

**Measurement and Modeling of the Fate of the Herbicide Atrazine
in the Lakes of Isle Royale National Park**

A Research Proposal Submitted to the U.S. Environmental Protection Agency

In Response to the Announcement

"Reducing Uncertainty in Risk Assessment and
Improving Risk Reduction Approaches - Air Pollutants"

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14 April 1995

Abstract. Atrazine is the most widely used herbicide in the United States. It is toxic to aquatic life and has been shown to alter phytoplankton community structure at low concentrations. Atrazine is a semivolatile organic compound and thus subject to atmospheric transport, potentially impacting pristine environments far distant from its point of application. Highly contradictory evidence exists regarding the environmental persistence of atrazine. Reported activities range from essentially conservative behavior to a half life on the order of days. Although distinctly seasonal in its application and transport, the dynamics of atrazine and its environmental fate following deposition are not well described. This lack of information serves as a barrier to the determination of ecosystem exposure and the ultimate risk associated with this herbicide.

Here we propose to utilize an integrated program of field monitoring, laboratory experimentation, and mathematical modeling to define the environmental behavior of atrazine in selected lakes at Isle Royale National Park on Lake Superior. Monitoring of the atmospheric flux of atrazine to the island, coupled with back trajectory analysis, will be applied in determining sources and rates of input of the herbicide to the island. Water column measurements and field and laboratory experimentation would be used to quantify the biological, chemical, and physical source/sink terms which mediate the environmental behavior of atrazine and its metabolites. Inputs, losses, and transformations of atrazine would be examined within the framework of a mass balance model to elucidate the fate and environmental partitioning of atrazine in this pristine environment and to predict changes in ecosystem exposure associated with future changes in herbicide use. Model inputs will be developed in a manner which facilitates application of the findings to studies of other atmospherically-derived contaminants and to other potentially impacted sites in the region.

Description of the Project

Current agricultural practices require chemically manufactured herbicides in order to be profitable. It is estimated that approximately 230,000 tons of 96 different active ingredient herbicides are used in the United States every year (Gianessi and Puffer, 1990). Atrazine (2-chloro-4-ethylamino-6-isopropylamine-s-triazine; Figure 1) is the most widely used herbicide in the United States, with over 27,500 tons applied annually (USDA 1993, USDA 1994). It is used primarily with pre-emergent corn (*Zea mays* L.) and grain sorghum (*Sorghum bicolor* L.) to control broadleaf weeds.

Atrazine acts to inhibit photosynthesis by blocking the Hill electron transfer of photosystem II. Being a photosynthetic inhibitor, atrazine is toxic to the plant communities of aquatic systems as well. Studies of the acute toxicity of atrazine indicate photosynthetic inhibition of phytoplankton at concentrations of 20 µg/L (Jones and Winchell, 1984; deNoyelles et al., 1982). Subacute effects, i.e. alteration of phytoplankton community structure, have been noted at much lower concentrations (0.1 to 1.0 µg/L; deNoyelles et al., 1982). Atrazine is a suspected carcinogen and is regulated in finished drinking water (Maximum Contaminant Level, MCL, of 3.0 µg/L).

Atrazine is mobile (aqueous solubility of 32 mg/L at 25° C) and thus appears in groundwater following application to land surfaces (Koplin et al., 1991). Researchers have estimated that 1-2% of the mass of atrazine applied to soil is transported to subsurface waters (Adams and Thurman, 1991; Barrett and Williams, 1989; Jury et al., 1987). Atrazine is found in lakes and rivers as well. An additional 1-2% of the mass of atrazine applied annually is washed from fields, making its way to rivers and reservoirs downstream of agricultural regions (Goolsby et al., 1991; Squillace and Thurman, 1992; Thurman et al., 1991; Thurman et al., 1992; Ulrich et al., 1994; Schottler and Eisenreich, 1994). In a 1992 study of atrazine in the mid-continental U.S., Goolsby et al. (1993) found that 16 of 74 reservoirs exceeded the MCL at least once during the monitoring period.

Atrazine is a semivolatile compound (vapor pressure of 3×10^{-7} mPa at 20° C; Henry's Law constant of 2.5×10^{-7}) and is thus also lost from fields through atmospheric pathways (Buser, 1990; Tierney, 1993; Spencer and Clith, 1990; Nash and Hill, 1990; Clendenen et al., 1990; Glotfelty et al., 1990; Eisenreich et al., 1981; Glotfelty et al., 1990; Nations and Hallberg, 1992; Wu, 1981; Richards et al., 1987; Goolsby et al., 1995; Cromwell and Thurman 1995). The volatilization rate

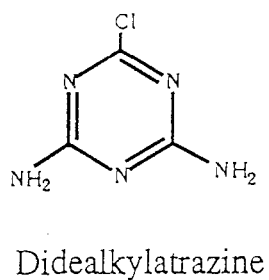
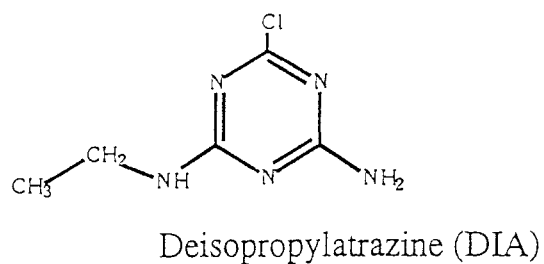
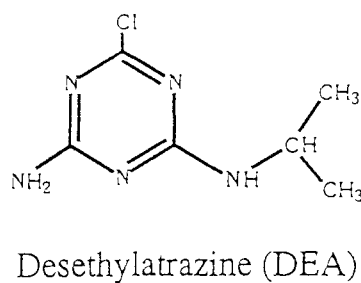
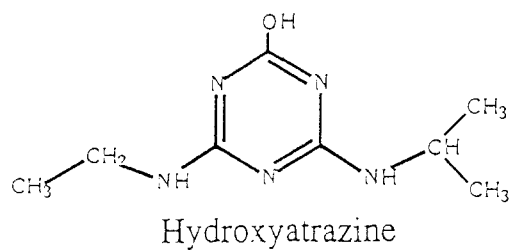
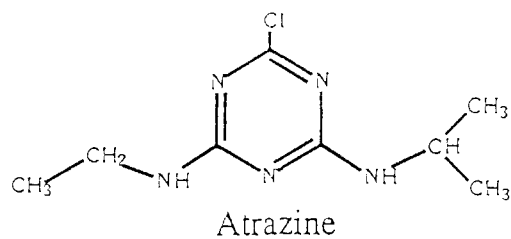


Figure 1. Structures of atrazine and its metabolites.

of atrazine is highest immediately after application and decreases logarithmically thereafter (Nash and Hill, 1990; Lending et al., 1990). Environmental conditions which favor volatilization include high winds, warm temperatures, and moist soils (Spencer and Cliath, 1990; Nash and Hill, 1990; Clendening et al., 1990). Gas phase loss of atrazine from fields is thought to be comparable in magnitude to that lost through aqueous pathways, i.e. 2-3% of the applied mass (Glottfelty et al., 1990). However, the atmospheric dispersal of atrazine is not as well defined as the mobilization to surface and ground waters. Additional sources of atrazine to the atmosphere include physical drift of the herbicide when sprayed atrazine and particle movement of both the pure chemical and of atrazine-laden soil particles.

Atrazine delivered to the atmosphere is subject to transport and subsequent deposition. A host of studies have identified atrazine as being present in rainfall (Buser, 1990; Glottfelty et al., 1990; Nations and Hallberg, 1992; Wu, 1981; Richards et al., 1987; Goolsby et al., 1995, Dankwardt et al., 1994; Cromwell and Thurman, 1995) with concentrations reaching 1-3 $\mu\text{g/L}$ proximate to the source (Clendening et al., 1990; Glottfelty et al., 1990; Eisenreich et al., 1981; Goolsby et al., 1995). In one study, rainfall received adjacent to a corn field contained 40 $\mu\text{g/L}$ of atrazine (Nations and Hallberg, 1992). Atrazine concentrations in precipitation tend to decrease with increasing distance from the source due to atmospheric dilution and possibly photochemical degradation (Pelizzetti et al., 1990; Goolsby et al., 1995, Cromwell and Thurman, 1995).

Despite the potential for dilution and transformation in the atmosphere, atrazine has been observed to travel great distances. Atrazine has been detected in rainfall at national park in Germany (Dankwardt et al., 1995) and in Swiss alpine lakes at altitudes well above those used for agriculture (Buser, 1990). Richards et al. (1987) detected atrazine in Maryland rainfall at a time when there was no local use and tracked the herbicide to applications in Florida (Richards et al., 1987). Goolsby et al. (1995) studied atrazine deposition across the mid-continental U.S. and observed atmospheric transport of atrazine as far as Isle Royale National Park in Lake Superior. A subsequent study by Cromwell and Thurman (1995) showed that atmospheric deposition of atrazine to Isle Royale is significant, with rainfall concentrations on the island sometimes equaling those observed in the cornbelt (2.3 $\mu\text{g/L}$; Goolsby et al., 1995). These studies illustrate the potential for long range transport of atrazine and confirm that quantities of the herbicide applied in agricultural regions are

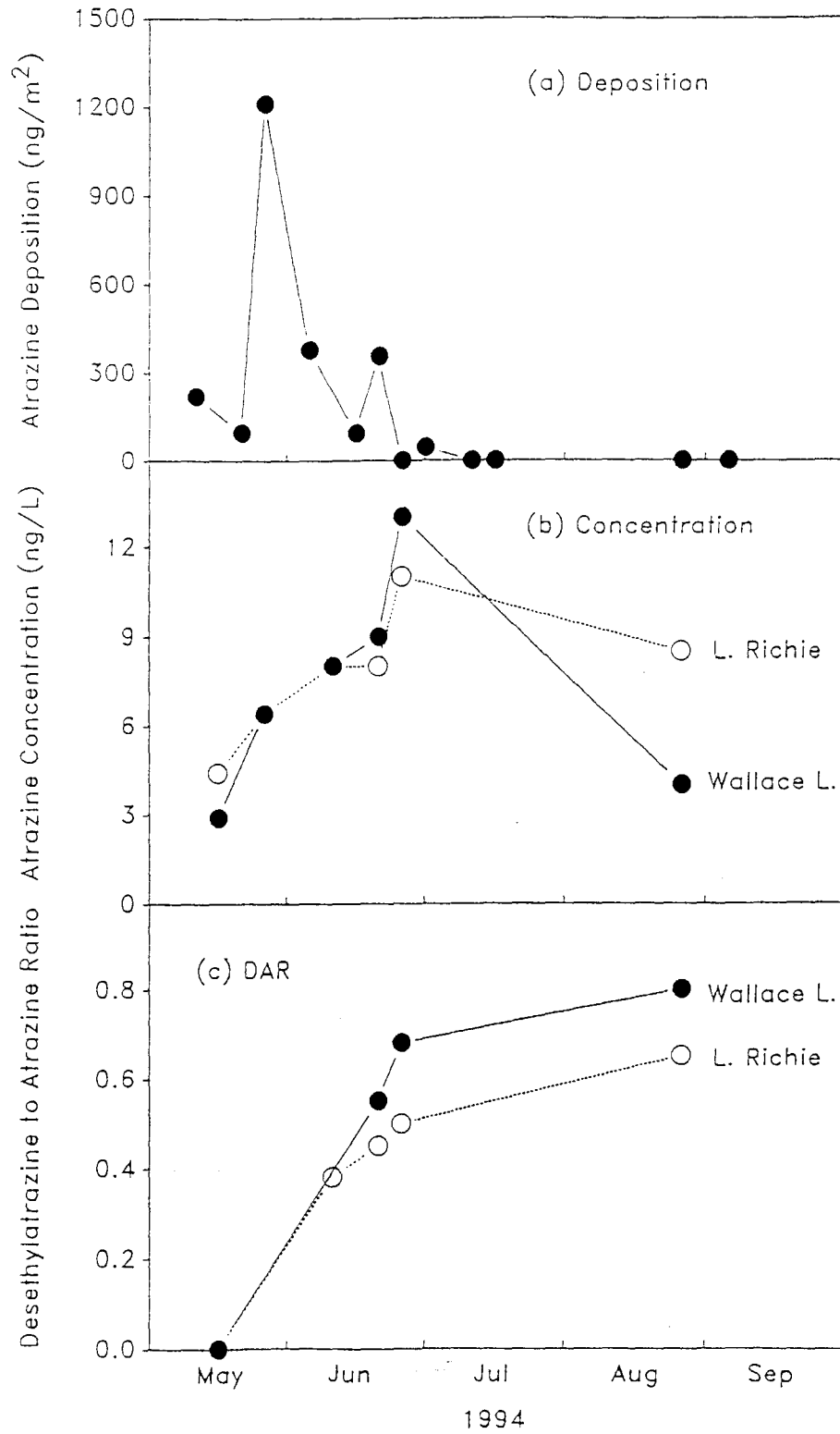
reaching far distant, often pristine, environments.

Although the presence of atrazine in lakes and rivers is well documented (Squillace and Thurman, 1992; Thurman et al., 1991; Thurman et al., 1992; Ulrich et al., 1994; Schottler and Eisenreich, 1994; Buser, 1990; Cromwell and Thurman, 1995), its fate in surface waters is poorly described. In fact, evidence provided by several recent studies is contradictory. Koplin et al. (1993) showed atrazine in surface waters to be highly reactive, with a half life in Iowa streams on the order of a few days. These findings are consistent with studies of atrazine degradation in soil environments where half lives of 60-100 days have been reported (Jury et al., 1987). Others have noted, however, that atrazine persists in midwestern reservoirs all year, despite its seasonal application (Goolsby et al. 1993, Fallon 1994). Studies on the Laurentian Great Lakes (Schottler et al., 1994) and on two lakes in Switzerland (Ulrich et al., 1994; Buser, 1990) suggest that atrazine behaves conservatively in those environments, i.e. there is no chemical or biological degradation.

A recent study of atrazine dynamics in two lakes at Isle Royale National Park on Lake Superior (Cromwell and Thurman, 1995) provides evidence that this herbicide does behave in a non-conservative fashion. Figures 2a and 2b illustrate atrazine deposition to Isle Royale and concentrations of the herbicide in Lakes Richie and Wallace over the May - September period of 1994. Increases in lake water atrazine levels in May and June correspond nicely to periods of high atmospheric flux and are consistent with patterns of application of the herbicide in the mid-continental U.S. Decreases in deposition after late June are reflected in decreasing water column concentrations following the July peak. Note, however, that atrazine is present in the lakes in mid-May, despite the fact that atmospheric deposition in fall and winter are negligible. Although not conclusive, these findings suggest that atrazine either persists in the lakes or their watershed or that atrazine is delivered to the island from other sources before spring applications commence in the mid-continental U.S.

It is not clear whether the marked reductions in atrazine observed in Lakes Richie and Wallace in late summer and fall occur through degradation or flushing. Hydrologic budgets have not been developed for these primarily seepage systems and thus losses to outflow cannot be determined. However, some evidence for the chemical or biological degradation of atrazine is available through analyses of one of its major metabolites, desethylatrazine (DEA, Figure 1). The DEA to atrazine ratio (DAR) in Lakes Richie and Wallace for the summer of 1994 is presented in Figure 2c (Cromwell and

Figure 2. Atrazine on Isle Royale



Thurman, 1995). Essentially absent from the lakes in the spring, DEA concentrations increase over the summer, nearly equalling those of the parent compound (atrazine) by September (DAR ~ 0.8). DAR values for Isle Royale rainfall are relatively constant at ~0.45. The fact that ratios observed in September are higher than those in the rainfall suggest the occurrence of transformations within the watershed. The results of this preliminary study of atrazine fate in the lakes of Isle Royale provide strong evidence that atrazine undergoes degradation in aquatic systems, but suggests as well that the herbicide persists over the winter in the lakes, in the watershed or in adjacent environmental reservoirs.

Here we propose to utilize an integrated program of field monitoring, laboratory experimentation, and mathematical modeling to define the environmental behavior of the herbicide atrazine in selected lakes of Isle Royale National Park on Lake Superior. Inputs, losses, and transformations of atrazine will be examined within the framework of a mass balance model to elucidate the fate and environmental partitioning of atrazine in these pristine aquatic systems and to predict changes in ecosystem exposure associated with changes in herbicide use.

Study Site

The study will focus on three lakes located in Isle Royale National Park (Figure 3): Siskiwit Lake, Lake Richie, and Wallace Lake). These are systems with documented atrazine contamination (cf. Goolsby et al., 1995; Cromwell and Thurman, 1995) and have contrasting physical characteristics (e.g. hydrology) Isle Royale offers an exceptional opportunity in its role as a wilderness laboratory and has served prominently in early studies of atmospheric contamination of lakes.

Isle Royale National Park

Isle Royale National Park is located in northwestern Lake Superior, approximately 16 miles from the Ontario/Minnesota shore and 43 miles from mainland Michigan. Isle Royale is 45 miles long and 9 miles wide and is the largest island in Lake Superior. More than 400 additional, smaller islands are located within the park boundaries. The main island is characterized by a series of parallel ridges and valleys and a shoreline marked by numerous islands, narrow peninsulas, and bays. Most of the

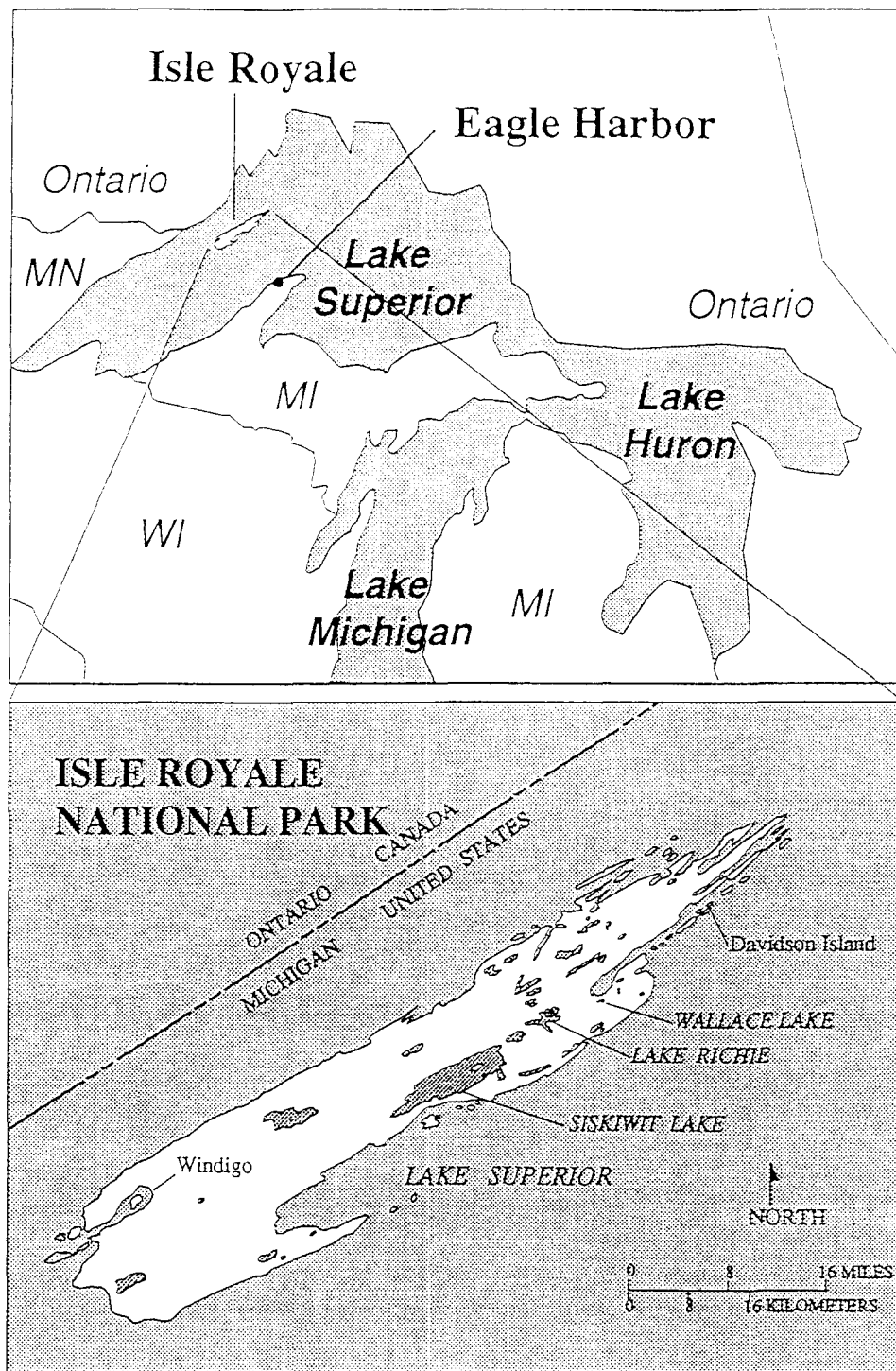


Figure 3. Location of study area.

land area is heavily forested, with numerous inland lakes, ponds, swamps, and bogs occupying lowlands between the ridges. Overstory vegetation represents the southern edge of the boreal forest and the northern fringe of the northern hardwoods. The park climate is heavily influenced by Lake Superior, which modifies both the severe cold of winter and warmer heat of summer typical of mainland Minnesota and Ontario.

There are over 50 inland lakes on Isle Royale, ranging in size from a few acres up to several square miles in surface area. Most of the lakes are fed by groundwater and support a diverse biological community. The lakes are, however, very poorly studied and are lacking in baseline limnological data. Recent studies of limited scope have shown that contaminants are present in the water column, sediments, and biota of these lakes, a likely result of the atmospheric input of pollutants.

Research and the Park Mission

Isle Royale National Park was formally created in 1931 to protect the islands as a wilderness area. Particularly noteworthy in the Congressional reports which accompanied the enabling legislation were references to the site as a location for scientific study. The park was formally designated as a Wilderness area in 1976 and as an International Biosphere Reserve in 1980. The Biosphere Reserve status was granted primarily because of the extensive history of scientific study in the park and the relative isolation of the site on Lake Superior. This isolation has in essence created a "natural laboratory", relatively free of the direct influence of human activity. Isle Royale is also designated a Class I airshed through provisions of the Clean Air Act. The specific value of Isle Royale as a study site for the proposed work lies in its protection from direct human influence and in its history as a site for research on toxic substances, especially related to the phenomenon of atmospheric transport.

History of Contamination on Isle Royale

Swain (1978) was the first to document the presence of anthropogenic contaminants on Isle Royale, reporting elevated levels of PCBs in fish collected from the island's Siskiwit Lake. Swackhamer and Hites (1988) conducted further studies of organochlorine compounds in the fishes

of Siskiwit Lake, pointing to the potential role of atmospheric transport at this location where no local sources of pollution exist. Other chemicals of likely atmospheric origin have been detected on Isle Royale, including elevated levels of sulfur and zinc in lichens (Wetmore, 1985; Bennett, 1995) and mercury in the Common Loon (including juvenile birds whose only exposure to mercury was on the island; Evers, 1992; 1993). The National Park Service (NPS) has monitored selected criteria pollutants (sulfur dioxide, ozone, aerosols, and acid precipitation) on Isle Royale since the late 1980s (cf. Sisler et al, 1993) and the U.S. Geological Survey (USGS) has conducted measurements of atrazine in rainfall and in selected Isle Royale lakes (Cromwell and Thurman, 1995).

Objectives

The objective of this project is to define the fate and environmental behavior of atrazine and its metabolites in the lakes of Isle Royale National Park (Lake Superior). The results of this effort will aid in the determination of the long-term environmental risks associated with herbicide exposure in this pristine environment. It is our goal to conduct the study and to develop the modeling interface in a manner which will facilitate transapplication to other contaminants and to other pristine lake systems in the U.S. and Canada. Specifically, we seek to:

- monitor the atmospheric deposition of atrazine and its principal metabolites to Isle Royale;
- utilize back-trajectory analysis to identify sources of atrazine;
- develop hydrologic budgets for selected Isle Royale lakes;
- measure atrazine and its metabolites in surface runoff, groundwater and the water column;
- conduct field and laboratory measurements of the transformations influencing atrazine fate;
- integrate the results of these efforts in a mass balance model describing the fate of atrazine and its metabolites in the lakes of Isle Royale.

It is our goal to make the best possible use of existing data on atrazine and its metabolites. Information on atmospheric deposition, concentrations in Isle Royale lakes, and kinetic transformations available from the scientific literature will be used to support the modeling effort.

New studies are proposed where existing information is insufficient (i.e. kinetic behavior) or where site-specific determinations are fundamental to the credibility and reliability of the resulting model. It is also our objective to seek cooperation and interaction with the body of scientists and engineers presently studying interactions between lakes and the atmosphere on Lake Superior and in the mid-continental U.S. and with those studying atrazine in other environments (e.g. Europe).

Results or Benefits Expected

The primary benefit of this study will be definition of the role of long range transport and subsequent kinetic behavior in determining levels of atrazine, the most widely used herbicide in the U.S., in the pristine waters of Isle Royale National Park, Lake Superior. Specific results and products associated with the project would include:

- quantification of the rates of atmospheric deposition of atrazine and its metabolites;
- identification of the sources of and seasonality in atmospheric deposition of atrazine and its metabolites to the lakes of Isle Royale;
- determination of the relative role of physical losses and biochemical transformations in mediating the fate of atrazine; and
- application of a mathematical model suitable for the prediction of atrazine dynamics in pristine lakes.

The importance of physical, chemical, and biological processes in mediating the fate of atrazine in aquatic environments has not been well characterized. The lack of information and conflicting results regarding the persistence of atrazine in lakes serve as barriers to the application of mass balance models for atrazine fate and transport. It is these basic deficiencies with respect to a wide-spread toxic contaminant which have led us to propose this research project. We plan to offer contributions to the pool of basic knowledge of this most widely used herbicide and to apply these findings so that the impact of its use on aquatic ecosystems may be facilitated.

Approach

The overall approach for the proposed research, integrating field monitoring, field and laboratory studies of atrazine kinetics, and the application of a mass balance model for atrazine fate and transport in selected Isle Royale lakes is presented below. An outline of the effort, scheduling proposed project activities are presented as a time-line in Table 1.

Table 1. Project Time Line

1995-96	1996-97	1997-98
Monitoring		
Initiate atmospheric deposition monitoring and lake sampling; develop data set for model calibration	Complete atmospheric deposition monitoring and lake sampling; develop data set for model verification	Completed
Modeling		
Develop model framework; utilize available data for preliminary model runs; results support design of kinetic experiments	Perform model calibration; refine monitoring and kinetics programs for verification year	Perform model verification and management applications; prepare model documentation
Kinetics		
Design kinetic experiments based on preliminary model output; define relative importance and rates of abiotic/biotic processes	Full scale laboratory experimentation; examine effects of environmental conditions on rates	Verification of laboratory-based kinetics in field microcosms

Field Program

Proposed field work on the three test lakes will include the development of hydrologic budgets and the characterization of loads and water column concentrations of atrazine and its metabolites. Hydrologic budget data is not available for Isle Royale lakes and is fundamental to the proposed mass balance modeling. Definition of inputs from surface runoff, groundwater, and precipitation, together with monitoring of water column levels of the herbicide will permit characterization of the non-conservative behavior of atrazine in Isle Royale lakes and provide the loading information and calibration data sets required for the mass balance modeling.

Hydrology

The mass balance approach proposed here to characterize the fate and transport of atrazine requires a knowledge of the hydrologic budget of the test lakes, specifically the rate at which water enters and is lost from those systems. Little is known about the hydrology of Isle Royale lakes, however, inspection of the basins suggests that most of the systems are fed by groundwater. Precipitation and tributary inputs will be monitored directly. Groundwater inputs will be quantified using a hydrogeological approach (Vanek, 1987) employing piezometers (Lee and Cherry, 1978) and seepage meters (Lee, 1977). Where possible, outflow will be measured directly; otherwise it will be estimated as the sum of the hydrologic inputs less losses to evaporation. Rates of evaporation will be calculated based on measurements of air temperature, relative humidity, and wind speed (Environmental Laboratory, 1982). Bathymetric surveys will be conducted for each lake and hypsographic curves developed (Wetzel and Likens, 1991), permitting calculation of lake volume. Hydraulic residence time will be calculated as the lake outflow divided by the lake volume.

Atmospheric Deposition Monitoring

Monitoring of soil water atrazine concentrations on Isle Royale (Cromwell and Thurman, 1995) suggest that inputs from surface runoff and groundwater are of negligible importance; that atmospheric inputs are dominant. Event-based measurements of atrazine and its metabolites in bulk precipitation have been made on Isle Royale on several occasions over the past five years (Goolsby et al., 1995, Cromwell and Thurman, 1995). Additional vapor-phase, particulate-phase and bulk

precipitation measurements are presently being made at an adjacent Lake Superior mainland site (Eagle Harbor, Michigan; U.S. Environmental Protection Agency and U.S. Geological Survey; Figure 3). Results of that monitoring effort will be examined to determine the need for multi-phase sampling and to identify correlations between mainland and island deposition of atrazine and its metabolites. In this way, monitoring data from the Eagle Harbor site may be used to calculate rates of atmospheric deposition during winter periods when access to Isle Royale is not permitted.

Pending the results of phase distribution studies, the protocols of Goolsby et al. (1995) and Cromwell and Thurman (1995) previously employed in studies of atrazine deposition on Isle Royale will be utilized. Rainfall will be collected at weekly intervals over the April - October period at sites on opposite ends of the park: Davidson Island on the east and Windigo Ranger Station on the west (Figure 3). Bulk precipitation will be collected using low-density polypropylene funnels connected to 4-L (liter) baked amber-glass bottles. After each rainfall event, bulk precipitation will be transferred from the collectors into baked amber-glass bottles and transported on ice to the laboratory for analysis. The collectors will then be washed in detergent and de-ionized water before being used again. Rain gauges at each site will determine the amount of rain in each event. If multi-phase measurements are required, hi-vol samplers such as those presently employed at Eagle Harbor, will be put in place on Isle Royale to track gas and particulate phase inputs.

Back-trajectory analysis will be utilized to identify source regions of atrazine deposition at Isle Royale, especially to separate inputs from herbicide applications in the mid-continental U.S. from contaminant reservoirs more local to the island. The analysis follows established methods of trajectory analysis (Merrill et al., 1989) and will make use of Lake Superior atmospheric deposition monitoring data collected at the Eagle Harbor, Michigan station.

Lake Monitoring

Preliminary studies by Cromwell and Thurman (1995) suggest that there is little vertical or horizontal variation in atrazine levels in Isle Royale lakes. This will be confirmed by an exploratory, spatially-intensive vertical and horizontal monitoring effort. Water samples will be collected at weekly intervals over the April - October period from Siskiwit Lake, Wallace Lake, and Lake Richie. Pending characterization of requirements for more intensive spatial resolution, it is proposed that

samples be collected at a single, central location in each lake, at depths of 1m below the surface and 1 meter above bottom. Samples will be collected using a Teflon-coated, 500 mL water sampler and will be placed in two, separate 125 mL baked amber-glass bottles. Samples will be kept on ice (4° C) and transported to the laboratory for processing and analysis.

Kinetic Studies

Dechlorination to form the hydroxy-substituted hydroxyatrazine, N-dealkylation to form desethyl- and desisopropylatrazine, and ring cleavage are the major transformation processes for this herbicide (Figure 1). Kinetics describing the non-conservative behavior of atrazine and the attendant production of its metabolites will be examined in field and laboratory studies. It is thought that both biotic and abiotic processes may mediate atrazine transformations (Buser, 1990). Experiments will be conducted to clarify the relative importance of physicochemical and microbial processes in governing atrazine degradation and to quantify the role of environmental conditions in determining the rate of transformation.

Lake water and sediment samples will be collected, spiked with atrazine, and maintained in the laboratory in the dark at 20 °C. Samples will be incubated under oxic and anoxic conditions. Aliquots will be withdrawn from the sample vessels at intervals and the concentrations of atrazine and its metabolites determined. Reaction orders will be determined from plots of concentration versus time and rate coefficients by mathematical transformations (i.e. log plots) of the data. Selected samples will be sterilized (autoclaving and treatment with a chemical biocide such as sodium azide) to separate biotic and abiotic effects. Parallel experiments will look at the importance of abiotic reactants such as nitrate, iron (II), sulfide, and organic in mediating transformations. Photolytic effects will be examined in environments where UV light has been excluded to avoid direct photolysis. Following identification of key mechanisms governing atrazine transformations, experiments will be conducted to determine the role of environmental conditions in regulating rates. Candidate parameters include temperature, nutrients, pH, and organic matter concentration. Algorithms describing the kinetic behavior of atrazine will be developed and field verified using experimental microcosms before use in the mass balance model.

Laboratory Analyses

Atrazine and its metabolites will be determined by solid phase extraction followed by GC/MS analysis (Thurman et al., 1990; Meyer et al., 1993). Solid-phase extraction will be performed on a Waters Millilab workstation (Waters-Millipore, Milford, MA) using extraction cartridges consisting of 360-mg of 40- μ m C₁₈-bonded silica (Sep-pak; Waters-Millipore). The cartridges will be prepped sequentially with pesticide-grade solvents (Fisher, Springfield, NJ): 2 mL methanol, 6 mL ethyl acetate, 2 mL methanol, and 2 mL distilled water. Next 100 mL of sample will be passed through the cartridge at a flow rate of 10 mL/min. The cartridges will then be eluted with 3 mL ethyl acetate followed by a transfer step to remove ethyl acetate (top layer) from the residual water (bottom layer) in the eluate. The ethyl acetate will then be evaporated to approximately 80 μ L for GC/MS analysis.

The GC/MS analyses will be performed on a Hewlett-Packard Model 5890A (Palo-Alto, CA) instrument with a selective detector (MSD). A 12m HP-1 fused-silica capillary column (Palo-Alto, CA) will be used for the separation of analytes. The column to be used is coated with a methyl silicone film of 0.33 μ m and has an internal diameter of 0.2 mm. Operating conditions for the GC/MS are those described by Meyer et al. (1993). Standard stock solutions will be prepared in methanol and deuterated atrazine d5 (U.S. EPA, Cincinnati, OH) will be used as an internal standard for GC/MS analysis. A blank or standard will be run between every actual sample to insure accuracy.

Modeling

A mathematical model will be utilized to define the environmental partitioning and fate of atrazine and its metabolites in selected Isle Royale lakes. It is proposed that MASAS (Modelling of Anthropogenic Substances in Aquatic Systems) be employed for this task. While it is often attractive (particularly to modelers) to develop a new tool for each chemical and for each environment, that choice seems imprudent here. MASAS is a versatile simulation tool which supports the development of mathematical models for describing the dynamic behavior of organic chemicals in lakes (Ulrich et al., 1994). The software provides for different levels of spatial resolution (1-box, 2-box, and continuous segmentation) and offers the user flexibility in designing the kinetic framework as well, an important consideration when considering application to a variety of contaminants.

Most importantly, MASAS has been successfully applied in simulating atrazine dynamics in a test lake system (Greifensee, Switzerland; Ulrich et al., 1994). In that model, inputs from tributaries, point source discharges, and the atmosphere were considered as source terms and losses to hydraulic flushing, sorption and sedimentation, gas exchange, photolysis, and chemical and microbial transformation as sink terms. Loads were measured directly and rate coefficients were estimated from literature data and model calculations (Henry's Law constants, octanol/water partition coefficients, etc.). No data regarding biological transformations were available. A continuous (32-box) approach was utilized, generating vertical profiles of atrazine (metabolites were not simulated) in the lake over the season. The model served well in describing the behavior, i.e. seasonality in the vertical distribution, of atrazine in the lake. It was concluded from the modeling effort that hydraulic flushing was the dominant sink term, but that elimination of atrazine indirect photolytic transformation or microbial degradation might play a role in mediating behavior as well. Application of the model here would provide an exciting opportunity to contrast atrazine behavior in the oligotrophic and pristine waters of Isle Royale with that in the highly-developed and eutrophic conditions of Greifensee.

Quality Assurance/Quality Control

Samples will be collected and analyzed under the auspices of the Michigan Technological University Environmental Engineering Center (MTU/EEC) and the U.S. Geological Survey Research Laboratory in Lawrence, Kansas (USGS). All data generated under the guidance of MTU/EEC will be validated for precision, accuracy, completeness, and comparability. Precision is defined as the ability to reproduce the analytical results of a given sample regardless of how well it compares to the *true* value. A minimum of 10% of the samples collected will be analyzed in duplicate. The acceptable limit of precision is a relative error of 15%. Accuracy is the ability to obtain results matching the *true* value. This will be monitored through the analysis of standards prepared in-house. The objective in achieving completeness is 100% of the samples. Samples will be collected in duplicate to achieve this goal. Comparability will be insured through the use of standard methodologies.

Atmospheric deposition sampling sites are established locations utilized by USGS, U.S. EPA,

and the National Park Service. Lake water sampling sites will be determined to be representative through spatially intensive sampling. Prior to use, all sample containers will be cleaned in accordance with approved EPA methods. Samples will be stored on ice and transported to the laboratory with minimum holding time. A chain of custody worksheet will be generated for each sample, recording conditions of sample collection, temperature, and holding times. Upon arrival at the laboratory, samples will be immediately logged into the data storage and retrieval system, stored in a walk-in refrigerator, and processed within the holding time of the analyte as recommended in Methods of Analysis of Drinking Water (E.P.A., Cincinnati, Ohio).

Analysis of atrazine and its metabolites will be according to a methodology standard to USGS (Thurman et al., 1990; Meyer et al., 1993), an established protocol of the USGS Central Laboratory in Denver, Colorado and approved for use throughout the agency. Over 20,000 ground water, surface water, and rainwater samples have been analyzed for atrazine using this protocol, establishing a baseline for several environmental matrices. Using solid phase extraction and selected ion monitoring, this method has been found to be robust and with few interferences. All extracts will be held in archive at -25 degrees C. Normal procedure will call for 10% blanks on each sample run, 10% duplicates, 5% spiked samples, and 20% controls. All records of sample storage and refrigeration, instrument maintenance, tuning, and quantitation will be held for reference.

Quality control of GC/MS procedures will be established by having blind and double blind samples analyzed by MTU/EEC and the USGS laboratories in Lawrence, Kansas and Denver, Colorado. All procedures will be written in the manual of laboratory protocols and will be available for inspection. The detection and quantitation limit for atrazine and its primary metabolite (DEA) according to this method is 2.5 ng/L. All laboratory blanks will be free of herbicides and metabolites. Experience with the method indicates spike recoveries of 90 to 110%. The variation of duplicates averages $\pm 5\%$ at one standard deviation and the correlation coefficient for standard curves average 0.998 ± 0.002 . Each sample analyzed will contain terbutylazine as a recovery surrogate. Recoveries may be calculated for every sample and typically average $95 \pm 10\%$.

Individuals responsible for performing the analyses will conduct data calculations, examining the data as it is generated and determining its validity by duplicate analysis, standards or performance audits. The Quality Assurance Officer will rule on all decisions to disregard original results as being

in error. Annual audits for sample preparation, storage, and quality assurance and control will be conducted. If irregularities are noted, the Quality Assurance Officer will be alerted and corrective action taken before analysis proceeds.

Additional Project Information

Research Team

The project team is comprised of four scientists and engineers offering a wide range of expertise bearing on the proposed research. Dr. Martin T. Auer will serve as project director. Dr. Auer has more than 15 years experience in the field of surface water quality and has designed and implemented a host of field monitoring programs. Dr. Auer specializes in the conduct of field and laboratory studies supporting the development of water quality models. At present, Dr. Auer supervises site operation at the U.S. EPA Atmospheric Deposition Monitoring Station at Eagle Harbor, Michigan. In addition to overall project coordination, Dr. Auer will be responsible for activities relating to mathematical modeling. Dr. Judith A. Perlinger offers expertise in the fate and transport of synthetic organic chemicals in the environment which special focus on experimental studies of chemical and biochemical transformations. Dr. Perlinger will be responsible for the design and execution of field and laboratory studies characterizing the biotic and abiotic degradation of atrazine and its metabolites. Mr. Aron E. Cromwell has three years experience studying atrazine in the Isle Royale environment. As project coordinator at the USGS Water Resources Division, Mr. Cromwell was responsible for the collection of lake water and precipitation samples, determination of the concentration of atrazine and its metabolites using GC/MS techniques, and the interpretation and presentation of results. Aron is presently a doctoral student at Michigan Technological University. Dr. E. Michael Thurman is a Research Hydrologist with the USGS District Office in Lawrence, Kansas. Dr. Thurman is an expert in the analysis of pesticides in atmospheric deposition, surface water and groundwater and has directed a suite of research projects relating to the environmental fate and behavior of herbicides. Dr. Thurman has pioneered the development of analytical methods for herbicide analysis; his laboratory has processed in excess of 25,000 herbicide samples in the past six years. Dr. Thurman will be responsible for analytical oversight and, within the

guidelines of the award, perform analyses as a subcontractor.

Relationship to Ongoing Programs

The studies described here are compatible with the goals and activities of several ongoing regional research efforts. As a result, significant conceptual, technical and logistic support will be available for the proposed projects. In turn, the results generated here help to support the mission of those programs. Several examples are provided below.

National Park Service: as evidenced from studies to date, that atmospheric pathways are important in the transport of contaminants to Isle Royale. It is fundamental to the NPS mission to understand impacts and threats to the resources under its care. Because they are so pervasive on the island and because their impacts are so little understood, atmospherically-derived contaminants are considered by park management to be perhaps the most serious threat to the Isle Royale ecosystem. NPS has a history of cooperation in the conduct of research on the island and offers limited logistical support to scientists, including transportation, housing subsidies, access to communications equipment, and occasional field assistance by employees. A letter of support is appended.

U.S. Environmental Protection Agency: the Lake Superior atmospheric deposition monitoring station at Eagle Harbor, Michigan is operated for U.S. EPA by Michigan Technological University. The data base for this site contains three years of data on meteorological conditions and contaminant concentrations in the vapor- and particulate-phase and in bulk precipitation. The data base contains limited information on atrazine and its metabolites. Space is available at the site for location and operation of additional monitoring equipment. Data from this site has been used by Michigan Tech researchers to quantify atmospheric inputs of PCBs to Lake Superior and to identify transport processes governing airborne PCB concentrations in the Lake Superior region.

Great Lakes Protection Fund: as part of its mission to improve the understanding of threats posed to the Great Lakes by toxic substances, the Great Lakes Protection Fund has supported studies of the sources of persistent toxic organic compounds to the atmosphere over Lakes Superior and Michigan, conducted by Michigan Tech. These studies, directed by Dr. Richard E. Honrath, have utilized back-trajectory analysis to identify emission locations. The proposed project expects to cooperate with this ongoing effort, sharing data on atrazine and its metabolites, as well as extant capabilities in the conduct of back-trajectory analyses.

U.S. Geological Survey: the primary mission assignment for the USGS laboratory in Lawrence, Kansas is to understand the chemistry, analysis, fate and transport of herbicides in the environment. The laboratory has supported several studies of atrazine fate, including a preliminary investigation of long range transport and deposition on Isle Royale. Present efforts include the collection of vapor- and particulate-phase atrazine at the Lake Superior atmospheric deposition

station at Eagle Harbor, Michigan. Communication and cooperation with USGS and their knowledge of atrazine transport and chemistry would be an asset to the proposed project. The findings of the proposed work would greatly benefit the efforts of USGS in understanding the environmental behavior of atrazine.

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