Zhangjiakou, Hebei Province, Changxing, Zhejiang Province and Siping District, Jilin Province.

The aim of this study is to investigate the source of ATR residue in the Guanting Reservoir and the concentration levels of ATR and its DPs in ground and surface waters in Yang River, Hebei Province, China.

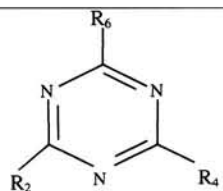
1 Experimental

(i) Material and method. The ATR standard was obtained from the Center of Country Standard Chemicals. Standards of DPs were gifts from Dr. Steinheimer (USGS) and Dr. Williams Hickey (Wisconsin Univ.). Table 1 lists the structures of ATR and its DPs, HA, DEA, DIA and DEDIA.

Surface water samples were collected in the Yanghe Reservoir in December of 2000. Ground-water samples were collected from the well of 130 m and 380 m depths near the pesticides plant (fig. 1). All samples were stored at 4 °C until analysis.

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Water samples were filtered before the SPE extraction. The concentration of ATR in water samples of the Guanting Reservoir was detected using SPE-LC-MS^[6,7]. ATR and its DPs were extracted by using an MCX cartridge. The pH of water was adjusted to pH 1.5 with HCl. Then the water samples were extracted in a vacuum manifold using 3 mL reservoir and a 60 mg MCX SPE cartridges that has been pre-treated as follows: (1) Condition cartridges by sequentially adding 3 mL of CH₃OH

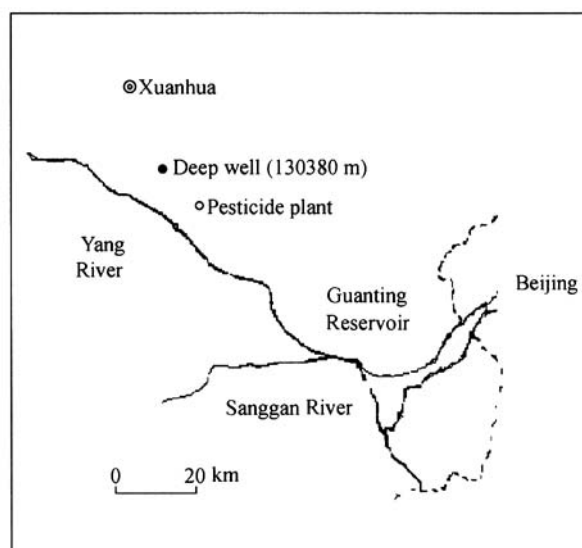


Fig. 1. Map of Zhangjiakou District and Guanting Reservoir.

and H₂O each; (2) pass a 50–500 mL sample through cartridges at a flow rate of 10 mL/min; (3) wash cartridge with 2 mL LC-grade water, methanol, and 2% NH₃·H₂O; (4) elute with 3 mL 4% NH₄OH in methanol; and (5) evaporate eluant to 100 μL under N₂ for HPLC-MS analysis.

The HPLC separation was performed by using gradient elution at a flow rate of 0.8 mL/min. Initial conditions were 10% acetonitrile and 90% aqueous buffer (ammonium acetate 1 mmol) with a linear gradient to 20% of acetonitrile within 5 min, then to 80% of acetonitrile within 15 min. The UV detector was set at 220 nm. The spectra were recorded on a mass spectrometer in the positive ion mode. The cone voltage was set at 14 V, and the corona voltage at 3.3 kV. The ion source was set at 150°C, and the probe temperature was 550°C. For full scan conditions, the scan range was *m/z* 100–300 at 0.3–1.05 s. The quantitative SIM conditions at 14 V are listed as follows: DIA, 8.0–11.0 min, *m/z* 174 and 176; HA, 9.0–13.5 min, *m/z* 198; DEA, 11.0–14.5 min, *m/z* 174; DEDIA, 3.0–6.0 min, *m/z* 146. The in source CID experiments at cone voltage of 36 V were conducted using the following conditions: DIA, 8.0–11.0 min, *m/z* 174 and 132; HA, 9.0–13.5 min, *m/z* 198 and 156; DEA, 11.0

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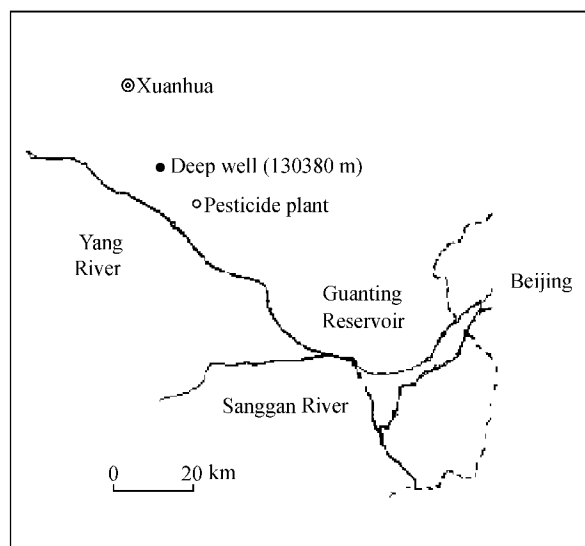


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2 Results and discussion

The DPs of ATR in water was extracted by using the MCX cartridge and analyzed by HPLC-MS. Although C18 cartridge is successfully applied to ATR extraction in water, its sorption capacity for DPs is limited^[8]. The sorbents of graphitized carbon black (GCB) and polymer resin have large breakthrough volumes in extraction of DEA and DIA in water^[8,9]. But in the meantime, matrix interferences that were of higher polarity were also extracted. To solve this problem, a new sorbent, sulfonated divinylbenzene-co-N-vinylpyrrolidone copolymer (MCX) was applied for a selective trace enrichment of polar DPs. Polymeric resin sulfonate has a great selectivity and recovery for DPs. The breakthrough volume of DEA, DIA and HA are all above 400 mL. The recovery rate for ATR, DEA, DIA and HA at the spiked level of 0.05 $\mu\text{g/L}$ in water is over 80% by using this cartridge.

The pK_a of DEA, DIA and HA ranges from 1.6 for chlorotriazines to 4.9 for HA. Therefore, the water containing 1 mmol/L ammonium acetate (pH = 6.5) was used. Large water sample volumes must be enriched in low level and much matrix interference would be coextracted at the same time. The LC-ESIMS method has been elaborated for simultaneously monitoring ATR and its six major DPs in natural waters^[10]. A new automated on-line immunosorbent phase extraction with an HPLC-APCIMS was also developed and used for detection of ATR and its DPs in environment water samples^[11]. In the present work, we detect ATR and its DPs using HPLC-APCIMS. The detection limits were 10—20 ng/L in environmental water. The mean relative standard deviation (RSD) was lower than 7.0%. More structural information could be obtained as cone voltage was 36. However, the detection limit was sacrificed to 0.25—0.6 ng/L at the same time.

ATR in drinking water and food has been paid more attention to because of its endocrine disrupting effect. The pesticides plant in Zhangjiakou District has produced ATR for 10 years^[12]. The residue of ATR and its DPs in surface and ground water was investigated.

The concentrations of ATR and its DPs in surface and ground water are listed in table 2, The mass spectra are shown in figs. 2 and 3. The data show that the levels of contaminates range from 1.7 to 8.6 $\mu\text{g/L}$ in surface water samples. Most of them are above the MCL for ATR. In ground water, HA has not been observed and the levels of

ATR are far below the MCL. The concentrations of DEA and DIA in the well-sampled water are much higher than what were expected, and the value of DEA is up to 7.2 $\mu\text{g/L}$.

DEA and DIA are the two major degradation chemicals in soil by the microbiological process, while HA is formed by chemical hydrolysis. These chemicals all occurred in surface water. In farmland, DEA is less adsorbed than ATR, while HA is more likely bounding with the soil matrix than ATR, DEA and DIA^[13]. Therefore, the con-

centration of ATR and its DPs in ground water has a great decrease with the increase of depth. However, HA is rarely detected in ground water. It is well observed that the shallow well always has more problems in terms of pollution. In well water of 130 m depth, ATR, DEA and DIA were all detected and concentrations were 10–100 times higher than that of 380 m. In well water of 380 m depth, only DEA and DIA were detected. The major pollutants of ground water in Zhangjiakou District were DEA and DIA.

Table 2 Concentration of ATR and its DPs in environmental water samples ($\mu\text{g} \cdot \text{L}^{-1}$)

	ATR	DEA	DIA	HA	SUM	SUM/ATR	(DEA + DIA)/ATR
Yanghe Reservoir	6.7 ^{a,b)}	1.7	3.2	8.6	11.6 ^{a,b)}	1.73	0.73
Water of 130 m depth well	0.72 ^{a)}	7.2	1.24	ND	9.16 ^{a,b)}	12.7	11.7
Tap water of Xuanhua	0.03	0.106	ND	ND	0.136 ^{a)}	4.5	3.5
Water of 380 m depth well	ND	0.046	0.13	ND	0.176 ^{a)}	∞	∞
Miyun Reservoir	ND	ND	ND	ND	–	–	–

a) Above EU standards (0.1 $\mu\text{g/L}$), b) above China EPA standards (3 $\mu\text{g/L}$). SUM = ATR + DEA + DIA; ND, not detected. Detection limit: ATR, 0.01 $\mu\text{g/L}$; HA, 0.06 $\mu\text{g/L}$; DEA and DIA, 0.05 $\mu\text{g/L}$.

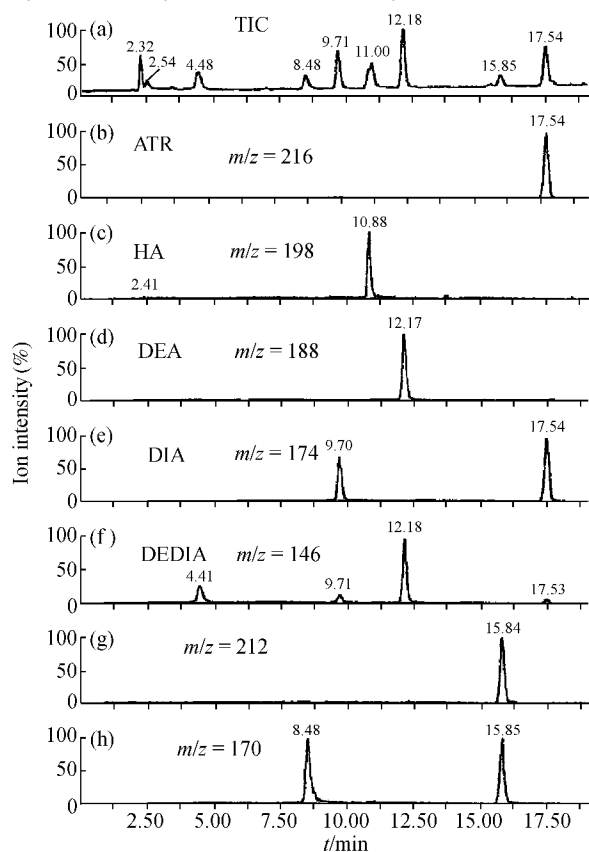


Fig. 2. HPLC/MS obtained by analyzing 500 mL water sample spiked with the five analytes at the level of 0.5 $\mu\text{g/L}$. (a) TIC: DEDIA 4.45 min, DIA 9.71 min, HA 11.00 min, DEA 12.18 min, ATR 17.54 min; (b) ATR m/z 216; (c) HA m/z 198; (d) DEA m/z 188; (e) DIA m/z 174; (f) DEDIA m/z 146; (g) m/z 212 and (h) m/z 170, they may be the degradation products of ATR. m/z 170 (8.48 min) and m/z 212 (15.85 min) may be deethylatrazine-2-OH (DEHA) and deethylhydroxyatrazine^[14] (4-amino-2-hydroxy-6-(isopropylamino)-s-triazine) respectively.

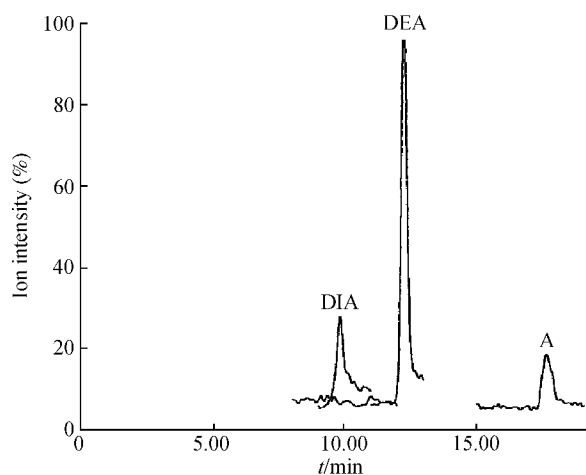


Fig. 3. Mass chromatography spectrum of ATR m/z 216, DEA m/z 174, and DIA m/z 188 in 150 mL water samples of well of 130 m depth of Anyuan village.

Because DEA and DIA are structurally and toxicologically similar to ATR, the total ATR residue (ATR + DEA + DIA) must be an important consideration for their environmental occurrence. Total ATR residue concentration was up to 11 $\mu\text{g/L}$ (two times that of ATR) in surface water, 9 $\mu\text{g/L}$ (12 times that of ATR) in well water of 130 m depth. Nevertheless, HA was rarely considered because of its low toxicity to human. The yields of corn dropped greatly when the local well water of 130 m depth was used to irrigate. The level of pollutants in water of well is not toxic enough to do harm to the crop, however, the concentration of ATR could increase dramatically due to the local arid weather. Therefore, the weather may be another major factor that influences the growth of corn. Overall, if ATR remains in the ground water for a long time, it would have potential

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time, it would have potential hazards to the local drinking water.

3 Conclusion

A valid and selective method consisting of the SPE and LC-MS has been developed for the determination of ATR and its DPs in the environmental samples. The ATR and its DPs residue in environmental water are investigated. ATR and its DPs have occurred in ground water of Zhangjiakou District, and the levels of DEA and DIA are far higher than the concentration of ATR, especially in deep well at the depths of 130 and 380 m.

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