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Atmospheric Transport and Fate of Herbicides
at Pristine Isle Royale National Park, Lake Superior

by

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Abstract

Herbicides used in agricultural areas are being transported atmospherically and deposited by precipitation onto pristine watersheds, such as Isle Royale National Park (an island park located in Lake Superior). Samples of rainfall, surface water, and soil water were collected during the summers of 1992, 1993, and 1994 and were analyzed by combining solid-phase extraction with either GC/MS or immunoassay. Atrazine, cyanazine, and two of atrazine's metabolites, desethylatrazine (DEA) and desisopropylatrazine were detected in Isle Royale rainfall from mid-May to early July at concentrations of less than 5 ng/L to over 2000 ng/L. Air parcel back trajectories indicate that most of the herbicides deposited on Isle Royale originate in the corn belt. The annual mass of herbicides deposited varied between years, with 1994 having the greatest mass deposited ($5.8 \mu\text{g}/\text{m}^2$). Furthermore, atrazine and DEA were found in concentrations of less than 5 ng/L to 30 ng/L in eleven lakes across Isle Royale. It is hypothesized that the degradation rate of atrazine is more rapid in shallow lakes and soilwaters and slower in deep lakes of Isle Royale. Degradation of atrazine in lakes of Isle Royale is estimated to be on the order of years for the deeper lakes, which is indicated by an increase in the DEA to atrazine ratio over time.

Introduction

In the twentieth century farmers have greatly improved crop yields by using chemically manufactured herbicides. The seven most frequently used herbicides in the United States are atrazine, alachlor, metolachlor, EPTC, 2,4-D, trifluralin, and cyanazine (1). Only one of these herbicides, trifluralin, is not applied to corn crops (2,3). The cultivation of corn (*Zea mays* L.) alone accounts for about one half of total national herbicide use in the United States (2,3). Atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine; 2-chloro-4-ethylamino-6-isopropylamine-s-triazine) is the most frequently applied herbicide in the United States with almost 55 million pounds of atrazine applied to corn crops in the United States (2,3).

Once applied atrazine undergoes rapid chemical and biological degradation. The biochemical half-life of atrazine in soil is estimated to be 64 days (14). However, not all of the atrazine applied to fields remains on fields to be degraded. Sources of atrazine loss from fields include surface runoff, transport to ground water, and volatilization. Each year 1-2% of atrazine is washed off the fields making its way to rivers and reservoirs down-stream from agricultural areas (4-11). Transport of atrazine to ground water has also been studied intensively (12-15). Factors affecting the transport of atrazine to ground water include distance to ground water, amount of organic matter in soil, amount of rainfall, and microbial populations (14). An additional source of atrazine loss from fields is through atmospheric transport (11,16-29). A study by Glotfelty et al. (27) found the volatilization losses of atrazine from fields to be about 2% of the applied mass, and a study by Goolsby et al. (26) found that about 1% of atrazine applied was deposited by precipitation on the mid-continent. Thus losses of atrazine due to volatilization are similar to losses of atrazine due to surface runoff, although atmospheric transport of atrazine has not been studied as thoroughly as surface and ground water transport.

Atrazine reaches the atmosphere through at least three pathways. First, physical drift can occur as the liquid pesticide mixture is being sprayed on a field. Because most

spray droplets eventually fall back to earth, drift is most likely a relatively insignificant source of atrazine in the atmosphere ; however, volatilization of drifting spray droplets may be significant (16). The second pathway for atrazine transport to the atmosphere is particle movement. Particle movement occurs when either soil containing atrazine or atrazine itself is picked up by wind and blown into the atmosphere. According to a technical paper by Ciba-Geigy (16) this is a much more likely source of atrazine in the atmosphere. The third pathway for atmospheric transport of atrazine is volatilization.

Studies indicate that volatilization of atrazine is a major source of transport (16-26). Volatilization can occur from evaporation of the herbicide as it is being applied or from evaporation of the herbicide from soil or plant surfaces after application. Volatilization rate is highest immediately after application, decreasing logarithmically thereafter (18,19). Environmental conditions that increase volatilization rate include wind, warm temperatures, and moist soil (17-19).

Once in the atmosphere, atrazine is transported by wind. Several studies have identified atrazine in rainfall (11,22-26,28). Near the source of the compound, concentrations of atrazine in rainfall reach 1-3 $\mu\text{g/L}$ (19-21,26) and in one study by Nations and Hallberg, a rain adjacent to a corn field contained 40 $\mu\text{g/L}$ atrazine (23). Atrazine concentrations in rainfall decrease with increasing distance from its source due to atmospheric dilution and possibly photochemical degradation (26,29). Despite this dilution and degradation, studies have detected atrazine being transported great distances (11, 25-27).

Richards et al. found atrazine in Maryland rainfall prior to local application (25). The timing of this early deposition coincided with application in Florida (25). Goolsby et al. studied atrazine deposition across the mid-continent and found atrazine to be transported atmospherically as far as Isle Royale National Park in Lake Superior (26). Dankwardt et al. determined that a German national park had atrazine input from rainfall (28). Buser found atrazine present in alpine lakes in Switzerland at altitudes much

greater than agricultural crops (11). The altitude of these lakes studies eliminates inflow from agricultural areas as a source and implicates rainfall as the route of atrazine transport. These studies show the potential for atrazine to be transported long distances. Furthermore, they indicate that atrazine is being transported from agricultural areas to pristine areas and deposited by precipitation.

Although some work has been done concerning the long range transport of atrazine and its subsequent deposition on pristine areas, the flux of atrazine in a pristine watershed has not been studied. With this goal in mind a three year study was conducted at Isle Royale National Park. The primary objectives of this study were (1) to identify herbicides in the rainfall of a pristine watershed and to quantify the mass of these contaminants being deposited per unit area; (2) to survey pristine lakes for the accumulation of atmospheric herbicide contamination; and finally (3) to determine the fate of herbicides being deposited onto pristine areas. To meet these objectives rain water, lake water, and soil water were collected in a US National Park and analyzed by GC/MS or enzyme-linked immunosorbant assay (ELISA) for atrazine, two degradation products of atrazine, desisopropylatrazine (DIA) and desethylatrazine (DEA), as well as other herbicides such as cyanazine, metolachlor, and alachlor. This paper discusses the results of that study.

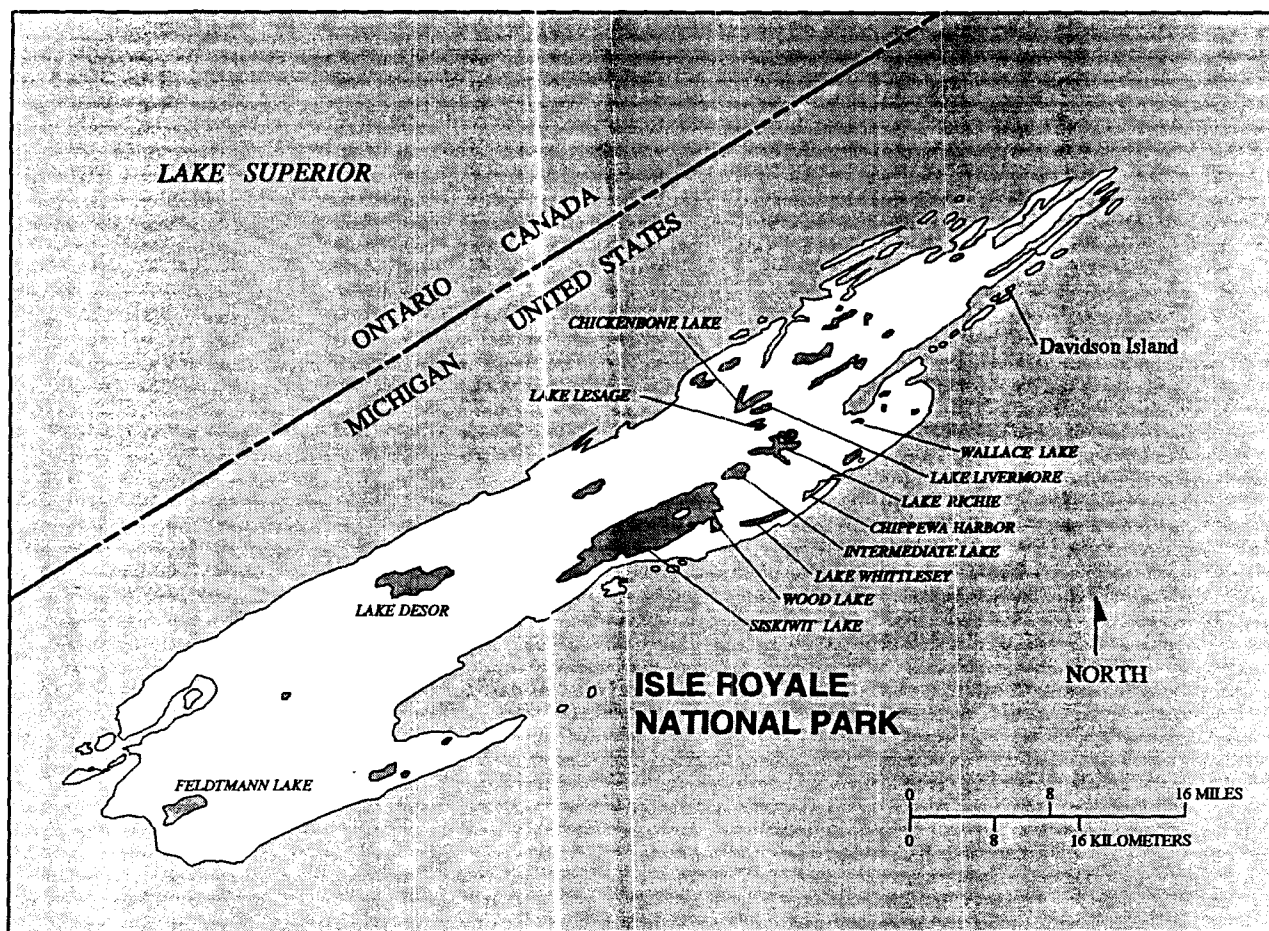
Experimental Section

Field Site and Sampling. The study area was Isle Royale National Park, Michigan, which is a 575-km² (square kilometer) island located in Lake Superior on the United States-Canadian border (figure 1). The park is protected from excessive human influence by its Congressional designation as Wilderness Area and its United Nations designation as an International Biosphere Reserve. Isle Royale has never had any history of herbicide application, and being an island, is isolated from inflow from herbicide-contaminated areas.

Two data-collection sites were established at Isle Royale. The sites were located near two lakes on Isle Royale, Lake Richie and Wallace Lake (figure 1). Samples were collected at these sites in 1992, 1993, and 1994. An additional data collection site was established in 1994 at Davidson Island (figure 1).

Bulk precipitation was collected using low-density polypropylene funnels connected to 4-L (liter) baked amber-glass bottles. After each rain, bulk precipitation was transferred from the collectors into either 125-mL or 1-L baked amber-glass bottles. The collectors were then washed in detergent and de-ionized water before being used again. In 1992 three of these collectors were placed at each of the two field sites. Approximately 10 rain events between May 16 and July 17 were collected during the 1992 season. In 1993 the number of rain collectors were increased to six at each site. Four rain events between May 13 and June 17 were sampled in 1993. In 1994, in order to accommodate a new ultra sensitive 1-L GC/MS method, the number of collectors at each of the three sites were increased to 10. In 1994, 14 rain events between May 15 and September 3 were collected.

Soil water was collected in suction-cup lysimeters in 1992 only. The polyvinyl-chloride lysimeters had porous porcelain cups at their base. Twelve lysimeters were installed near Wallace Lake, and six lysimeters were located near Lake Richie. Lysimeters at both sites were paired at depths of 15 and 30-cm. After each rain sampled



Index map

Figure 1. Location of study area.

in 1992, a hand pump was used to apply a vacuum to the lysimeters. The following day, the water in the lysimeters was pumped into 125-mL baked amber-glass bottles. Precleaned Teflon¹ tubing was used for the transfer.

Surface-water was collected and analyzed in order to determine the extent of herbicide contamination in the watershed. Samples were collected in 125-mL or 1,000-mL baked amber-glass bottles at a depth of 0.5 meters. Different lakes across Isle Royale were sampled in August of 1992, 1993, and 1994. In the summer of 1994 surface water was collected at frequent intervals from three lakes.

Analysis by GC/MS. Methanol, ethyl acetate, and acetonitrile (Fisher, Springfield, NJ) were the pesticide-grade solvents used. The SPE cartridges that were used for SPE-ELISA analyses and 100 mL GC/MS analyses contained 360-mg of 40- μ m C₁₈-bonded silica (Sep-pak from Waters-Millipore, Milford, MA). The SPE cartridges used for 1000 mL GC/MS analyses were ENVI-Carb from Supelco (Bellefonte, PA). These cartridges contained 250-mg of Carbpak-B. Standard stock solutions were prepared in methanol, and deuterated atrazine d₅ (U.S. EPA, Cincinnati, OH) was used as an internal standard for GC/MS analysis.

Solid-phase extraction by carbopak-B was carried out by using a vacuum manifold (Supelco, Bellefonte, PA) to pass liquids through the cartridge. The cartridges were prepped sequentially using 3 mL each of ethyl acetate, 20:80 acetonitrile : methanol, and distilled water. One L of water was sucked through the prepped carbopak-B cartridge by connecting a Teflon tube from the cartridge to a water sample. After passing the sample through the cartridge the cartridges were dried by passing air through the cartridge for several hours. This drying step eliminated residual water in the cartridge, which could complicate GC/MS analysis. After drying, the cartridges were eluted with 20:80 acetonitrile : methanol. The eluates were then evaporated to

approximately 80 μ L for analysis by GC/MS. Carbopak-B GC/MS method detection limit was 5 ng/L for atrazine, DEA, alachlor, and metolachlor.

Solid-phase extraction by C-18 was carried out using a Waters Millilab workstation (Milford, MD). Cartridges were prepped sequentially with 2 mL methanol, 6 mL ethyl acetate, 2 mL methanol, and 2 mL distilled water. Next 100 mL of sample was passed through the cartridge at a flow rate of 10 mL/min. The cartridges then were eluted with 3 mL ethyl acetate followed by a transfer step to remove the ethyl acetate (top layer) from the residual water (bottom layer) in the eluate. The ethyl acetate was then evaporated to approximately 80 μ L for GC/MS analysis. This method is described in detail in Thurman et al. 1990 (8) and Meyer and others, 1993 (30).

Gas chromatography/mass spectrometry procedure was for C-18 and Carbopak-B preparations. The analyses were performed on a Hewlett-Packard Model 5890A (Palo-Alto, CA) with a mass selective detector (MSD). A 12m HP-1 fused-silica capillary column (Palo-Alto, CA) was used for the separation of analytes. The column was coated with a methyl silicone film of 0.33 μ m and had an internal diameter of 0.2 mm. Operating conditions from both were identical to those described by Meyer and others, 1993 (30).

Analysis by Enzyme-Linked Immunosorbent Assay (ELISA). Atrazine ELISA was performed on rainfall samples to screen concentrations. Additionally, some analysis of Isle Royale surface waters was done by combining SPE with ELISA. Some of the SPE-ELISA samples were analyzed on-site at Isle Royale. The SPE-ELISA method is described in detail by Aga and Thurman, 1993 (31).

The ELISA analysis was performed with Ra-PID assay kits (Ohmicron Corp., Newtown, PA). This immunoassay kit uses polyclonal antibodies coated on paramagnetic beads. The samples were analyzed according to the directions supplied with the kits. The optical densities were read using a RPA-1 photometric analyzer

(Ohmicron, Newtown, PA) which also calculated the analyte concentrations based on a linear regression of linear/logit-transformed data. The calibration standards for atrazine were prepared at concentrations of 5.0, 1.0, 0.10, and 0 $\mu\text{g/L}$ using 20/80 (% v/v) methanol/water solvent, the same solvent used to reconstitute the analyte. When performed at Isle Royale a standard of 0 ppt, 10 ppt, or 25 ppt atrazine separated every sample processed through SPE in order to ensure the quality of the field data.

Results and Discussion

Herbicides in Rainfall. Herbicides were detected in rainfall of Isle Royale in concentrations ranging from less than 5 ng/L to over 2000 ng/L. Concentrations were determined predominately by C18 prepped GC/MS. This analytical method has been used in many studies and has been shown to be very reliable (3,5-9,21,23). Rain water was prepped on a robotic workstation with blanks placed between every sample. All blanks were analyzed and were found to contain no traces of herbicides. The quantitation limit for atrazine for the C18 prepped GC/MS was 25 ng/L.

During 1992, 1993, and 1994 herbicides were detected in rainfall as soon as sampling began (mid-May) and were present until early July (figure 2). The data suggest a seasonal pulse of atrazine occurs in Spring, with little or no atrazine present between July and May. This temporal trend is noted in other studies of herbicides in precipitation (10,17,18,20,21). However, in Wu's 1981 study of atrazine in rainfall of Maryland (19) no seasonal difference in atrazine concentrations was detected.

Figure 2 represents the mean concentration of atrazine in rainfall from 1992, 1993, and 1994. Typical concentrations between mid-May and mid-June were between 100-500 ng/L. The maximum atrazine concentration was 2344 ng/L occurring on June 3, 1992.

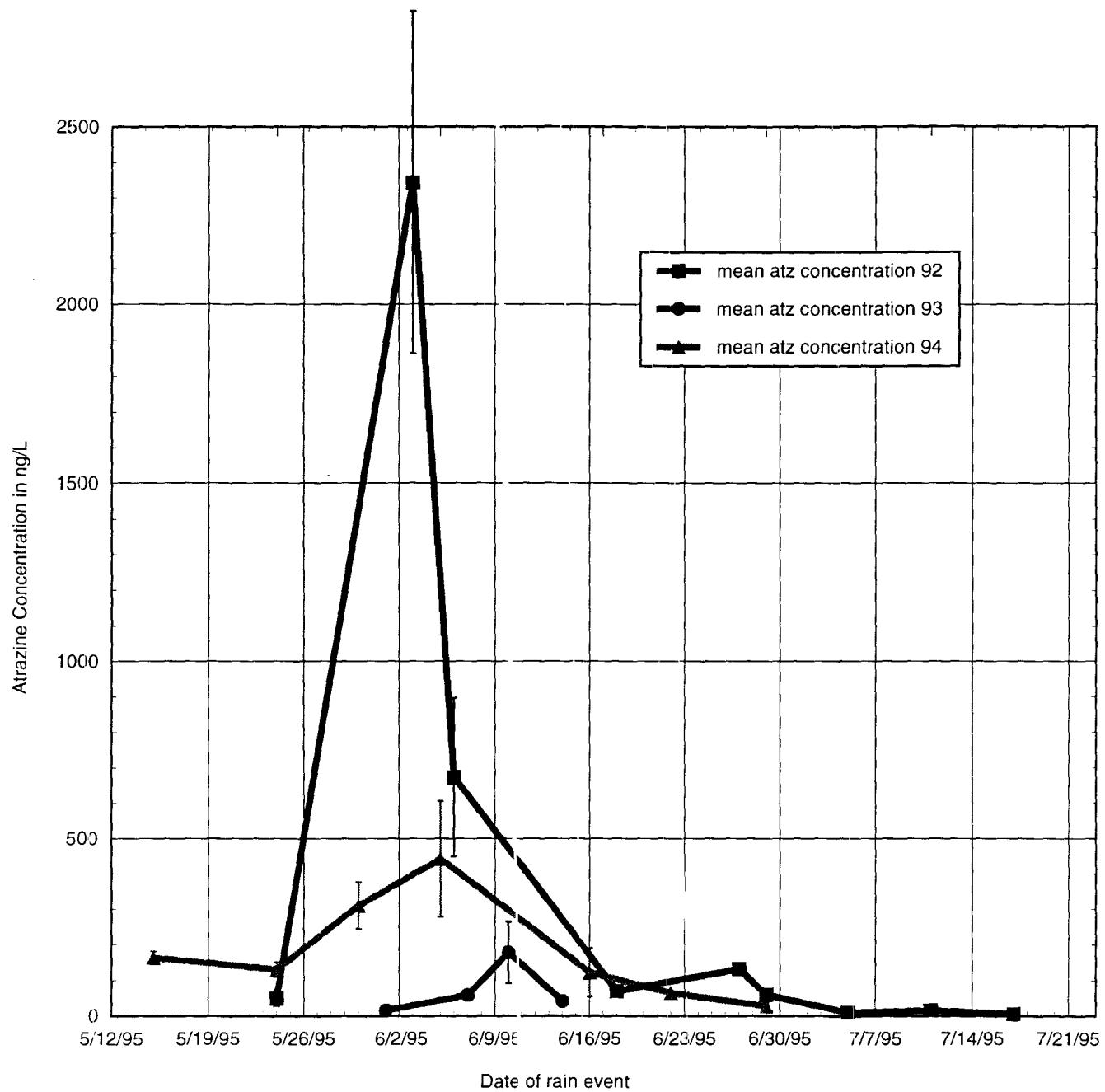


Figure 2. Mean concentration of atrazine in rainfall from 1992-1994 at Isle Royale. Concentration determined by GC/MS. Error bars are standard deviation of data.

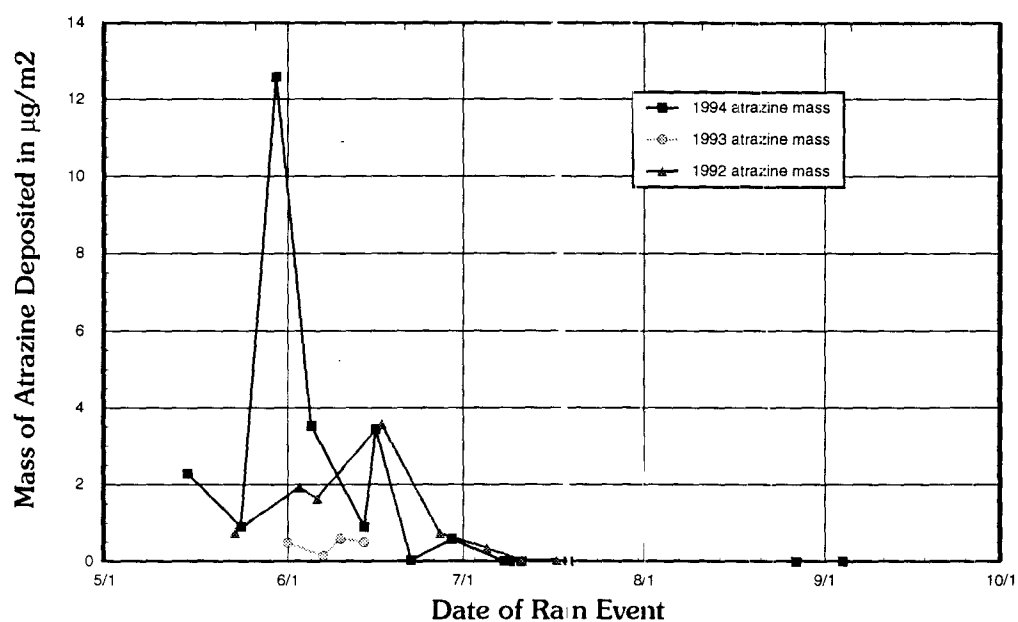
Since the amount of rainfall can be vastly different between events it is important to include it in calculations. By figuring the mass of atrazine deposited from each rain event the differences in rain volume are corrected. The mass of atrazine deposited is a more useful number than the concentration because the total amount of atrazine being deposited on an area can be calculated. Additionally, the mass of atrazine deposited over a period of time can be calculated. One can not sum the concentrations of atrazine in rainfall and obtain any useful figures. Mass is reported in ng/m² which is easily calculated because 1 mm of rain has a volume of 1 L per square meter. Thus by multiplying the concentration of atrazine in ng/L times the volume of rain in mm (or L/m²) one is left with ng/m².

The difference between atrazine mass and atrazine concentration can easily be seen. For instance, the rain event containing 2344 ng/L only deposited 1 mm of rain. the mass of atrazine deposited from this event was therefor only 2340 ng/m². The rain event with the greatest mass occurred on May 30, 1994. This rain had a mean concentration of 310 ng/L (over 7 times lower than the June 3, 1992 event) but contained 40 mm of rainfall. The mass deposited on May 30, 1994 was 12410 ng/m².

The mass of atrazine deposited with each rain event in 1992, 1993, and 1994 is depicted in figure 3. The temporal trend noted in concentration data is present in mass data as well. Early June was the time of greatest atrazine deposition on Isle Royale. While figure 2 showed that 1992 was the year with the highest atrazine concentrations, it is clear in figure 3 that 1994 had greatest atrazine masses in rainfall.

Table 2 contains the yearly mass totals for atrazine, DIA, DEA, and cyanazine. The amounts of these chemicals deposited varies considerably from year to year. 1993 is seen to have a much lower mass of herbicide deposition than the other two years although nearly as much atrazine was applied in 1993 as in 1992 (1,2). This could be due to several factors. First, rainfall was collected for only one month, mid-May to mid-June. This is, however, seen to be the peak herbicide deposition time. According to the 1992

Figure 3. Mass of atrazine in $\mu\text{g}/\text{m}^2$ deposited on Isle Royale by rain events in 1992, 1993, and 1994. Mass determined by GC/MS concentration multiplied by volume of rain.



$$\begin{array}{r} 1000 \\ 1000 \end{array} \cdot 6 = 6000$$

.36

$$3 \times 10^6$$

$$3 \text{ g/sm}$$

$$\frac{200}{600 \text{ g}}$$

	Isle Royale (land only) 575 km ²		Lake Superior 82100 km ²
	µg/m ² deposited on Isle Royale	kg deposited on Isle Royale	kg deposited from rain on lake surface
92 Atrazine	9.0	5.2	424
92 DIA	0.0	0.0	0
92 DEA	2.6	1.5	125
92 Cyanazine	0.4	0.2	17
92 Total	12.0	6.9	566
93 Atrazine	1.7	1.0	82
93 DIA	0.0	0.0	0
93 DEA	0.8	0.4	36
93 Cyanazine	1.0	0.5	45
93 Total	3.5	2.0	162
94 Atrazine	24.5	14.1	1155
94 DIA	7.3	4.2	346
94 DEA	10.1	5.8	475
94 Cyanazine	16.3	9.4	768
94 Total	58.2	33.4	2744

Table 2. Projected deposition rate and loadings for Isle Royale and Lake Superior. Yearly mass is calculated by summing the GC/MS concentrations of compound in rainfall multiplied by amount of precipitation in rain event. Area of Isle Royale does not include any Lake Superior waters belonging to the park. Surface area of Lake Superior is from Eisenreich et al. (16).

and 1994 data approximately 85% of atrazine should have been deposited during the month sampled in 1993. An additional reason for the lower herbicide levels in 1993 could be the flood of 1993. The unusually high rainfall for the midwest (2) could have scavenged atrazine out of the atmosphere before it could be transported to Isle Royale. Richards and others (20) as well as Nations and Hallberg (18) report that atrazine is rapidly scavenged out of the atmosphere during a rain event.

In addition to atrazine, DEA and DIA (two degradation products of atrazine), cyanazine, alachlor, and metolachlor were all analyzed for in Isle Royale rainfall. Table 2 contains yearly masses of atrazine, DEA, DIA, and cyanazine deposited on Isle Royale. Metolachlor and alachlor were only seen in trace levels in rainfall. This is an interesting find as these compounds are used in abundance in the cornbelt (1,2). Furthermore metolachlor and alachlor have vapor pressures almost 100 times those of atrazine and cyanazine. The higher vapor pressures of metolachlor and alachlor mean that they are more volatile than atrazine or cyanazine. Alachlor and metolachlor have been seen in rainfall studies (18,20,21). Data from Goolsby's study (21) indicate that in the corn belt the ratio of alachlor applied to alachlor deposited by rainfall is in fact greater than the ratio of atrazine used to atrazine deposited by rainfall. However, this study also indicates that alachlor is deposited closer to its source than atrazine is. The only slight detection of alachlor and metolachlor in rainfall of Isle Royale may indicate that alachlor and metolachlor are not as prone to long-distance transport as atrazine, or cyanazine.

Herbicides in Surface Water Atrazine was detected in surface waters of Isle Royale with concentrations ranging from below 5 ng/L up to about 30 ng/L. Concentrations of atrazine varied from lake to lake across Isle Royale. Table 3 illustrates how at any one time the concentration of atrazine in one lake may be more than 4 times the concentration in another lake. The data represented in table 3 is from a lake survey taken in August of 1992. Similar samplings were done in August of 1993 and 1994 with similar results.

Table 3. Concentrations of atrazine in surface-water samples taken in August 1992. Concentrations are determined by GC/MS. Locations can be found in figure 1.

Lake	Concentration in ng/L
Chickenbone	12
Desor	22
Feldtmann	17
Intermediate	10
LeSage	11
Livermore	5
Richie	10
Siskiwit	11
Wallace	7
Whittlesey	7
Wood	15

In order to determine if atrazine was entering the lakes of Isle Royale by groundwater seepage the concentration of atrazine was examined in soil water. The day after a rain event containing atrazine occurred a vacuum was applied to the lysimeters. The next day the soil water was transferred to 125 or 1000 mL bottles for analysis. Due to the low concentrations of atrazine in soil water and the small volumes of sample available, SPE-ELISA analysis was performed. Approximately 80% of soil water samples analyzed by SPE-ELISA had atrazine concentrations below the detection limit of 5 ng/L. Data for a typical lysimeter is depicted in figure 8. To confirm the lack of atrazine in soil water carbo-pak GC/MS analysis was performed. Soil water from adjacent lysimeters was pooled in order to have the 1 L sample volume necessary for analysis. Only one of the ten pooled samples which were analyzed by GC/MS contained atrazine above the 10 ng/L detection limit. The negligible concentrations of atrazine in the soil water, despite relatively high concentrations of atrazine in rainfall, indicate that atrazine is not being transported to the ground water of Isle Royale.

This finding virtually eliminates ground water as a potential herbicide input to lakes of Isle Royale. With ground water a negligible source of atrazine input, lakes of Isle Royale would be receiving all of their atrazine by precipitation directly onto the surface of the lakes, runoff of precipitation and inflow from other lakes receiving direct deposition or runoff.

The concentration of atrazine in the three lakes increases as atrazine is deposited by precipitation in late-May and June. The peak concentration of atrazine in lakes was found to occur just after the peak deposition of atrazine by precipitation.

Figure 9 depicts the atrazine concentration between summer of 1992 and spring of 1994 in three Isle Royale lakes. There is seen to be a decreasing trend in atrazine concentration in the lakes during this period. This trend can be attributed to the very small mass of atrazine deposited in 1993. With little atrazine input the concentration

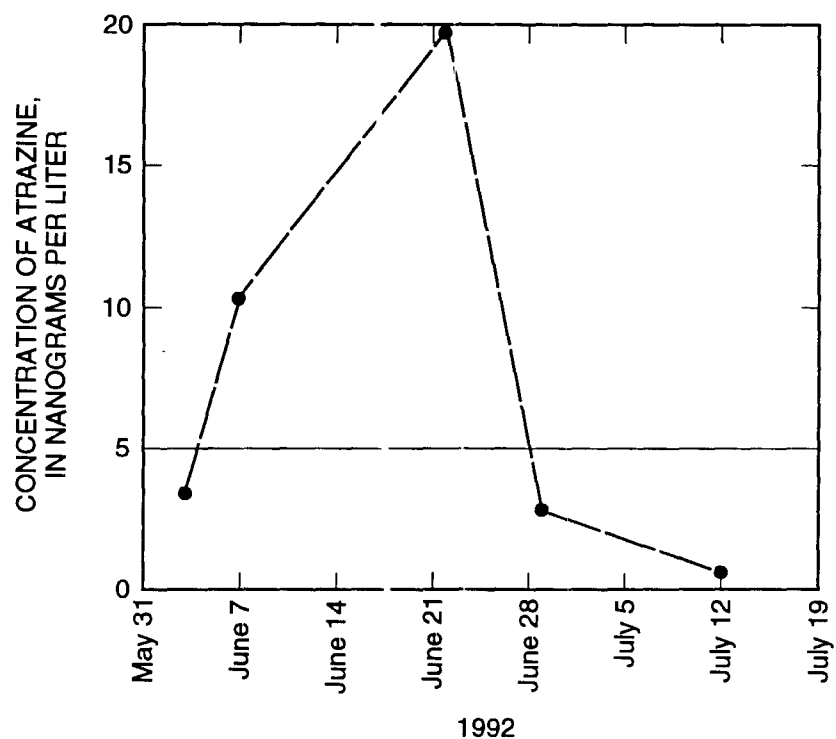
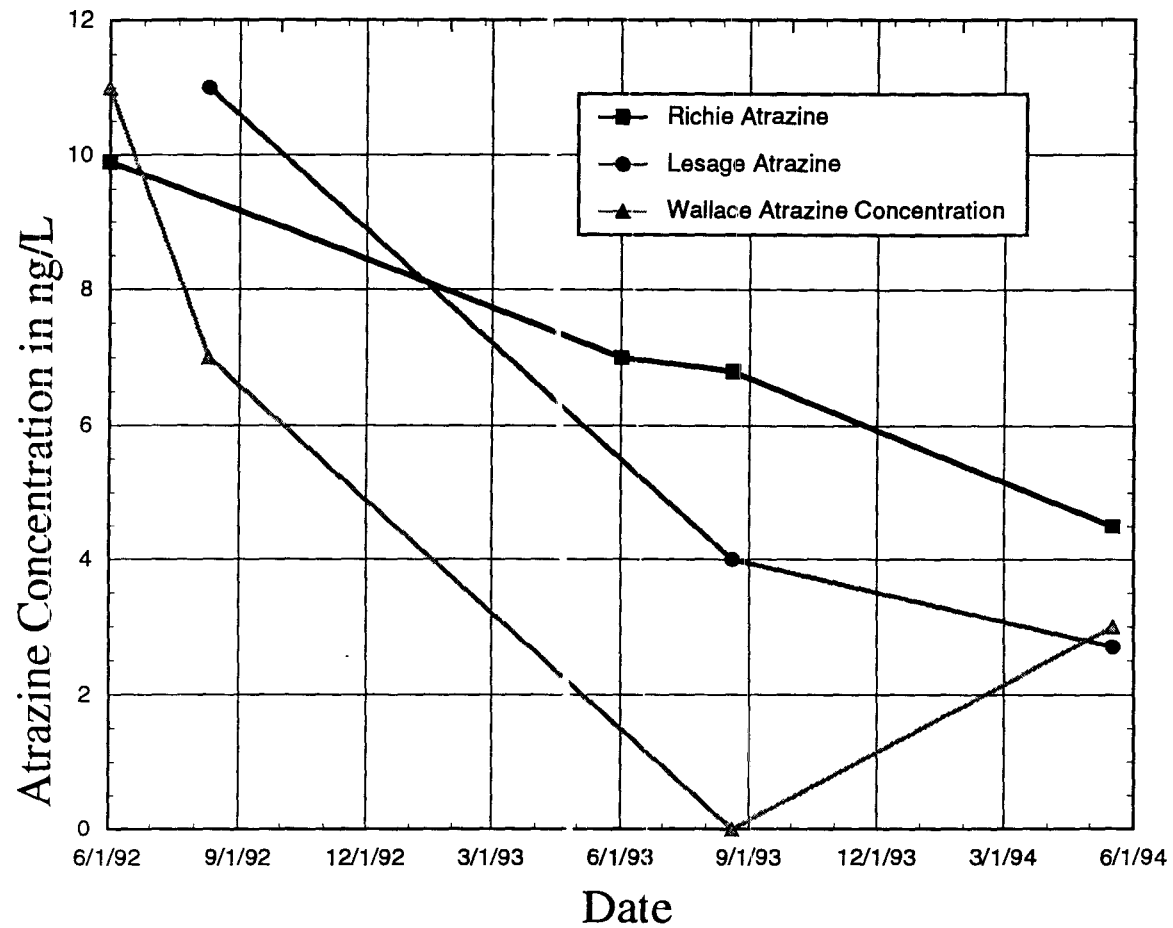


Figure 8. Concentration of atrazine in soil-water samples collected from a lysimeter near Wallace Lake, Isle Royale National Park. Concentrations determined by enzyme-linked immunosorbent assay. Detection limit is 5 ng/L.

Figure 9. Atrazine concentration in three Isle Royale lakes between Summer 1992 and Spring 1994. Concentrations determined by GC/MS



steadily decreased due to dilution and metabolic decomposition. With deposition of 1994 atrazine the concentration in the three lakes rapidly increased until sampling ended in late June (figure 10). When these lakes were resampled in August the concentration had fallen again.

Evidence for degradation of atrazine is shown in figure 11. Figure 11 shows the DEA to Atrazine Ratio, the DAR. An increase in the relative amount of the metabolite DEA to parent compound atrazine is indicative of biological degradation (6,23). The rate of atrazine disappearance from Isle Royale lakes appears to be on the order of years. This is evidenced from the fact that atrazine is present in Isle Royale lakes in early May, before deposition. Atrazine detected before the current year's transport is indicative of persistence of atrazine originating from last year's transport. Additionally, 1993 had very little atrazine deposition yet atrazine concentrations did not fall below the detection limit in all of the lakes. These facts suggest a persistence of atrazine in lakes of Isle Royale on the order of years. This persistence of atrazine is supported by recent research in the Great Lakes (9) and Switzerland(8,10).

Cyanazine could not be detected in greater than trace levels in lakes of Isle Royale. This was probably due to problems with GC/MS analysis such as poor cyanazine response and a tendency for cyanazine to "hang-up" on the column at low concentrations such as would be expected. Due to these problems cyanazine concentrations could not be quantified in Isle Royale lakes.

Air Parcel Back Trajectories. The source of pollutants deposited onto an area can be determined by examining the source of surface winds. This is accomplished by projecting wind vectors backwards from the destination in three hour steps. This procedure is known as air parcel back trajectory and was developed by David Yap of the Air Resources Branch of the Ontario Ministry of the Environment (25,26). Mr. Yap generously calculated the source regions of surface winds for several deposition events at Isle Royale. These calculations show where air in the 0-1000m range has come from

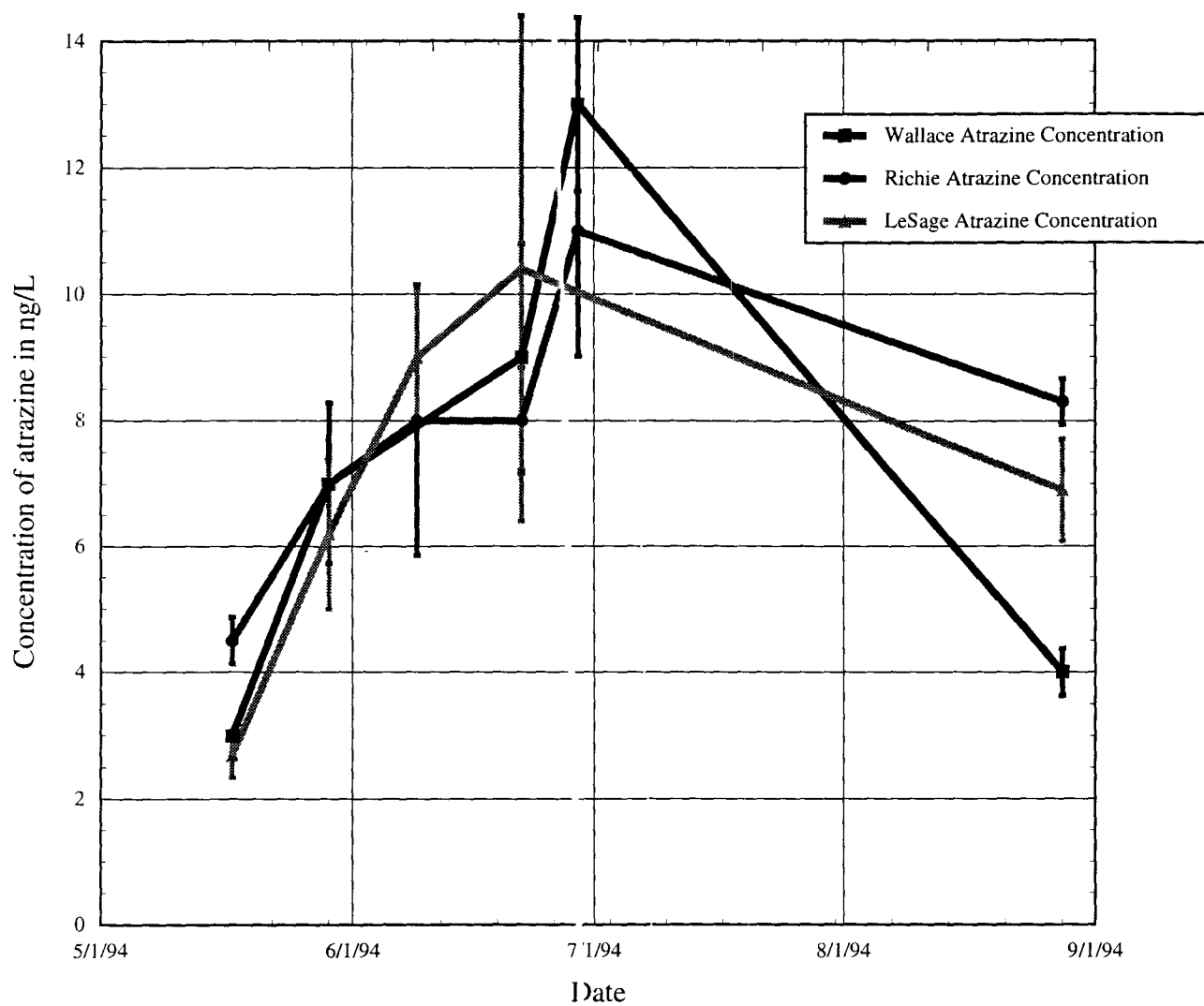


Figure 10. Atrazine concentration over time in three Isle Royale lakes. Concentration determined by GC/MS.

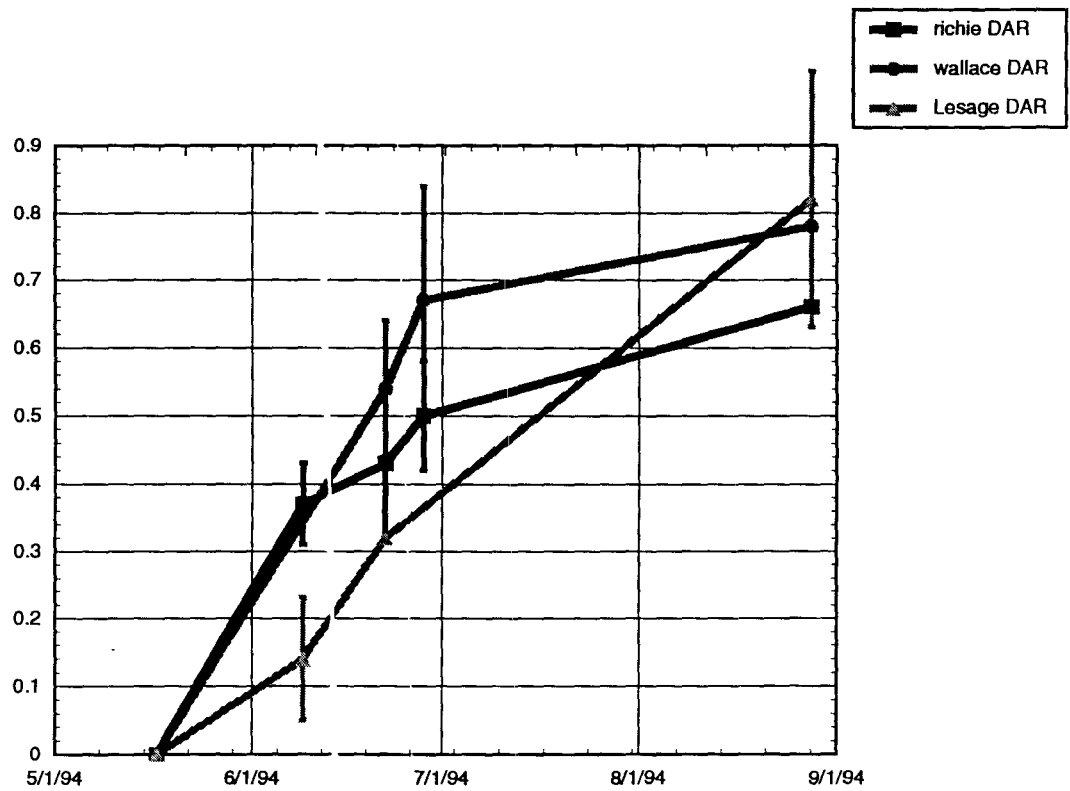


Figure 11. The DAR over time in three Isle Royale lakes. Desethylatrazine and atrazine concentrations determined by GC/MS. Increasing DAR is indicative of degradation.

within the past 48 hours. These calculations are not accurate for air above the 1000m height. Typically winds are slightly more westerly at greater heights. Figures 5 and 6 illustrate the results obtained from 48 hour surface geostrophic back trajectories from rain events in 1992 and 1994 containing high levels of herbicides. The source appears to be predominately south-west of Isle Royale. As shown in figure 2 this region includes some areas of high herbicide use. Alachlor, atrazine, cyanazine, and metolachlor are all used in abundance in this area. It is interesting to note that metolachlor and alachlor are applied in levels close to or exceeding levels of atrazine application and yet only traces of metolachlor and alachlor were seen in rainfall of Isle Royale.

Figure 7 represents the results of 48 hour surface geostrophic back trajectories calculated for rain events containing no herbicides. It appears from the back trajectories that these rain events would have been scavenging air which passed through areas of lower atrazine use than those events containing high masses of herbicides. Since these events with no herbicides occurred much after application it is unlikely that they would have contained high levels of herbicides even if the source air had been from areas of intense corn farming. The fact that the air originated in areas of low corn production contributed to the fact that no traces of herbicides could be detected even at the 5 ng/L level.

DARs in Rainfall. Figure 4 depicts the DAR values of rainfall at Isle Royale. 1994 was the only year which showed an increase in the DAR over time. The small number of samples make the verification of this trend impossible. It is however likely that there would be only a slight tendency for increased DARs over time in rainfall since DEA probably has a lower volatilization rate than atrazine (21). This lower volatilization rate would mean that though DEA would be increasing with time in agricultural soils, the atrazine would be preferentially volatilized. If this were the case than year round DARs should be lower than the 0.4 average for rainfall at Isle Royale. The elevated DARs in precipitation are most likely indicative of photodegradation in the atmosphere. The fact

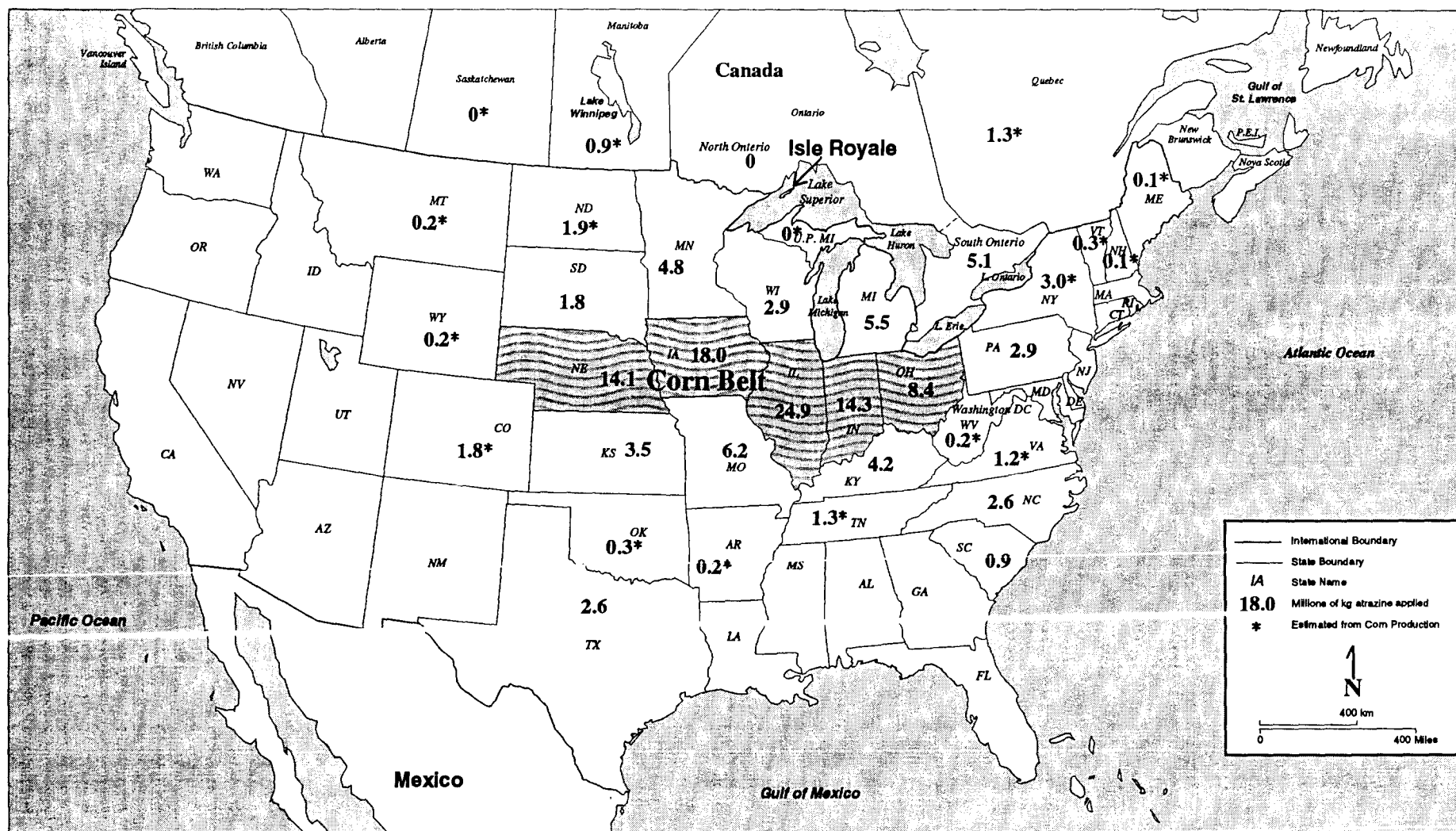
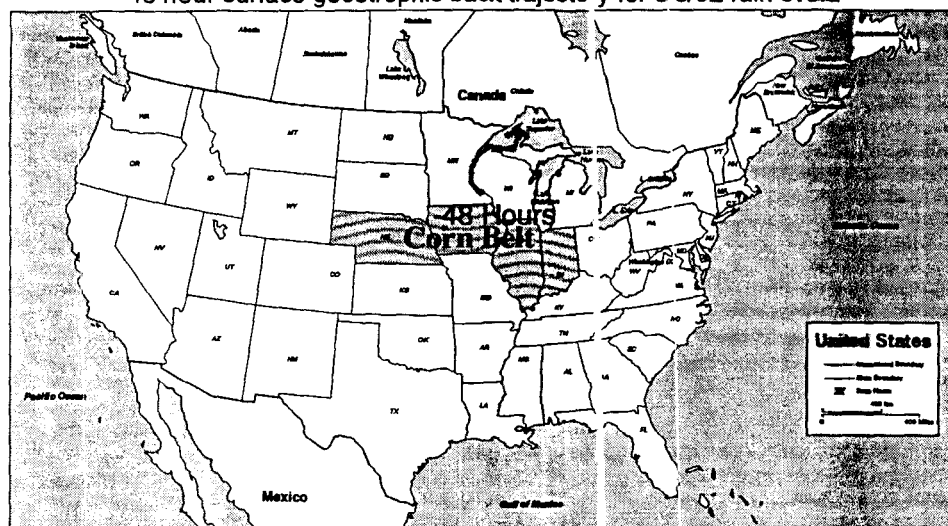


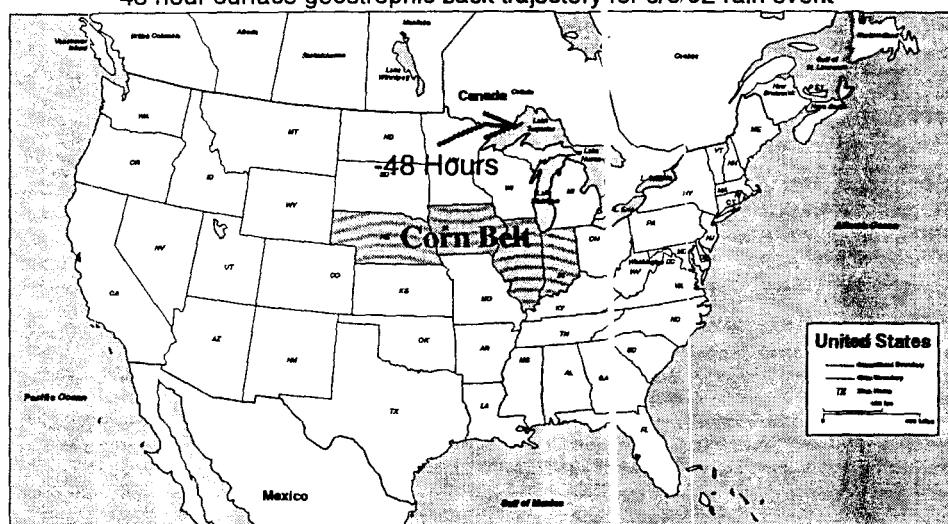
Figure 2. Millions of kilograms of atrazine applied in 1992. US data is from USDA Agricultural Chemical Usage, 1992 Field Crops Summary, March 1993. Canadian figures are from the Ontario, Saskatchewan, and Manitoba Ministries of Agriculture. Atrazine use was estimated from corn production figures in provinces without herbicide statistics. States and Provinces without figures are assumed to have relatively little atrazine use due to relatively little corn production.

48 hour surface geostrophic back trajectory for 6/3/92 rain event



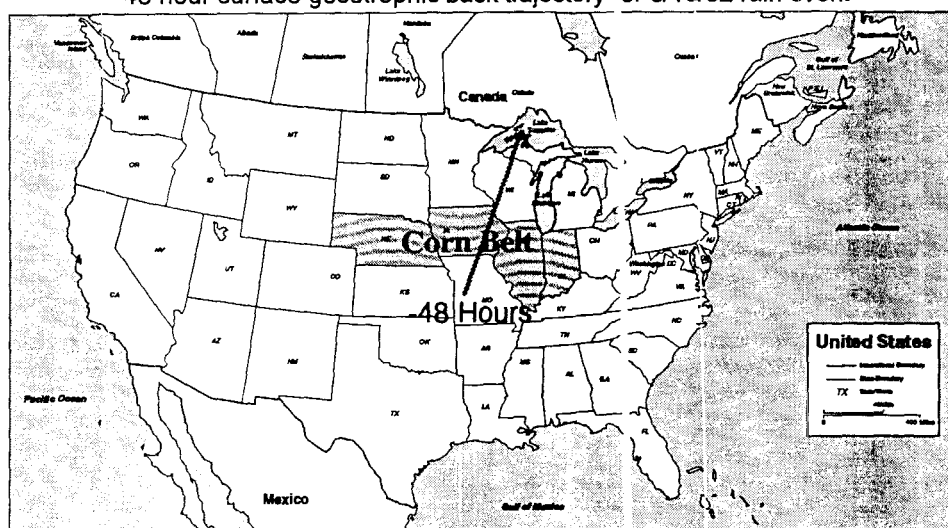
6/3/92 Rain
192 ng/m² atrazine
12 ng/m² DEA
0 ng/m² DIA
37 ng/m² cyanazine

48 hour surface geostrophic back trajectory for 6/6/92 rain event



6/6/92 Rain
163 ng/m² atrazine
53 ng/m² DEA
0 ng/m² DIA
0 ng/m² cyanazine

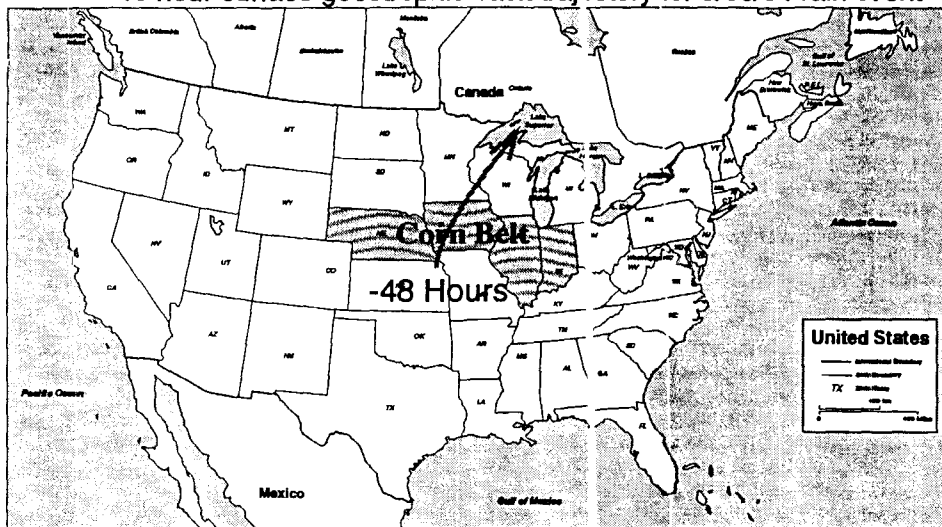
48 hour surface geostrophic back trajectory for 6/18/92 rain event



6/18/92 Rain
358 ng/m² atrazine
126 ng/m² DEA
0 ng/m² DIA
0 ng/m² cyanazine

Figure 5. 48 hour surface geostrophic back trajectories for the 3 rain events in 1992 with the greatest mass of herbicides.

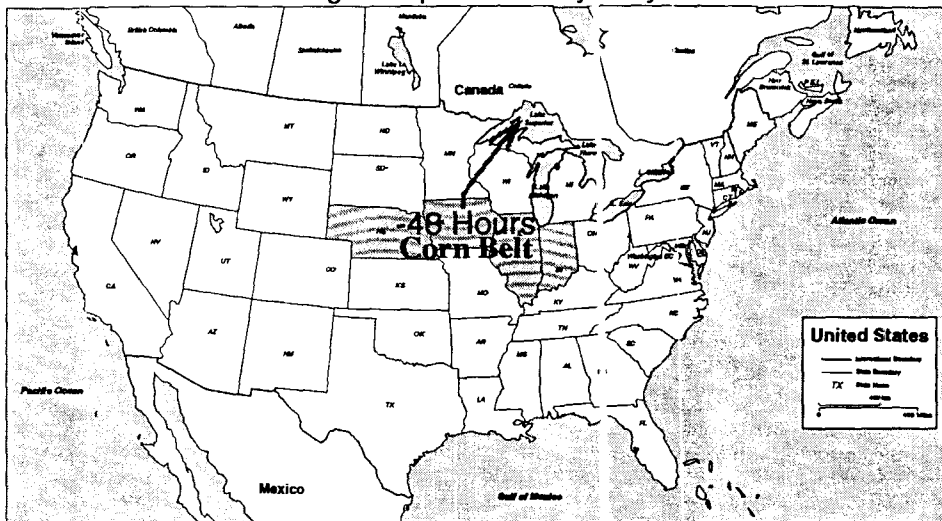
48 hour surface geostrophic back trajectory for 5/30/94 rain event



5/30/94 Rain
1260 ng/m² atrazine
540 ng/m² DEA
470 ng/m² DIA
720 ng/m² cyanazine

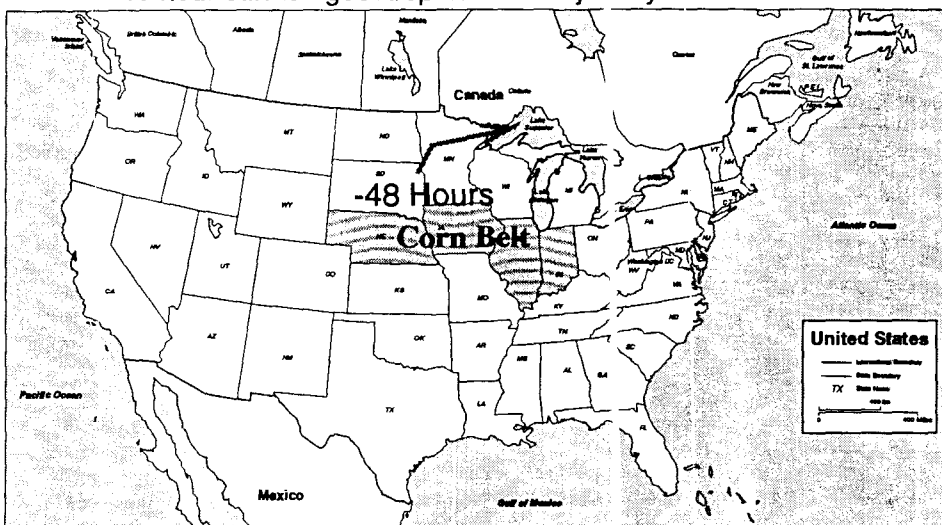
CORN BELT

48 hour surface geostrophic back trajectory for 6/5/94 rain event



6/5/94 Rain
355 ng/m² atrazine
135 ng/m² DEA
117 ng/m² DIA
413 ng/m² cyanazine

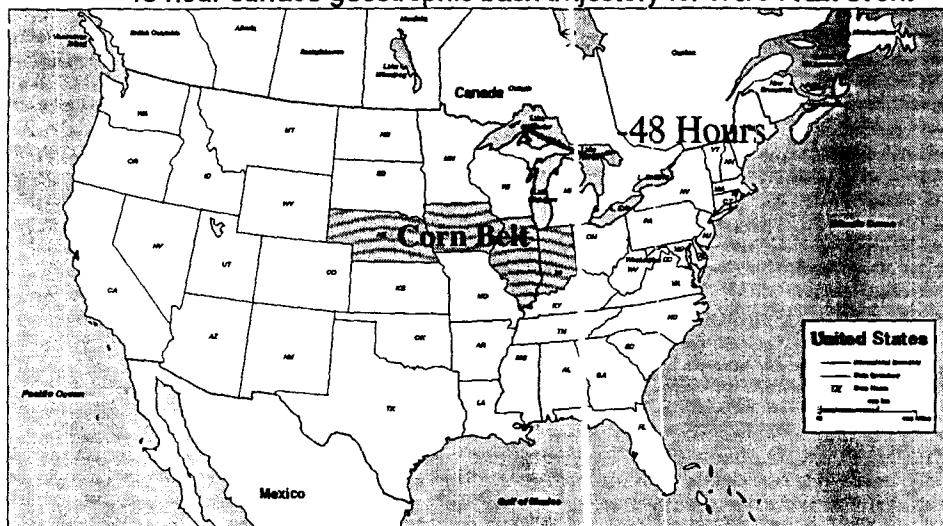
48 hour surface geostrophic back trajectory for 6/16/94 rain event



6/16/94 Rain
345 ng/m² atrazine
169 ng/m² DEA
85 ng/m² DIA
0 ng/m² cyanazine

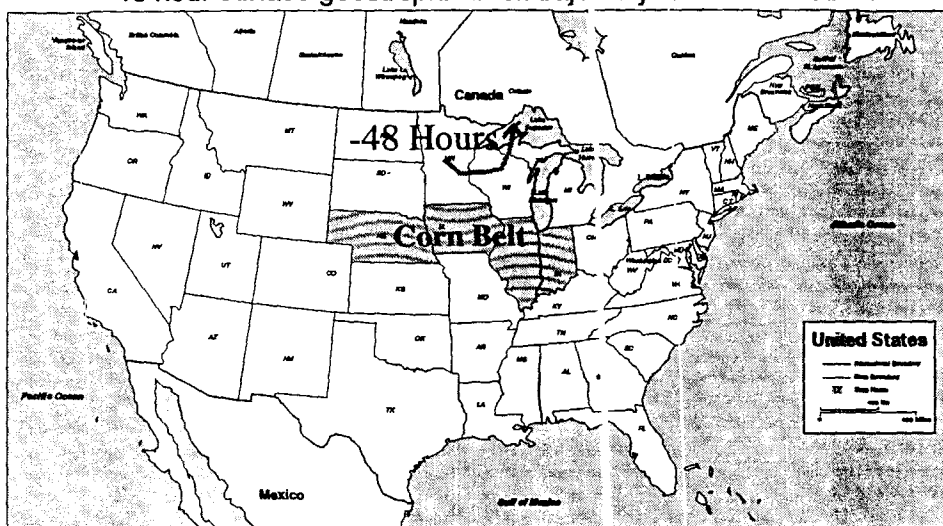
Figure 6. 48 hour surface geostrophic back trajectory for the 3 rain events in 1994 with the greatest mass of herbicides.

48 hour surface geostrophic back trajectory for 7/8/94 rain event



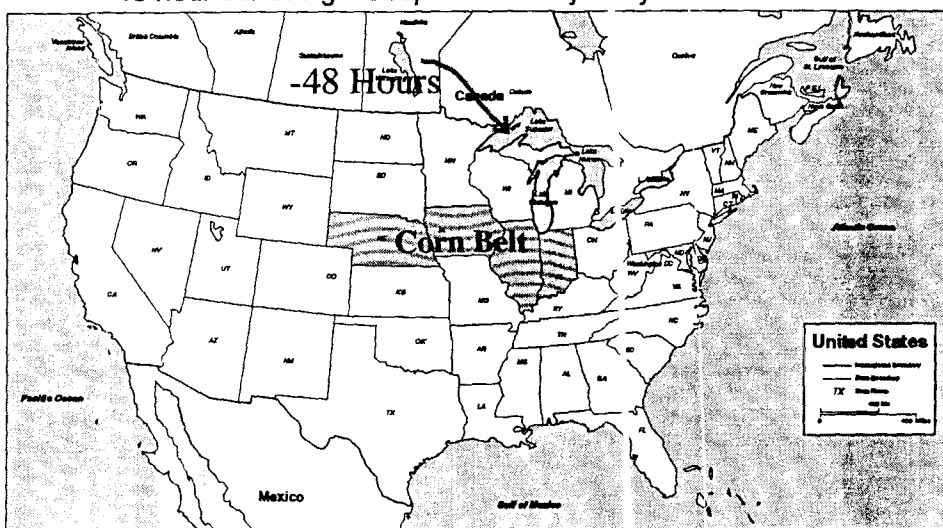
7/8/94 Rain
No herbicides detected

48 hour surface geostrophic back trajectory for 7/19/94 rain event



7/19/94 Rain
No herbicides detected

48 hour surface geostrophic back trajectory for 8/27/94 rain event



8/27/94 Rain
No herbicides detected

Figure 7. 48 hour surface geostrophic back trajectories for 3 rain events in 1994 with no detectable herbicides.

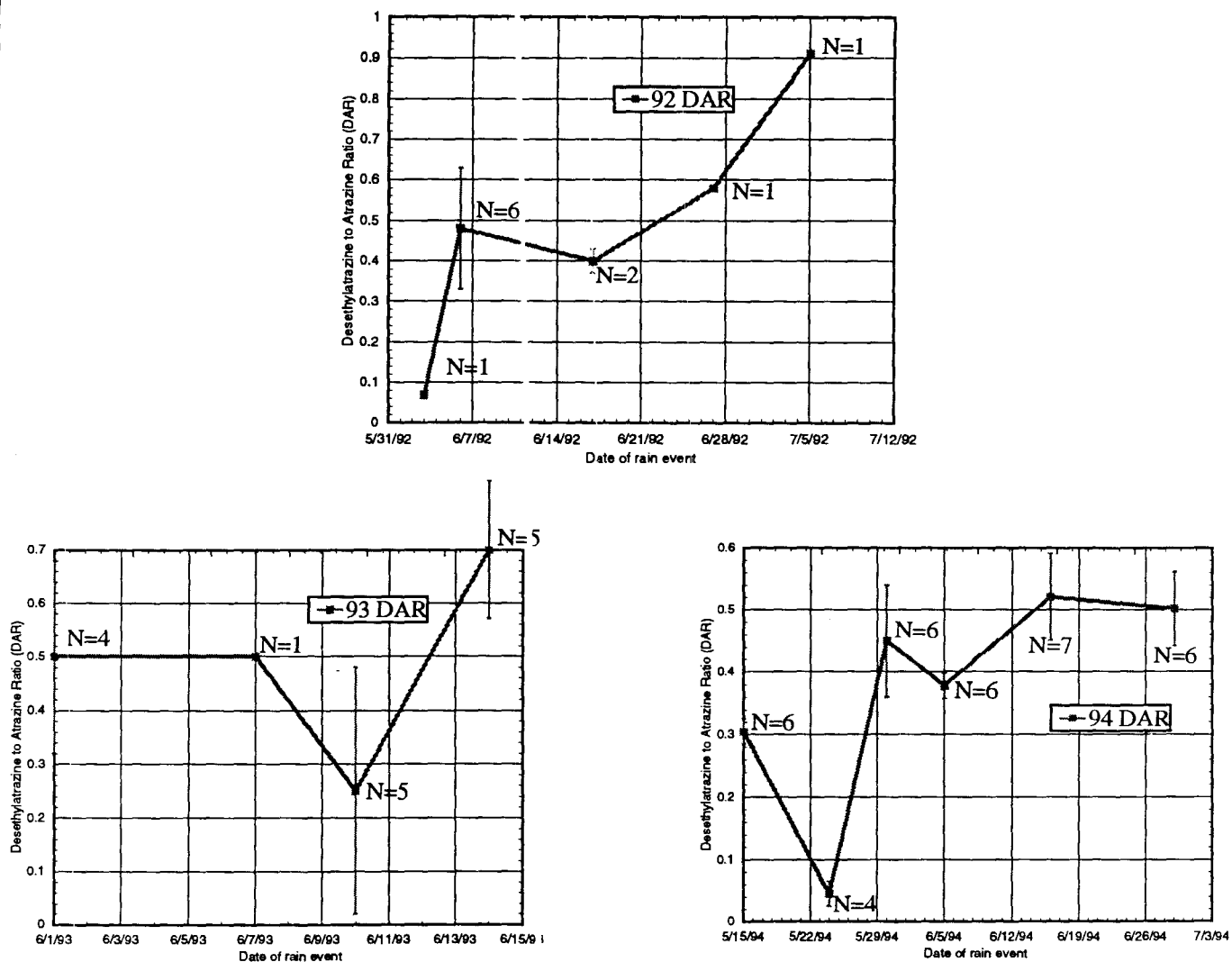


Figure 4. Average DAR for rain events in 1992, 1993, and 1994. DAR determined by GC/MS DEA concentration/ GC/MS atrazine concentration. Error bars illustrate standard deviation. Sample size denoted by N.

that atrazine degrades to DEA by photo-oxidative processes has been shown by Pelizzetti and others (22). If atrazine was degrading to DEA in the atmosphere, only a slight increase in the DAR over time would be seen. This slight increase is seen in the 1993 and 1994 rain DAR graphs in Figure 4. The 1992 DARs show a much more pronounced trend than would be expected under the hypothesis of atmospheric degradation. This can be explained by the fact that in 1992 fewer samples were analyzed by GC/MS. This lack of sample size makes it impossible to quantify any apparent trend. In a study by Goolsby in which nearly 2200 precipitation samples from throughout the mid-continent were analyzed (21), the median DAR was 0.5 for those samples which could be quantified for both atrazine and DEA regardless of the date of the rain event. These findings are consistent with the theory that atrazine is degrading to DEA in the atmosphere.

Summary and Conclusions.

Results from this study indicate that atrazine is capable of being transported atmospherically and deposited in significant amounts onto pristine areas. Once deposited on pristine areas, atrazine is detectable in surface water. The probable methods of transport include atrazine-laden precipitation falling directly onto lakes, and surface runoff of atrazine-contaminated rainfall flowing into lakes. Ground water transport of atrazine into lakes was eliminated as a possible transport mechanism by the data showing minimal atrazine concentrations in soilwater.

Atrazine is seen to undergo metabolic degradation in lakes of Isle Royale. However, this degradation is slow enough that one year of very minimal deposition (1993) accompanied by constant dilution and degradation did not eliminate atrazine from the system.

Additional work needs to be done in determining the half life of atrazine in different waters, and what various controlling factors to this half life time exist. The half-life of atrazine in water is of great importance because atrazine is toxic to aquatic plants

and animals at significant concentrations (28-30). Additionally, the community structure has been seen to be altered at concentrations as low as 100 ng/L (31). Data from this study indicates that atrazine is probably not going to build up to these levels at Isle Royale. However, there is a potential for other pristine areas to be affected by atmospherically deposited herbicides. This is why it is important to understand the mechanisms involved with the long-range transport of these toxic chemicals. Moreover, understanding of the fate of herbicides once in the surface waters used for drinking water is critical for policy makers worldwide.

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