Editor's Perspective—Atrazine Becomes Important Regulatory Issue

John A. Simon

From time to time, in this Editor's Perspective we focus on chemicals that appear to be prime for increased regulation or enforcement. Recent attention to the herbicide atrazine has increased the awareness of the widespread agricultural use of this chemical and other herbicides. This increased awareness primarily results from a recent study published by the Natural Resources Defense Council (NRDC) entitled *Poisoning the Well—How the EPA Is Ignoring Atrazine Contamination in Surface and Drinking Water in the Central United States* (NRDC, 2009). This study received national press coverage, including a cover story in the Sunday edition of the *New York Times* on August 23, 2009 (Duhigg, 2009).

As a result of the NRDC study and media coverage, on October 7, 2009, the U.S. Environmental Protection Agency (EPA) announced that it intends to review the health effects of atrazine. The US EPA's review, which is expected to be completed in 2010, will be used to assist the Agency in deciding whether to revise its risk assessment for atrazine. The study results could further scrutiny of atrazine and, possibly, prompt the US EPA to impose new restrictions on atrazine use to protect human health and ecological resources. Ultimately, this could lead to atrazine becoming a more highly regulated chemical and even lead to additional soil, sediment, and groundwater investigations and remediation to remove potential atrazine exposures.

In this Editor's Perspective, an overview of atrazine is provided, along with a discussion of the NRDC study, the potential health and ecological effects of atrazine, and the development of remediation technologies that can potentially be applied to soil and groundwater with atrazine contamination.

ATRAZINE OVERVIEW

Atrazine is a common herbicide used to kill weeds to promote the growth of various agricultural products—most commonly, corn, sugarcane, sorghum, and evergreen trees. It is also commonly used for weed control along roadsides. Atrazine is the second most used herbicide in the United States, and more than 60 million pounds are applied in the United States each year.

The chemical formula for atrazine is 6-chloro-N-ethyl-N′-(1-methylethyl)-triazine-2,4-diamine. The chemical is sold under a variety of trade names and formulations. Due to health concerns, atrazine-containing chemicals can only be applied by certified herbicide users; however, atrazine is used on residential properties by commercial applicators.

As a result of the potential health risks of atrazine and alleged exposures to herbicides containing the chemical, a lawsuit was filed in Madison County, Illinois, in 2004 against

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Syngenta, the manufacturer of atrazine, by the local sanitary district, and additional plaintiffs were sought. As of September 2009, this legal action was ongoing.

Many states are becoming concerned about the risks of atrazine. For example, in Wisconsin, atrazine application is prohibited in areas where atrazine concentrations in groundwater exceed the applicable standard of 3 μg/L (the same as the federal maximum contaminant level). As of 2006, Wisconsin had established 102 prohibition areas covering 1.2 million acres (http://www.datcp.state.wi.us/arm/agriculture/pest-fert/pesticides/atrazine/index.jsp). Similarly, Iowa restricts atrazine applications in pesticide management areas to one-half the federal application rate. This restriction applies to 7 counties and 16 townships (http://www.agriculture.state.ia.us/Pesticide/pdf/Ag_CH45_Pesticides.pdf).

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NATIONAL RESEARCH DEFENSE COUNCIL STUDY

The US EPA has two substantial monitoring programs for atrazine: (1) the Ecological Watershed Monitoring Program, in which surface-water samples are collected by companies registering atrazine (required as a result of a lawsuit by the NRDC against the US EPA), and (2) the Atrazine Monitoring Program, in which the same companies are required to sample raw (untreated) and finished (treated) water supplies. The NRDC obtained data from these programs and conducted a detailed evaluation, which was published in the August 2009 report referenced earlier.

The results of the Ecological Watershed Monitoring Program showed that 75 percent of surface water and 40 percent of groundwater in agricultural areas contain atrazine. In surface water bodies, atrazine concentrations as high as 237 μg/L were detected. A table from the NRDC study showing atrazine concentrations in surface-water bodies is included as Exhibit 1.

The drinking-water system data from the Atrazine Monitoring Program indicate that greater than 90 percent of the raw water samples collected in 2003 and 2004 contained detectable levels of atrazine, that three water systems contained atrazine concentrations consistently above the 3 μg/L maximum contaminant level established under the Safe Drinking Water Act, and that 39 percent of the water systems tested contained a one-time peak of atrazine above the maximum contaminant level.

HEALTH AND ECOLOGICAL EFFECTS OF ATRAZINE

According to the Agency for Toxic Substances and Disease Registry (ATSDR, 2003), there is insufficient evidence to evaluate the carcinogenic effects of atrazine. However, the US EPA has classified atrazine as not likely to be carcinogenic to humans. Similarly, the International Agency for Research on Cancer has determined that atrazine is not classifiable as to its carcinogenicity to humans. The NRDC report challenges the US EPA's current conclusion regarding the carcinogenicity of atrazine and references several scientific reports that suggest that atrazine may be a carcinogen, including epidemiological studies of occupational exposures. The additional toxicity study being performed by the US EPA should provide additional insight into the chemical's potential carcinogenicity.

Atrazine is considered to be an endocrine-disrupting chemical that has the potential to adversely affect the reproductive systems of aquatic life. For example, studies have shown

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Exhibit 1. Ten watersheds with the highest peak concentrations of atrazine, Ecological Watershed Monitoring Program

		Atrazine Concentration (ppb)		
Watershed Name	**Sampling Year**	**Max. Peak**	**75th Percentile**	**Average**
Little Pigeon Creek, IN 2005	2005	237.5	5.02	18.56
South Fabius River, MO*	2005	182.75	8.82	9.61
Big Blue River, Upper Gage, NE	2006	125	5.1	17.61
Big Blue River, Lower Gage, NE	2005	112.19	1.54	7.85
Middle Loup Creek, NE	2006	82	0.4	2.79
Rock Creek, IN	2004	78.1	0.68	2.76
Little Sni-A-Bar Creek, MO	2004	59.03	3.88	4.42
Youngs Creek, MO	2004	53.75	9.69	8.89
Horse Creek, IL	2006	50.7	0.85	2.58
Muddy Creek, NE	2005	49.87	1.97	4.67

*The South Fabious River watershed had 3 of the 15 highest peak concentrations: 182.75 ppb (2005), 106 ppb (2006), and 82.8 ppb (2006).
Source: Table 1 (NRDC, 2009).

that exposing frogs to atrazine impairs the development of the reproductive organs and even cause the development of female characteristics in male frogs (a phenomenon referred to as *intersex species*, as discussed in prior Editor's Perspectives discussing endocrine-disrupting chemicals in the Spring 2005, Winter 2006, and Summer 2007 issues).

The U.S. Fish and Wildlife Service has examined the potential effects of atrazine on two endangered aquatic species at the request of the US EPA: the Alabama sturgeon and the dwarf wedgemussel. The request was made in conjunction with the re-registration of pesticides containing atrazine as an active ingredient. Although the facts are somewhat complicated, the Fish and Wildlife Service concluded that it does not concur that re-registration would not adversely affect the two species studied, and additional formal consultation is warranted (U.S. Fish and Wildlife Service, 2008).

ATRAZINE REMEDIATION

The above discussion regarding the health and ecological effects of atrazine is indicative of a growing concern regarding the liabilities associated with the presence of the herbicides in soil and groundwater. For example, an environmental professional conducting a Phase I environmental assessment of an agricultural property should consider whether herbicides, including atrazine, have been applied and, if so, how the chemicals were managed. This is of particular concern if groundwater is shallow or if there is a water supply well on the property.

The prevalence of atrazine in groundwater is exemplified by an analysis of the US EPA's Pesticides in Ground Water Database conducted by the Center for Environmental

Quality at Wilkes University (2009) in Wilkes-Barre, Pennsylvania. This analysis showed that atrazine was detected in 22 percent of the private water systems in the corn-producing regions of Pennsylvania. This incidence is of sufficient significance to pose a concern in the context of a Phase I environmental assessment.

Atrazine can be remediated by several different methods. These include phytoremediation, bioremediation, iron-enhanced oxidation, and traditional pump-and-treat systems. The potential application of the first three of these technologies is briefly discussed in the next subsection.

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Phytoremediation

The process through which plants can uptake atrazine-contaminated groundwater has been studied since the 1990s. A study published in 1996 by Joel Burken of the Missouri University of Science and Technology and Jerald Schnoor of the University of Iowa demonstrated in laboratory tests that poplar trees can remove atrazine from contaminated soil (Burken & Schnoor, 1996). There has been substantial additional research since that time on the subject of phytoremediation of atrazine, including work conducted in Switzerland and Iran (Dehghani et al., 2007; Marcacci, 2004); however, it does not appear that there have been any full-scale applications of the technology.

Bioremediation and Iron-Enhanced Oxidation

Bioremediation of atrazine-contaminated soil has been performed on a limited basis, although successfully. A detailed overview of the biodegradation of s-triazine herbicides, including atrazine, is presented in a book chapter by Mandelbaum et al. (2008). This discussion provides an overview of bioremediation efforts, including the treatment of 19,000 cubic meters of atrazine-containing soil at a Ciba-Geigy plant in St. Gabriel, Louisiana, using land farming and bioaugmentation techniques. The technique, as reported in Finklea and Fontenot (1995), demonstrated that atrazine was reduced from as high as 300 ppm to less than 2 ppm.

Another demonstration of using bioremediation to treat soil contaminated with atrazine was a study performed by researchers at the University of Minnesota in which soil containing up to 2.9 percent atrazine was treated using killed, recombinant *Escherichia coli* and phosphate. The study showed reductions of up to 77 percent, which is significant considering the high initial contaminant concentrations (Strong et al., 2001).

More recently, soil contaminated with both atrazine and cyanazine was extracted from the field and treated in laboratory-scale experiments with combinations of zero-valent iron, ferrous sulfate (a catalyst), and emulsified soybean oil (Waria et al., 2009). Based on the field tests, a chemical-biological approach consisting of zero-valent iron, ferrous sulfate, and emulsified soybean oil was utilized in a field-scale application. The test involved applying the solution to soil windrows and covering the windrows to maintain temperature and water content. Post-treatment sampling indicated overall losses of the two herbicides ranging from 79 to 91 percent.

The use of *in situ* bioremediation to treat atrazine-contaminated groundwater has also been studied in various laboratory tests, although no full-scale applications have been

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identified in the literature. The laboratory tests have consisted of the following technologies:

- Isolating a specific bacteria, *Pseudomona* sp. Strain ADP, capable of removing atrazine and nitrate (a common co-contaminant) from groundwater (Katz et al., 2000; Mandelbaum et al., 1995; Shrestha et al., 2006).
- Using permeable reactive biobarriers to treat groundwater with atrazine, ammonium, and other volatile and semivolatile contminants (Patterson, 2002). The concept tested involves dual barriers in which oxygen is delivered through the first barrier to transform ammonium to nitrite/nitrate and then ethanol is added to the second barrier as a carbon source to further degrade the nitrite/nitrate to nitrogen gas. The atrazine and other contaminants are degraded in the process. The concept has been conducted in laboratory column studies and is planned for field testing (CSIRO Land and Water, 2009).
- A similar process as above was tested by the U.S. Department of Agriculture in laboratory columns, except with only a single biobarrrier consisting of soybean oil and a consortium of atrazine-degrading microorganisms. The test showed that the microbes were using atrazine as a source of nitrogen and that there was competition between atrazine and nitrate (Hunter & Shaner, 2009).
- Treating atrazine- and nitrate-contaminated groundwater using zero-valent iron (Chew et al., 1998). Laboratory testing utilizing columns showed greater than 98 percent atrazine removal using powdered iron (0.02-micron size), and lesser removal efficiencies with industrial-grade iron powder (0.5-micron size), and rusted industrial-grade iron powder (also 0.5-micron size).

CONCLUSION

The NRDC report on the prevalence of atrazine in surface waters and water-supply systems has received widespread media coverage and appears to have prompted the US EPA to conduct additional research on the health effects of atrazine. There is documented evidence that atrazine is an endocrine-disrupting chemical and can cause other adverse ecological effects. However, there currently does not appear to be sufficient evidence to determine whether the chemical is a carcinogen.

The recent flurry of activity surrounding the prevalence and potential risks associated with atrazine by the NRDC and other environmental action groups, the scientific and regulatory communities, and the media highlights the importance of atrazine and, potentially, other herbicides to environmental professionals involved in assessment, investigation, and, to the extent required, remediation activities.

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John A. Simon is the editor-in-chief of *Remediation*. He is also an executive vice president of WSP Environment & Energy, an environmental consulting firm specializing in investigation, remediation, and environmental liability transactions. He frequently consults private industry on the assessment and remediation of hazardous sites, as well as environmental liability and risk-transfer issues. He also participates in the Sustainable Remediation Forum and on the ASTM Green Cleanup Task Group. He received his BE in civil and environmental engineering from Vanderbilt University and his MS in civil engineering, environmental engineering, and science from Stanford University.

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