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Risk Assessment of Atrazine polluted Farmland and Drinking Water: A Case Study

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Atrazine (2-chloro-4-[ethylamino]-6-[isopropylamino]-s-triazine) is a herbicide widely used for the protection of corn, sugarcane, grain sorghum, tea, and fruit crops. Since the introduction of atrazine to China in the early 1980s, its consumption in China has been increasing by 20% each year (Shu, 2000). Atrazine has been detected in the surface water and groundwater of several European Union countries (Siebers, 1994). The maximum contaminant level of 0.1 μg/L in drinking water has been detected in European Union countries, and 3 μg/L has been detected in the United States and China (Wüst et al., 1992). At a low soil pH, protonized atrazine becomes more hydrophilic, with the result that this compound moves downward to groundwater through water infiltration of soil. Furthermore, the higher the organic matter and clay contained in soil, the stronger the atrazine bond to the soil solid phase. An investigation conducted in Nebraska, USA, showed that 0.07% of the total atrazine applied to a sandy loam infiltrated down to 1.5 m below the surface (Capriel et al., 1986). In the case of paddy fields, frequent irrigation facilitates atrazine leaching in soils. It has been proposed that leaching and degradation are the two main pathways of atrazine dissipation in paddy fields, whereas the contribution of surface runoff is less important than these two pathways (Alissara and Thomas, 2001).

In late May 1997, a large-scale pollution incident occurred in the rice-growing area of Changtu County, Liaoning Province. During this incident, more than 2,800 ha of rice fields were heavily contaminated by atrazine during a short period of irrigation by atrazine-polluted waters from two rivers across the rice fields: the Tiaozi and Zhaosutai Rivers. An official investigation was conducted subsequently to trace the sources of atrazine in the rivers. It was found that an accidental leakage occurring in Siping City, Jilin Province, located on the upper reaches of the two rivers, resulted in a substantially higher concentration of atrazine upstream in the rivers.

Rice seeds died in many of the contaminated fields, leading to a direct loss of about US$ 4.4 million (National Pharmacy Water Pollution Control Center [NPHC], 2005). A 6-month monitoring study was conducted immediately after the accident. According to the report issued by the Pesticides Safety Evaluation Center (PSEC) in July 1997, atrazine concentrations measured around Bamiancheng, one of the major rice-growing regions in Changtu County, ranged from 0.06 to 0.29 mg/L in the Tiaozi River, from 0.23 to 0.36 mg/kg in soils, and from 1.07 to 2.26 mg/kg in young rice shoots. Atrazine concentrations around Baoli, another rice-growing region of the County, was 0.03 to 0.06 mg/L in the Zhaosutai River, up to 0.08 mg/kg in soils, and 0.28 mg/kg in young rice shoots. Given the unusually high concentration and persistence of atrazine in environments, a concern is raised. How long will this accident affect the local ecosystem and environment?

The current study aimed to determine atrazine residues in soils, rice grains, and drinking water in the contaminated area from November 1997 to October 2001 after the

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Fig. 1 Location of Chuangtu County in Liaoning Province and a schematic map of the water system in Changtu County

accident to gain a better understanding of the persistence and mobility of atrazine in the environment, and to assess atrazine exposure risks in the polluted area.

Materials and Methods

Changtu County is located in the northern part of Liaoning Province in Northeast China (42°33′–43°29′ N, 123° 32′–E 124°26′ E). The county is adjacent to Siping City in Jilin Province, as shown in Fig. 1. The Zhaosutai and Tiaozi Rivers are the two main sources of irrigation water for the rice-growing areas of Baoli and Bamiancheng, respectively.

The field measurements were taken from October 2 to 3, 2001. The sites for soil and rice grain sampling were located on farmland in Bamiancheng (heavy polluted) in 1997. When the incident occurred during this year in this area, and Tiaozi River, which also was polluted during the incident, ran across Bamiancheng. About 950 ha of farmland were polluted in this region. The Zhaosutai River ran across Baoli (lightly polluted), and the area of polluted farmland was about 1850 ha. Samples were collected from three farmlands in both polluted areas according to the direction of the rivers during the rice harvest period. The size of each soil sample was about 0.2 ha.

A stratified sampling strategy to examine the ubiquity of atrazine in the soil was adopted, and a total of 18 soil profiles were sampled covering both polluted areas (Baoli and Bamiancheng). Stainless steel shovels were used to obtain the soil profiles. Soil horizon samples were collected according to the sequence of soil genesis from the topsoil to the bottom layer in each soil profile (a depth of 100 cm). The boundaries of the horizons were 0 to 20 cm, 20 to 40 cm, 40 to 60 cm, 60 to 80 cm, and 80 to 100 cm from the soil surface, respectively. An equal number of soil samples were taken from each area. Each sample, weighing about 1.5 kg, was stored in brown glass bottles before analysis of atrazine. Rice plant samples were collected simultaneously and stored in a hop pocket, which was stored in the refrigerator intraday. Groundwater and surface water samples were randomly taken from 10-m wells and local reservoirs, which also were contaminated during the incident. The remaining water in pipes was drawn out before the sampling. Two independent samples were taken from each well and tap and stored in plastic bottles. The volume of each sample was about 2 L. The samples were kept in the refrigerator that day.

Table 1 Physicochemical properties of the two contaminated soils

Location	Pollution status	OM (%)	pH(KCl)	Sand (%)	Coarse silt (%)	Fine silt (%)	Clay (%)
Baoli	Lightly	1.37	8.14	25.0	30.5	14.5	30.0
Bamiancheng	Heavily	1.20	6.37	16.4	53.1	22.1	8.4

Soil pH was analyzed using combined measuring and reference electrodes in 0.1-mmol/L KCl extracts, and the ratio of soil and KCl was found to be 1:2.5. Soil organic matter was determined using a potassium dichromate oxidation method, and soil particle distribution was determined by densitometry (Li et al., 2003). The physical and chemical properties of the two contaminated soils are listed in Table 1. The calcareous paddy soil at lightly polluted Baoli had higher organic matter and clay contents than the soil at Bamiancheng.

Atrazine in the hexane solution was determined using a Hewlett-Packard 5890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a 1.2×2-mm glass column (2.5% OV-17 and 3.3% QF-1 coated on W AW DMCS, 800–100 mesh). The temperatures of oven, inlet, and detector were kept at 170°C, 200°C, and 250°C, respectively. The carrier gas used was N_2, and the flow rate was 50 mL/min.

The GC/MS was equipped with a TRACE2000 GC and MD800 MS, a 30-m DB-1701 column with an inner diameter of 0.25 mm and a film thickness of 0.25 μm. In the analysis, an injection volume (1 μl) with split injection, an injector temperature of 220°C, and transfer line temperatures of 300°C were adopted. The carrier gas was helium, with a constant flow rate of 1.5 mL/min. The GC oven temperature was programmed as follows. Initially, the temperature was set up at 90°C and held for 0.5 min, then increased at a rate of 15°C/min to 160°C. Thereafter, the GC oven was heated to 280°C at a rate of 25°C/min. The electron ionization (EI) source was kept at 70 eV. The instrument was operated in selective ion mode (m/z) at 173, 200, and 205, respectively.

The soil sample extraction experiment was conducted as follows. A set of fresh soil (10 g) was added to 100-mL glass centrifugal tubes containing 10 mL of $CaCl_2$ solution (0.010 mol/L) and 20 mL of methanol solution (methanol:water of 1:1), which then was mixed in a whirlpool and left for 12 h. Finally, the mixed solution was disposed by ultrasonic wave (100 HZ/s) in 25°C for 25 min and then centrifuged (4,000 rpm). The supernatant was taken. Each treatment was repeated three times (10 mL of methanol added the last two times). The mixed centrifugal solutions were transferred to a 250-mL extraction funnel through quantitative filter paper. The funnel was washed several times using 100 mL of distilled water, then extracted by 20 mL of dichloromethane (CH_2Cl_2). The extractions were collected in a 100-mL receiving bottle. The extraction process was repeated twice. All extracts were dried by rotary evaporator (EYELA, Tokyo, Japan). The atrazine extracts were dissolved in hexane completely, and then the hexane solution was desiccated by passing it through a small funnel filled with 2 g of anhydrous Na_2SO_4. A small amount of treated absorbent cotton was placed in the small funnel in case of Na_2SO_4 overflow. The volume of the extract was adjusted to 5 mL for analysis.

For the measurement, 10 g of rice grain (40 meshes) samples were weighed. The treatment process followed the same method described earlier rather than the liquid–liquid extraction process. In the case of emulsification, 5 g of NaCl were added before dichloromethane.

Atrazine in water was extracted using solid phase extraction techniques and analyzed by GC-MS, as described by Ren et al. (2002). One liter of water sample was passed through 0.45-μm-thickness film, with vacuum filtration enriched in a column filled with activated C_{18} purchased from Supelco (Bellefonte, PA, USA) (by 10 mL of methanol and 5 mL of redistilled water) at a flow rate of 3 mL/min. It was centrifuged subsequently to remove residues of water and eluted by methanol solution. The extract was collected in the range of 10 to 60 mL. Other processes were performed in the same manner as for soil extraction.

Statistical analysis was performed using the SPSS 10 software package. The differences were compared using one-way analysis of variance (ANOVA) after post hoc separation at a significance level of 0.05.

Results and Discussion

The vertical distribution of sampled atrazine is illustrated in Fig. 2. No significant difference was found in atrazine concentration among the soil layers at either site ($p > 0.05$). However, atrazine residues in the soil profile were considerably higher in the lightly polluted soil at Baoli than in the heavily polluted soil at Bamiancheng ($p < 0.05$). Given that the partition coefficient of atrazine is determined by

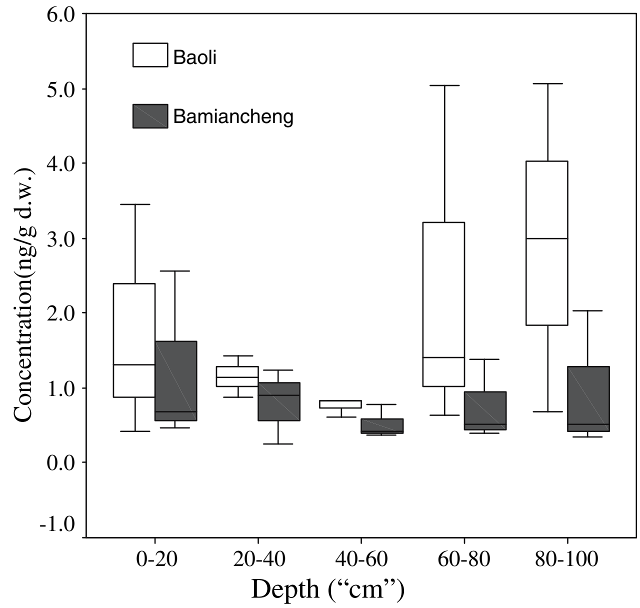

Fig. 2 Mean concentration and standard deviation of atrazine at different depths at two field sites

soil organic matter and clay content, it is expected that dissipation of atrazine via leaching would be stronger in soils with low organic matter or coarse textured soils. A possible explanation for the higher atrazine residues in the lightly polluted soil at Baoli may be that the organic matter and clay contents were higher in the soils at Baoli than in the other soils (Table 1). Organic matter and clay in soil lead to high atrazine affinity to the soil. As a result, the transportation of atrazine to the deep soil will be slow.

The concentrations of atrazine in the surface paddy field soil were 225 to 355 μg/kg at Bamiancheng and 126 to 323 μg/kg at Baoli Farm after the incident occurred in November 1997. Our measurements show that the concentrations ranged from 0.46 to 2.56 μg/kg and 1.31 to 5.05 μg/kg at two sites in October 2001, respectively. At both locations, the concentrations were lower than the maximum permitted residue limits of 50 μg/kg for corn in China.

The results of water sample analysis showed that dissolute atrazine concentrations were between the maximum contamination levels of 0.1 μg/L (European Union) and 3 μg/L (the United States) for drinking water. For instance, at heavily polluted Bamiancheng, the atrazine concentrations were higher in surface waters (0.10–0.32 μg/L) than in groundwater (0.07– 0.10 μg/L), whereas the atrazine concentration in the groundwater at lightly polluted Baoli was below 0.0026 μg/L.

After the polluted incident occured, atrazine still was detected in the agroecosystems of the affected areas during 4 years. Although concentrations of the herbicide in rice grains and drinking water were below or close to the statutory limits, because of its long half-life and bioaccumulation, atrazine would continue to be an environmental concern in the contaminated areas. Further studies still are needed to investigate the long-term trend and fate of atrazine concentrations in multiple compartments to gain more insight into the impact on environments from the accidental release of toxic pollutants.

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