FINAL REPORT

EXPOSURE TO ENDOCRINE DISRUPTERS FROM LONG-RANGE AIR TRANSPORT OF PESTICIDES

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CENTER FOR THE BIOLOGY OF NATURAL SYSTEMS
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I. INTRODUCTION

This project was designed to develop and test the usefulness of a computer model that can trace the movement of endocrine disrupters from the sources that emit them, through the air to avenues of exposure, for example, surface drinking water supplies. The project was motivated by the expectation that such a model could rank the multiple sources of the endocrine disrupters with respect to their contribution to the levels of exposure experienced in different localities and thereby facilitate preventive measures directed to the most important sources.

The new model is based on one that we had previously developed to trace dioxin from its numerous sources (most of them incinerators and other forms of combustion) to the Great Lakes. This model (HYSPLIT/TRANSCO) successfully predicted the amounts of dioxin that would be deposited in each of the Great Lakes over the course of a year (1993) and ranked more than 1300 sources by the amount that each of them contributed to the total. The model was originally developed by the National Oceanic and Atmospheric Administration (NOAA) in order to trace the movement of radioactive material — for example, from a nuclear accident — in time to warn people who might be exposed to it. It incorporates detailed weather data for the United States, southern Canada and northern Mexico for a grid of 924 points, 183 km apart, at six levels up to 5,000 meters, recorded at two-hour intervals for every year since 1988. The input data — the information that is entered into the model — include not only the weather pattern but certain physical and chemical properties of the substance that determine its fate as it travels through the air. For example, its sensitivity to light will determine how much of the substance is destroyed during the daytime en route, and the substance's solubility in water will determine how much of it is washed out of the air when it rains. Together, such processes determine the atmospheric lifetime of the substance and hence how far the weather pattern can carry it from its origin at the source.

The selection of a particular endocrine disrupter for the development of the new model was also influenced by several considerations: the availability of the necessary physical and chemical data; the amounts of the substance that might be emitted into the air, which will, of course, determine whether significant amounts of material will be deposited at distant sites; practical evidence that the substance does indeed travel through the air to places distant from its sources; the availability of measurements of the amounts brought down from the air to particular geographic locations, against which the validity of the model can be tested.

Atrazine, a herbicide and known endocrine disrupter, met these requirements and was selected as the basis for the model. Atrazine usage in the United States is larger than that of any other pesticide, amounting to 31-33 thousand metric tons per year in 1995 (Aspelin, 1997). Measurements by the U.S. Geological Survey show that atrazine occurs in rainfall in areas where it is not in fact used; they show that atrazine is subject to air transport and provide a convenient way to test the validity of the atrazine model.

Atrazine is applied to the soil during various times in the early growth stages of certain crops — chiefly corn, sorghum and sugar cane — in amounts that range from one-half to two kg per acre. It is very widely used, but there is particularly heavy usage in the Corn Belt states; they used about 80% of the national total of 32 thousand metric tons (in 1991). Atrazine is soluble in water, so that after it is applied to the soil, some of the atrazine drains away, reaching streams and lakes; some is converted by microbial action in the soil; the remainder is volatilized, becomes airborne, and therefore subject to atmospheric transport.

The basic input that is required to operate the model is the amount of the substance emitted into the air over time. In the case of a substance like dioxin, this is known from the operation of the sources that emit it, for example, each of the incinerators in the country, which generally emit dioxin continuously through the year. The atrazine situation is much different. Crop application of atrazine occurs only during the early growing season, mostly from April through June. Moreover, it is applied at several different times during this period. The amounts applied and the times of application vary from one farming region to another (and perhaps from farm to farm). Application times also depend on the weather; for example, atrazine is not applied when rain is expected, since much of it would then be carried away by runoff. Finally, the fraction of the atrazine applied to the soil that volatilizes and enters the atmosphere depends a great deal on soil conditions; for example, when the soil is wet and warm, this fraction, the “emission factor,” is particularly high. In sum, in modeling atrazine it is insufficient to consider only the total amount emitted into the air over the year. Instead, we estimated that amount week by week, over a 20-week period in the spring and early summer.

In order to localize the sources of atrazine emissions, they must be estimated separately for areas that may differ in any of the factors that determine the emission rate. The key agricultural statistic that is needed to estimate emissions, the acres planted in atrazine-requiring crops, which in turn determines the amount used, is available for separate counties. Accordingly, we have generally adopted the practice of defining each source analyzed by the model as a county. In southern Canada, the sources are defined as 127x127 km zones. In some cases we have found it useful to define sources in more detail, as Zip code areas.

Thus, in practice we have used the available agricultural statistics to estimate, for each of the 3,141 U.S. counties and the 855 larger zones in southern Canada, the amounts of atrazine emitted to the air during each week in the period March 5-July 23, 1991. The agricultural data used for this purpose are described in Section II below. The other essential source input required by the model is its location. This is specified as the latitude and longitude of the centroid of each county or zone, which is available from a Geographic Information System (GIS).

At the other end of the atmospheric route that the atrazine travels — the receptor — the situation is much simpler. We need to know its location and the local weather

conditions, which determine how much of the atrazine in the air over that location is actually deposited there. The location is given by the receptor's latitude and longitude, and the weather conditions are built into the data contained in HYSPLIT for 1991.

A crucial aspect of model development is evaluation. For this purpose, the model's estimate of the atmospheric concentration or the amount of atrazine deposited at a given point or area is compared with the amount actually measured there. The model is capable of separately estimating atmospheric concentrations and the amount of atrazine deposited in rainfall ("wet deposition") or in its absence ("dry deposition"). Dry deposition is very difficult to measure and few (if any) measurements of atrazine dry deposition have been attempted. Also, unfortunately, there have been very few measurements of the concentration of atrazine in the atmosphere in regions away from heavy use areas. Fortunately, a set of measurements were made by the USGS in 1990 and 1991, weekly, of the atrazine content of rainfall in an extensive series of locations in the Midwestern and Northeastern states (USGS, 1995). Our validation process consisted of comparing the USGS weekly wet deposition measurements with the model's estimates of wet deposition during those same weeks in 1991.

II. METHODS

A. Creation of the Atrazine Emissions Inventory:

1. Introduction:

The objective of the atrazine emissions inventory is to provide the HYSPLIT/ TRANSCO air transport model with estimates of emissions of atrazine from each source during each week in the period March 5-July 23, 1991. Since no actual data are collected for this purpose, the atrazine emissions inventory must be constructed from a variety of available agricultural data.[1] Our analysis is based solely on the use of atrazine in agriculture.

Agricultural atrazine is the most used pesticide in North America — approximately 30.6 million kilograms in 1991 (see Table II-1). Despite efforts to curtail its use, the latest estimate, for 1995, is expected to be between 28 and 33 million kilograms (Aspelin, 1997). In the U.S. over 80% of atrazine was used on field corn in 1991, 90% of which was applied in 17 major corn crop states (NASS, 1992). The planting is concentrated in the Corn Belt. Another major use of atrazine is on sorghum in the U.S., with almost 3.3 million kilograms applied. Sorghum and field corn account

[1]If all states and provinces would follow the lead of California, this would not be the case. In California, all agricultural applications must be filed with the state in regards to application amounts, timing, crop, and location. California makes this database available in electronic form for marketing and research. New York is developing a similar system. Advocacy of this system would greatly assist pesticide environmental fate research.

Table II-1 Atrazine Use Estimates 1991

Application and Country	Atrazine Kgs	Percent			
		Sub-Category	U.S.	Source Inventory	U.S.& Canada
U.S. Crops - Source Inventory					
Field Corn	26,128,726	85.28	81.68	82.01	78.68
Sweet Corn	201,632	0.66	0.63	0.63	0.61
Sorghum	3,286,536	10.73	10.27	10.32	9.90
Sugar Cane*	726,001	2.37	2.27	2.28	2.19
Pasture	234,992	0.77	0.73	0.74	0.71
Sod	54,061	0.18	0.17	0.17	0.16
Millet	5,415	0.02	0.02	0.02	0.02
Seed Crops	2,861	0.01	0.01	0.01	0.01
Total U.S. - Source Inventory	**30,640,225**	**100.00**	**95.78**	**96.17**	**92.27**
U.S. Non-Crop - Excluded from Inventory					
Fallowland	456,274	33.83	1.43		1.37
Turf and Rangeland	635,029	47.08	1.99		1.91
Other Professional Applications	238,136	17.66	0.74		0.72
Roadways	61,235	4.54	0.19		0.18
Industrial Facilities	40,823	3.03	0.13		0.12
Horticulture	6,804	0.50	0.02		0.02
Remainder	129,274	9.58	0.40		0.39
Home & Garden	19,278	1.43	0.06		0.06
Total U.S. - Inventory Excluded	**1,348,717**	**100.00**	**4.22**		**4.06**
Total U.S.	**31,988,942**		**100.00**		**96.33**
Canada Crop - Source Inventory					
Field Corn	1,133,999	93.03		3.56	3.41
Sweet Corn	31,316	2.57		0.10	0.09
Blueberries	52,616	4.32		0.17	0.16
Canola (rapeseed)	884	0.07		0.00	0.00
Total Canada Source Inventory	**1,219,000**	**100.00**		**3.83**	**3.67**
Total U.S. and Canada Inventory	**31,859,225**			**100.00**	
Total U.S. and Canada	**33,207,942**				**100.00**

Sources: CBNS estimates from: Arnold Aspelin, *Pesticide Sales and Use Survey*, U.S. Environmental Protection Agency; *Agricultural Chemical Usage: Field Crops Summary*, NASS, USDA; *1992 Agricultural Census*, U.S. Commerce Department; Heather Atkinson, Pesticide Sales Survey: 1991, Unpublished Data, Environment Canada, *1991 Census of Agriculture*, (1992) Statistics Canada, Ottawa, Ontario; Ontario Ministry of Agriculture, Food and Rural Affairs, *Pesticide Usage Survey, 1989 and 1993,* Toronto, Ontario; Leonard P. Gianessi and James Earl Anderson (1995) *Pesticide Use in U.S. Crop Production*, National Center for Food and Agriculture Policy (NCFAP), Washington, DC; Whitmore, Roy W., Janice E. Kelly, Pamela L. Reading (1992) *National Home and Garden Pesticide Use Survey*, Research Triangle Institute (RTI), Research Triangle Park, NC for Office of Pesticides, USEPA, March; Judy Shaw (1997) Correspondence. Novaritis Canada, Crop Protection, Mississauga, Ontario, Canada; Tom Parsely (1997) Correspondence. Novartis, Greensboro, NC Ciba-Geigy *1997 Sample Labels*, Ciba Crop Protection, Greensboro, NC; *Farm Chemical Handbook*, Meister Publishers, San Francisco.

for over 95% of the agricultural use of atrazine in the U.S. For our source inventory we included minor crop use as well; these, together with corn and sorghum, account for nearly 96% of atrazine use in U.S. agriculture in 1991.

We estimate that non-agricultural uses account for only 4.2% of the total amount of atrazine used in the U.S. The largest non-crop use is for turf and rangeland, which is concentrated in the Gulf Coast, Southwest and West (Novartis; Parsely, 1997). A survey of Federal and state government agencies did not reveal forestry or highway use of atrazine in 1991 in Minnesota, Wisconsin and Michigan, but private or local use could have occurred. Most of the railroad companies surveyed near our receptors did not reveal any significant use.

In Canada atrazine was restricted in use for corn, sweet corn, canola (rapeseed) and blueberries in 1991 (see Table II-1). Most of the atrazine is used on corn (we estimate 96%). No non-agricultural use of atrazine is permitted in Canada. Label changes reducing use were introduced in 1991 in Canada, after atrazine was detected in drinking water, but usage did not immediately decrease. By 1997 Novartis (the manufacturer of atrazine) estimated that Canadian usage dropped 28% from 1991, and Ontario usage by 38%. Over 90% of Canadian usage is concentrated in Ontario (66%) and Quebec (26%) (Environment Canada 1997 and CBNS estimates).

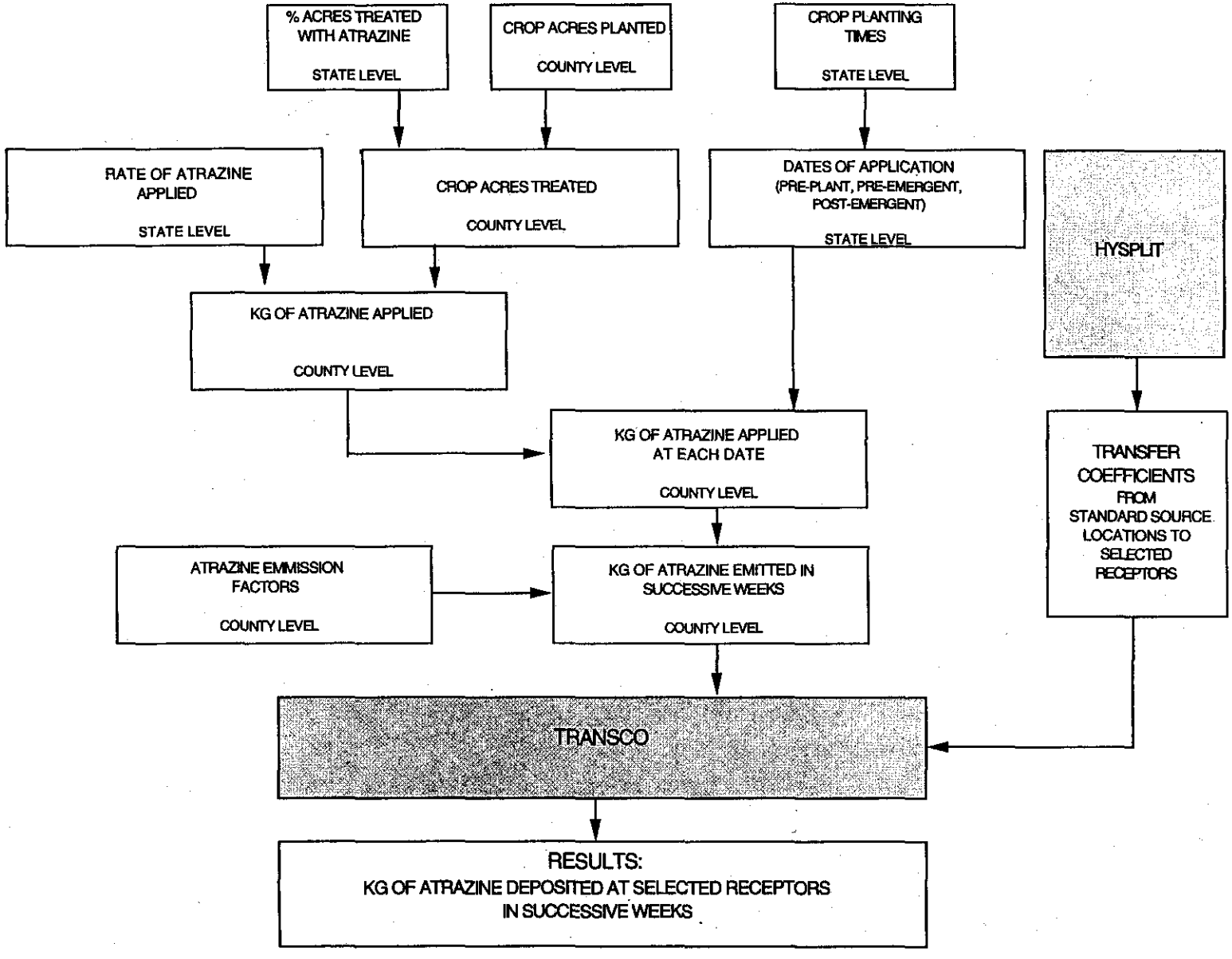
The procedures that we have used to develop the inventory are summarized in a flow chart (Figure II-1). The methods used to carry out each of the sequential steps are summarized below.[2]

[2]For the first runs of our model we used a less refined emissions inventory. We employed successive improvements in quantity, timing and spatial resolution. This allows us to assess the sensitivity of our transport model to the emissions inventory and its robustness (see appendix). The knowledge we have gained will greatly assist efficient targeting of our inventory work in future projects. What is presented in the body of the report is our latest, most accurate emissions inventory.

FIGURE II-1

SOURCE/RECEPTOR RELATIONSHIPS OF AIRBORNE ATRAZINE

METHODOLOGY FLOWCHART



2. Atrazine usage in the United States:

a) Acres planted:

The primary data source for acres planted was the USDA/NASS 1991 Crop Survey for the major crops: corn, sorghum, and sugar cane at the county level for most states. In some cases data were censored for non-disclosure reasons, and were only available in the broader category of NASS districts. These category totals were used to estimate acres planted for censored counties by distributing them according to the counties' areas.

The primary data source for minor crops and states not covered by NASS was the 1992 Census of Agriculture. The USGS (Thelin, 1997) kindly provided us with a data file that combined the 1992 Census and the National Center for Food and Agricultural Policy (NCFAP) 1989-1994 atrazine usage database (Gianessi and Anderson, 1995) (see below).

b) Acres treated :

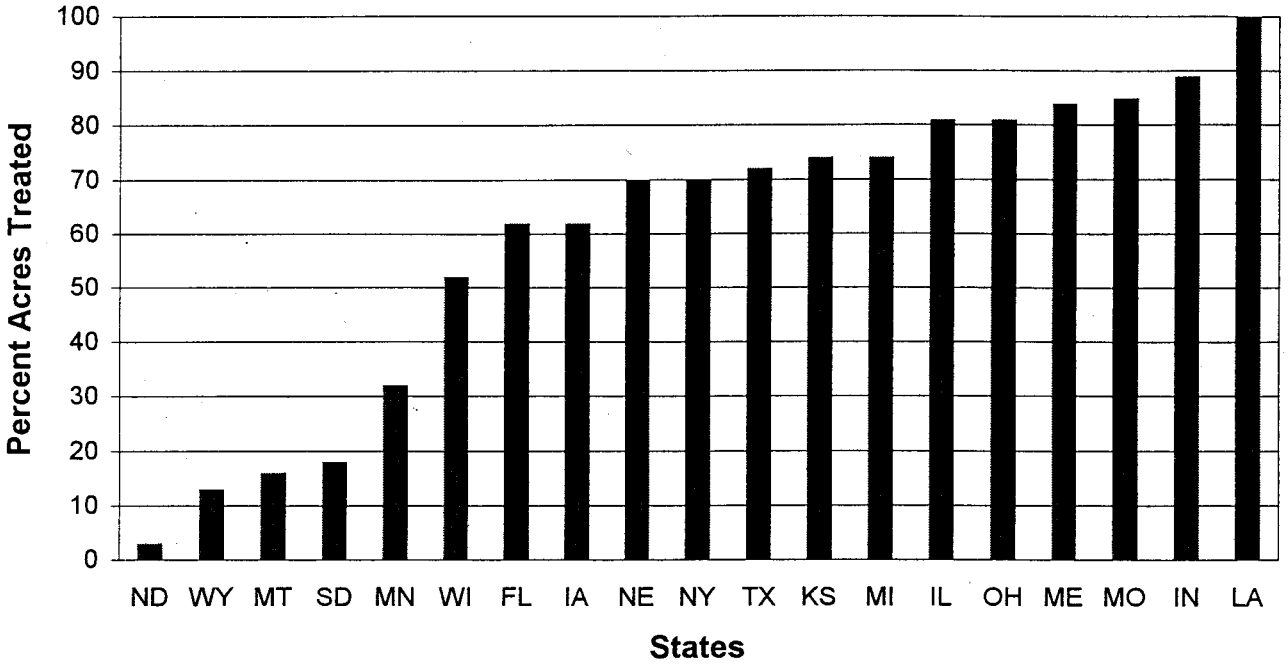
Although the USDA/NASS 1991 Survey data on acres planted was at the county level, the corresponding source of data for percent acres treated was at the state level. The main source of these data was USDA Agricultural Chemical Usage (ACU) 1991 Field Crop Summary, which includes 17 states in the case of corn and three states for sorghum (see Fig. II-2). These data were supplemented with data from Gianessi (1995), which included other states and crops, and was based on the 1992 Agricultural Census. Another source of data on acres treated at a county level was made available by Gail Thelin (USGS), and this was used to supplement our USDA/NASS Survey county level data for minor states and crops. This information reported acres treated with atrazine and the pounds of atrazine applied (1988-1994).

In order to calculate the actual usage of atrazine the rate of atrazine applied per acre treated was needed. The combination of data sources used for the percent of acres treated (ACU/Gianessi) also had these rates available at the state level. Similarly, the data from Thelin included an estimate of atrazine usage at the county level, which was used when other data sources weren't available.

3. Atrazine usage in Canada:

Unlike the U.S., regional variations in percent acres treated and rates of use are not generally available in Canada, therefore a different method was used to estimate local use. The primary data sources come from sales and marketing surveys conducted by Environment Canada and the manufacturer of atrazine, Novartis. We analyzed the Ontario Ministry of Agriculture, Food and Rural Affairs usage survey of 1989 and 1993 to assess the accuracy that the sales data and private marketing

Figure II-2
Field Corn Percent Acres Treated With Atrazine 1991
Selected States



surveys provide.[3] We found the Novartis estimate for total use of 1.22 million kilograms for 1991 to be reasonably accurate. For allocation to the local level, we were able to take advantage of Ortech's 1989-90 atrazine usage database, which consists of estimates for a grid of 127 km x 127 km square regions (Scholtz *et al*., 1997). Ortech's estimates were readjusted with a coefficient that conforms with the total Canadian 1991 atrazine use, to yield an improved estimate of atrazine use in each Canadian grid region.

4. Timing of atrazine application:

The regional atrazine usage data must be allocated to application dates for input into the HYSPLIT/TRANSCO air transport model. The primary reference date for application is the crop planting date, from which the distribution of application over time can be generally derived. Herbicide application dates are typically divided into three periods:

a) *Pre-planting*, either soil incorporation during tilling (common with corn) or aerial application

b) *Pre-emergent*, at the time of planting, before the crop plants and weeds have emerged

c) *Post-emergent*, after the crop plant and weeds have emerged from the soil.

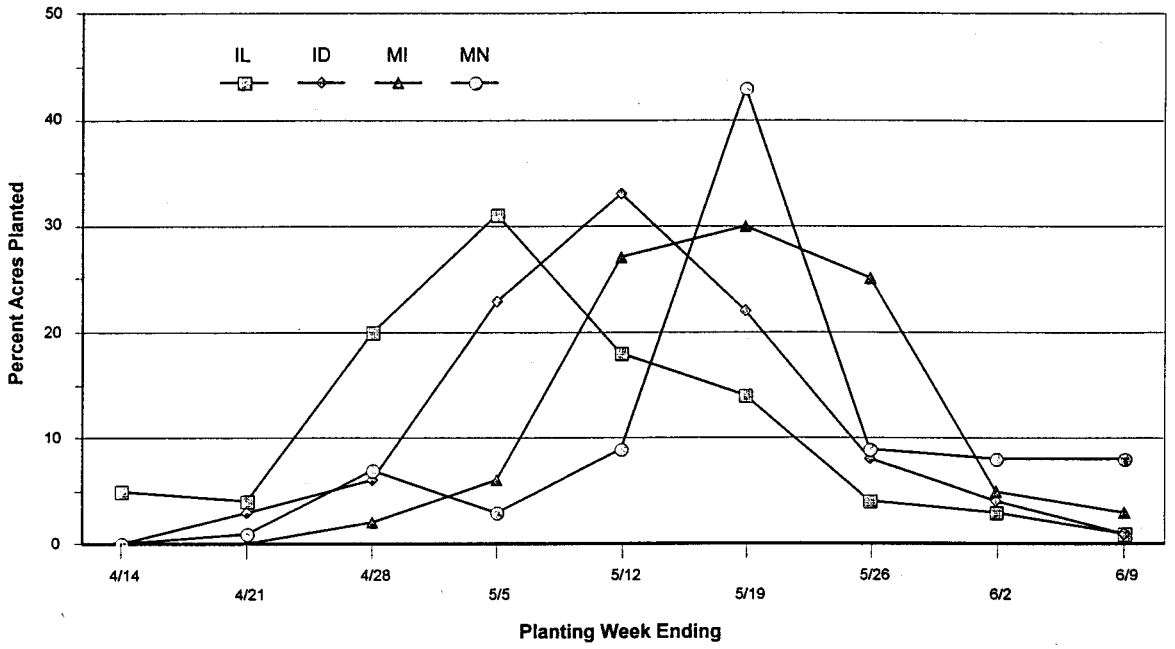
Timing patterns were developed on a state or regional basis, and then assigned to the counties or grids as in the usage inventory.

5. Planting date distributions.:

Fortunately, for major corn and sorghum states, there exists the 1991 USDA-NASS Weekly Crop Progress and Condition database, which has weekly percentages of acres planted (see Figure II-3). For the largest corn states, and for the states with significant use near receptors, state USDA Agricultural Statistics Services kindly supplied us with unpublished survey data at their reporting district level, usually nine

[3]The Ontario Ministry of Agriculture, Food and Rural Affairs conducted the most accurate survey of atrazine use for Ontario corn in 1989 and 1993. Interpolating these rates of application, 1991 Agriculture Census crop planting data, and the recommended application rates by Novartis, we estimate a mid-range value of 1.323 million kilograms in 1991. Environment Canada kindly provided CBNS a total 1990 sales figure of 1.211 million kilograms from unpublished survey data. Novartis kindly supplied CBNS an estimate of 1.219 million kilograms of Canadian use in 1991 from its own sales and marketing surveys.

Figure II-3: Crop Planting Times: Field Corn for Selected States 1991



regions within each state[4]. When planting time data are not readily available, as is the case of minor states and minor crops, we estimate planting dates from local climate data[5] and crop planting practices, or by surveying local crop specialists.

6. Derivation of pre-planting and post-emergent application distributions:

Once the planting time is allocated for each crop and location, the time period for pre-planting and post-emergent applications can be derived. For corn, pre-plant application is typically within two weeks of planting, often incorporated into the soil during tilling.[6] Sorghum and millet have similar recommendations for pre-plant application. The incentive is to apply atrazine close to the planting date, so that less will be lost due to degradation and transport.

Ideally, post-emergent applications are made when weeds have significantly emerged (about one and a half inches) but before the crop plant has reached twelve inches (Ciba-Giegy, 1996). For corn, this is usually the fourth week after planting, but varies depending on growing conditions. For sorghum and millet, the period of application can stretch out for a longer period of time.

We constructed a timing database for each application period, state and provincial agricultural region. Because of the variation in the distribution of pre-plant and post-emergent applications, we built into our databases the flexibility of developing alternative scenarios of distribution.

[4]We applied two different planting time scenarios to our model. One, with only state level data, and the other with supplemental regional data. The deposition estimates were generally within the same order of magnitude. The regional data scenario, however, had significantly better temporal agreement with USGS-measured data (see below).

[5]Climate data were provided by NOAA (1991, 1993) and Environment Canada (1991a, 1991b, 1992). Planting time for corn, for instance, can be estimated from the last spring frost. In regions with short growing seasons, for the best yield, corn for grain is planted very close to the last frost date. In regions with longer growing seasons, and for silage, corn can be planted over a longer period for a good yield.

[6]For corn, it is recommended by the manufacturer that pre-plant applications be within 2 weeks prior to planting, or up to 45 days prior in some cases with soil types that can retain water over longer periods.

7. Allocation between pre-plant, pre-emergent and post-emergent applications:

The USDA Economic Research Service (ERS) and NASS conduct an annual "Crop Practices Survey," from which they estimate much of their published data (e.g., the aforementioned Agricultural Chemical Usage reports). We were able to use their raw survey sample file (stripped of reporting farmer's identity) to estimate the proportions that farmers applied atrazine between pre-planting, pre-emergent and post-emergent for each major corn and sorghum state[7]. We used a weighted average for minor use states. Novartis (Shaw 1997) kindly supplied us with their estimates for Canada. There has been a recent trend towards post-emergent use to minimize polluting runoff in the rainier pre-planting and pre-emergent seasons and to reduce unnecessary preemptive applications.

8. Planting timing and usage database:

The timing database was developed from U.S. state NASS reporting districts and Canadian regional information. These data are assigned to the county, Zip code or Canadian zone level by the same procedure used in atrazine usage, according to the cropping patterns on the more local level. Consequently the local data are assigned uniformly; intra-state and intra-regional differences have not been accounted for.

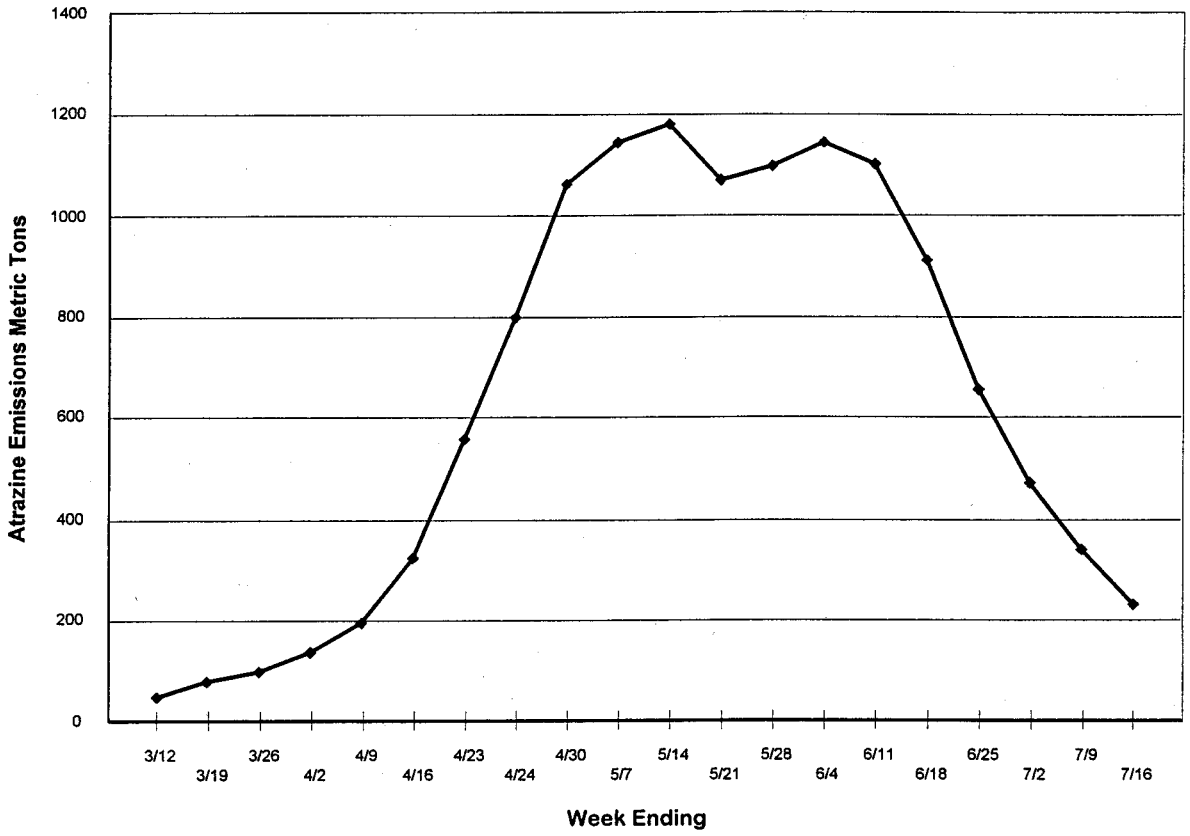
The timing data are ultimately expressed in the database as the percent of the atrazine applied in a particular week for each crop on the level of county or Canadian zone. The total atrazine applied in the county or zone for each crop (estimated in previous analysis) is then multiplied by this percent to yield the amount in kilograms applied in each week. The atrazine applied to minor crops was assigned to either the corn or sorghum timing patterns and included in the inventory.

9. Emission factors:

Ortech developed emission factors, expressed as ranges, on a 127 square kilometer grid system covering the United States and Canada. These were allocated to counties and Zip codes through GIS data processing (see section B below). The emission factors are divided into three categories: minimum range, mid-range and maximum range. The usage data by week for each county, Zip code and zone are multiplied by the emission factors to yield quantities of atrazine emitted from applications during each week (see Fig. II-4). The emissions are then spread over a

[7]When Ortech (1997) developed the regional emissions factors, they used a different time period (1989-1990) and a single allocation scenario, quite different than ours (see Table A-1, appendix). For comparative reasons, we ran our model with the Ortech allocation and with our state level data. We found, as in the case of planting time resolution, that our overall deposition results had the same order of magnitude, but our temporal agreement with USGS-measured results improved more significantly.

Figure II-4 Atrazine Emissions 1991 in the U.S. and Canada by Week



four week period corresponding to experimental data. The result is inputted into TRANSCO to yield contribution by week and source county/Zip code/zone to each receptor. For use in our model, the limits of the ranges of emission factors used in the Ortech color code were taken as minimum and maximum values for a given county or zone, and a midpoint value was given by using half the difference between them.

10. The Time Course of Emissions After Application

After application, atrazine is emitted at varying rates over a long period of time. The emissions rate at any time depends on a number of factors, including the method in which atrazine was applied, the characteristics of the soil environment (soil type, moisture content, temperature, etc.), the nature of the above-ground vegetative canopy (which, for example, may intercept atrazine emitted from the soil), the local meteorological conditions (e.g., wind speed, precipitation, temperature, relative humidity). Ortech's reported estimates of overall emissions factors were the cumulative results of their attempt to model the evolution of this complex process over time.

For the purposes of our calculations, the overall emissions factor (i.e., the annual fraction of applied atrazine that was emitted) was insufficient: we needed to know the fraction of applied atrazine that was emitted with a higher degree of temporal resolution. To yield a reasonable estimate of the time course of emissions after application, measurements of atrazine volatilization reported in the literature were reviewed, including the detailed laboratory and field-based studies of Burt (1974), Dorfler *et al.* (1991ab), Foster *et al.* (1995), Gish *et al.* (1995), Glotfelty *et al.* (1989), Schneider *et al.* (1992), Whang *et al.* (1993), Wienhold *et al.* (1993), and Wienhold and Gish (1994).

Analysis of the experimental results presented in these papers yielded the finding that while the total amounts emitted varied widely from study to study, the time course profile of volatilization after atrazine application was relatively consistent. That is, the *fraction of the total emissions* that were emitted in each week following application exhibited a fairly uniform profile even under different soil, weather, tilling and application conditions. Thus, it was possible to estimate an average time course profile from these experimental data, and, have some degree of confidence that it was a reasonable representation of the actual profile. In constructing this average profile, more weight was given to the field-based measurements than the laboratory-based measurements. In this average profile, 51% of the *total volatilization expected to occur* was estimated to occur in the first week after application, 25% in the second week, 12% in the third week, 6% in the fourth week, 3% in the fifth week, 1.5% in the sixth week, and 0.75% in the seventh week after application.

In sum, estimates of the weekly amount of atrazine applied in each source region were developed, as described above. The geographically-resolved total emissions factors estimated by Ortech were applied to each source region each week to estimate the total amount of atrazine expected to be volatilized from each source

region due to each week's application. Finally, the average time-course profile discussed immediately above was factored in to create an estimate of fraction of this total volatilization that would occur in each week following a given weekly application at a given location.

While we believe the approach above yielded reasonably accurate temporally-resolved emissions estimates, it is recognized that improvements in accuracy can probably be made. In future work, we hope to develop and evaluate a detailed soil/crop herbicide volatilization model and incorporate it directly into our modeling system.

B. The Use of Geographic Information Systems (GIS) Technology:

The use of GIS technology[8] was of strategic importance in the implementation of this project. This technique was used in the development of electronic databases, data analysis, and the display and analysis of the results.

As noted earlier, we relied on the Ortech study for our inventory of atrazine emission factors. These data were provided in the form of a color-coded map depicting the ranges of emission factors in each of 855 zones in a 127x127 km polar stereographic grid. Our model computations for Canada were based on these grids. However, since U.S. agricultural data were available at a much greater detail, for counties or Zip codes, it was necessary to convert the data in the Ortech grid to this more detailed level. For this purpose the Ortech grid was first replicated in electronic form. Then the Ortech emission factor values were entered into an electronic database and geocoded. This information was used to create a file (and maps) of emission factors for all U.S. counties and in some regions for Zip codes.

As indicated earlier, the atrazine usage inventory for the U.S. was developed from multiple data sources and organized at the county level. For the purpose of estimating the atrazine emissions in each county, the grid-based emissions for the U.S. that were gleaned from the Ortech study had to be translated to the county-level resolution. For that purpose the county base map (based on the U.S. Bureau of the Census Tiger/Line files) containing the emissions factors for the U.S. were organized in a common coordinate system and superimposed on each other. Each county was assigned its atrazine emissions factor by means of the GIS polygon processing technique. The same process was also applied in the transformation of county-based data sets to the U.S. Zip code level.

[8]Two software packages were used (MapInfo 4.0 and AtlasGIS) for various GIS operations such as: polygon overlay analysis (the ability to topologically overlay two or more GIS layers and create a new layer by storing information from the original map layers whose boundaries may not coincide), point in polygon analysis, spatial query, and distance calculations.

C. Modeling the Atmospheric Fate and Transport of Atrazine:

1. Introduction:

The atmospheric fate and transport modeling simulations performed in this project represent an effort to answer the following basic question: How much of the atrazine emitted to the air from a particular location (**source**) where it is used in agriculture is deposited at a **receptor** site (e.g., a drinking water reservoir) at another location? In order to answer this question, we defined each of the 3,141 U.S. counties and 855 larger zones in southern Canada as sources; this recognizes that atrazine is widely used in agriculture. We also defined 33 locations, chiefly in the Midwest, as receptors and investigated the relationship between each of them and each of the 3,996 sources. For each of these 131,868 source-receptor pairs, we estimated the amount of the atrazine emitted by the source that is deposited at the receptor. The effort to create such a comprehensive picture of these source-receptor relationships is a unique and challenging feature of this work.

Among the selected receptors is a set of locations at which the U.S. Geological Survey measured the amount of atrazine deposited in rainfall; these serve as a direct means of evaluating the overall modeling system. The degree to which the predicted deposition in rainfall at these sites matches the measured deposition is an indication of the accuracy of the emissions and of the atmospheric fate/transport estimates of the model.

Our approach to this complex analytical problem is based on a four-step procedure: *first*, a model is developed to simulate the fate and transport of atrazine emitted from a single source point; *second*, this model is used to estimate the atmospheric behavior of the individual emissions from each of a series of hypothetical standard source points, including its deposition of atrazine at each of the selected receptors; *third*, the source-receptor relationships for the numerous actual source points are estimated by means of an interpolation procedure based on the standard points; *finally*, the source-receptor relationships are coupled with an emissions inventory to estimate the actual amount of atrazine deposited at a given receptor from each of the sources in the inventory. These procedures are described below.

2. Simulation of the Atmospheric Fate and Transport of Atrazine Emitted from a Given Source Point

We have used the HYSPLIT air transport model, originally developed at the National Oceanic and Atmospheric Administration (NOAA) by Roland Draxler, as the starting point for this simulation. HYSPLIT is classified as a Lagrangian air pollution model because it attempts to follow the behavior of individual air parcels or puffs emitted from a given source. The model works in the following way:

- The total amount of atrazine emitted at a specified source point over a given period of time is simulated as a series of “puffs” of equal atrazine content;

- At each time step (which varied from 1 minute to 15 minutes in these simulations) the puff is dispersed by atmospheric diffusion and advected by the winds;

- Also at each time step, the fate of the atrazine in the puff is estimated, including its chemical transformation in the atmosphere and its wet and dry deposition to the earth’s surface; “wet” deposition in rainfall and “dry” deposition in the absence of rainfall are estimated separately.

In the simulation of real-world emissions, a series of puffs are emitted over time from a given source and each is tracked and analyzed with respect to its location and atrazine content. Atrazine applied to the soil is expected to be volatilized and emitted primarily during the day, as volatilization rates rise quickly as the temperature increases. This has been experimentally verified in the field (Glotfelty *et al.*, 1989; Whang *et al.*, 1993). In order to capture the basic diurnal pattern of emissions, in our simulation puffs were emitted only from 8 AM to 4 PM each day.

HYSPLIT incorporates NOAA-generated weather data for the United States, southern Canada and northern Mexico for a grid of 925 points, 183 km apart, at six levels up to 5,000 meters, recorded at two-hour intervals for every year since 1988.

In our earlier work, several modifications were made to HYSPLIT, including the effect of vapor/particle partitioning of semivolatile organic compounds in the atmosphere and a mass accounting procedure to estimate the deposition to user-defined area receptors (Cohen *et al.*, 1995). The earlier modifications were retained in the present work, and additional ones were added to account for the distinctive features of the emission and transport of atrazine. The primary modifications and refinements made in the present work include the following:

- the addition of a simulation of the hydroxyl radical reaction, which, for atrazine, is probably one of the most important atmospheric fate pathways;

- the addition of a capability to estimate the deposition at a *point* receptor such as one of the USGS rainfall deposition measurement sites (as opposed to an area receptor, such as one of the Great Lakes)

A screening analysis of the processes that influence the atmospheric fate of atrazine was performed. The results, presented in Table II-2 below, suggested that perhaps the most important fate mechanism that would affect airborne atrazine would

be the reaction with hydroxyl radical. This required the addition of the procedures to estimate hydroxyl radical reaction to the model.

The hydroxyl radical is extremely difficult to measure in the atmosphere due to its very low concentrations and extreme reactivity. Atmospheric transport models which attempt to quantitatively include hydroxyl radical reactions generally must rely on model-estimated concentrations. Lu and Khalil (1991) present a series of calculations that estimate the hydroxyl radical concentration as a function of time of day, season, latitude, elevation, and the levels of other pollutants in the atmosphere. These were used to create an algorithm within HYSPLIT that estimates the hydroxyl radical concentration as a function of time of day, season, latitude, and elevation. Thus, for a given puff, the hydroxyl radical concentration is estimated at each of its locations and times of transit so that the rate of reaction with atrazine could be estimated as well. The dominant feature that governs the variation of the atmospheric hydroxyl radical concentration with time and location is the diurnal pattern. There is very little hydroxyl radical at night, and during the day the concentration peaks at approximately the time of maximum sunlight intensity (generally around noon).

Reaction rates with hydroxyl radical have been experimentally determined for a number of compounds, but apparently not for atrazine. (The cost of such experimental measurements is rather high.) Accordingly, it is common practice to estimate the reaction rate of a particular compound by means of structure-activity correlations, which suggest how the rate is influenced by various aspects of the molecular structure.

Atkinson and coworkers have made a number of the experimental measurements of hydroxyl radical rate constants and have developed a structure-activity model for reactions with organic compounds (Atkinson, 1987, 1988; Atkinson and Aschmann, 1992; Kwok *et al.*, 1995ab). Meylan and Howard (1996) have utilized the structure-activity relationships of Atkinson and colleagues to create the Atmospheric Oxidation Rate Program. This program was used to make estimates for atrazine, yielding a first-order hydroxyl radical rate constant of 27.3×10^{-12} cm^3 $molecule^{-1}$ $sec^{-1.}$ This estimated rate constant was used in our simulations.

Table II-2. Summary of a Screening Analysis of the Atmospheric Fate of Atrazine			
	Atmospheric Removal Process	**Approx. Time Scale for Atrazine Removal (days)**	**Notes**
Transformation Processes	Reaction with atmospheric hydroxyl radical	1/4 - 1/2	Reaction Rate Constant Estimated using QSAR; typical atmospheric OH concentrations used to estimate rate of destruction
	Reaction with other atmospheric reactants	> 1	Generally assumed to be less important than hydroxyl radical reaction for this compound, although little data
	Photolysis	1 - 10	Estimated from comparison with literature values for pentachlorophenol, and measurements of the relative rate of photolysis of atrazine and pentachlorophenol
Deposition Processes	Dry Deposition of Vapor-Phase Material	1 - 7	Estimated by analogy to modeling results for 2,3,7,8-TCDD and HgCl2
	Dry Deposition of Particle-Phase Material	1 - 7 (or longer)	Simple vapor/particle partitioning theory suggests that atrazine will exist mainly in the vapor phase, leading to the conclusion that particle-mediated fate mechanisms will not be very important. However, some measurements have found significant proportions of atrazine on particles, and so, this mechanism may be somewhat significant.
	Wet Deposition of Vapor-Phase Material	3 - 10	Atrazine will be fairly effectively removed by precipitation, but, Lagrangian time scale for precipitation events is on the order of 3 - 10 days
	Wet Deposition of Particle-Phase Material	3 - 10 (or longer)	As noted above, atrazine may exist primarily in the vapor phase; however, to the extent that it exists on particle, this could be more significant; at its fastest, it would have a half-life of 3-10 days, similar to that of vapor-phase wet deposition.
Overall Transformation and Removal from the Atmosphere		**1/4 - 1/2**	**Governed by rate of reaction with hydroxyl radical**

3. Selection of a series of standard hypothetical source points and simulation of the atmospheric fate and transport of their emissions:

The simulation of emissions of atrazine from a single source point over a period of 20 weeks (the time frame used in this study) takes on the order of 3-6 hours on a 200 MHz Pentium computer. Given that we were considering emissions from thousands of counties in the U.S. and hundreds of source regions in Canada, it was impractical to run the model for each of them. Instead, the model was run for a series of standard source locations and the results were used in an interpolation model (TRANSCO) to estimate air transport and source-receptor relationships for the more numerous actual source locations. Three types of standard source locations were selected.

First, standard source locations were selected in the regions of heaviest atrazine use in order to provide data on the source-receptor relationships for the largest

emissions we expected to encounter. Approximately 20 such sites were selected, predominantly in the Corn Belt. Second, a few standard source locations were selected in regions distant from the chosen receptors (e.g., in Oregon) to allow estimates of long-distance source-receptor relationships. The effects of these distant sources are expected to be small, because atrazine has a relatively short atmospheric lifetime, but nevertheless important to estimate quantitatively. A total of 27 standard source locations of these two types were established for this analysis. Their locations are shown in Figure II-5.

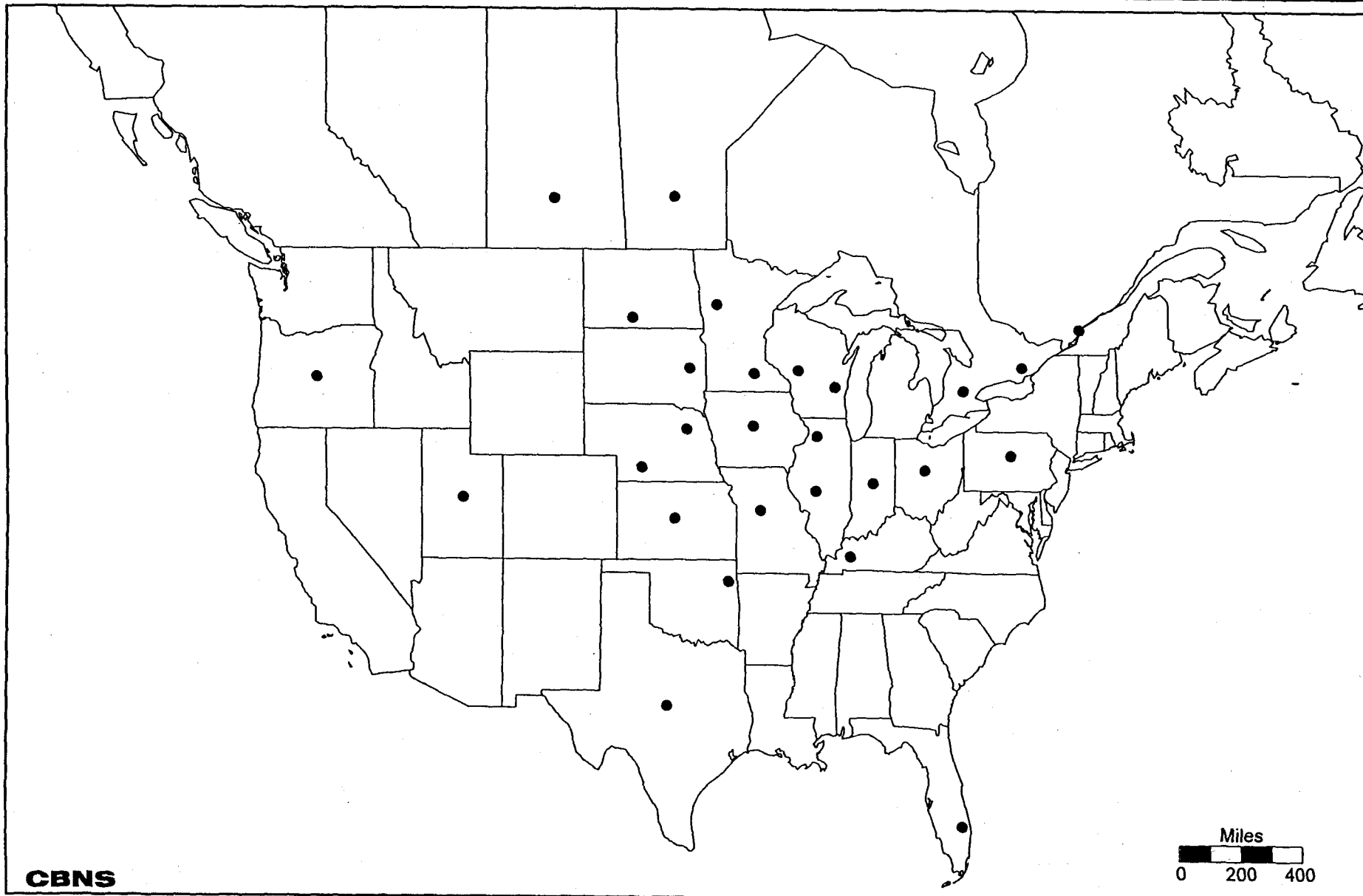
Finally, approximately 10 standard points were established within 75 miles of certain receptors to account for the impact of nearby sources on deposition at the receptor. Atrazine usage was generally low in regions close to the receptors, but such close-in sources might nevertheless have a significant impact on deposition at the receptor. Close-in standard source locations were established around each of eight of the USGS test sites studied and around an area receptor, Grand Traverse, MI. (Close-in modeling simulations for the other USGS receptor sites and the other selected receptors are currently underway, but, as discussed below, it is unlikely that these additional simulations will dramatically change the current results for these receptors.) The close-in runs required a reduced model time-step, and therefore increased computational resources. Even though a much smaller area was being simulated, each of these runs also took about 3-6 hours on a 200 MHz Pentium computer.

As noted earlier, atrazine is applied at specific times during the year, which vary from region to region. Weather conditions also vary with time; for this reason and, because the USGS data used for evaluating the model were weekly measurements of atrazine deposition, particular attention was given to the timing of emissions and the variation of source-receptor relationships with time.

This was accomplished as follows. A twenty-week period was chosen to encompass the dominant period in which atrazine is used and emitted in the U.S. and Canada: March 5 through July 23, 1991. Each weekly USGS rainfall measurement began and ended on a Tuesday at about 3 PM. To allow a direct comparison of the model predictions with the measurements, our model weeks coincided with these measurement weeks. Twenty separate model simulations were performed for each standard source location. The first simulated the fate and transport of atrazine emitted in the first week (March 5 - March 12), the second simulated the fate and transport of atrazine emitted during the second week (March 12 - March 19), and so on. Each of the twenty weekly emissions were tracked by the model for one additional week in order to account for delayed deposition of atrazine emitted in the previous week. However, very little of the deposition (on the order of a few percent) was generally accounted for by these later depositions. Nevertheless, as with many other aspects of the simulation, we did not want to assume *a priori* that these contributions would be negligible.

As noted earlier, it was assumed that atrazine was emitted only during the peak daylight hours (from 8 AM to 4 PM). A standard emissions unit of 3 grams per hour was

Fig. II-5: General Standard Source Locations (Type 1 and Type 2)
Used in this Analysis



adopted for this eight-hour period, representing a total of 24 grams per day, or the equivalent of 1 gram per hour. During each simulation, the wet and dry deposition flux of atrazine (grams deposited per square meter) was estimated for each of the selected receptors. For the receptors that represented areas rather than points (i.e., lakes and counties), the estimates considered the deposition flux to each of a series of subregions of known area. The contribution to each of the subregions was summed to estimate the total contribution to the receptor area.

An example of the results obtained from these unit-emissions, unit-week simulations, is shown in Figure II-6, for the amount of atrazine deposited on Lake Superior due to a hypothetical source in central Iowa emitting one gram of atrazine per hour. The results, which are typical of the model output, show that during about half of the studied weeks, little or none of the atrazine emitted by the source was deposited in Lake Superior. This might result from wind patterns carrying the emitted atrazine in directions away from Lake Superior — which can certainly happen — or from heavy rains falling between the source and receptor, which might wash atrazine out of the atmosphere in transit, effectively intercepting it before it reaches the Lake. Figure II-6 also shows that the relative proportion of wet and dry deposition varies from week to week, and that wet deposition generally — but not always — is the most important deposition pathway in a given week. Finally, it can be seen that the amount of predicted deposition varies quite a bit from week to week. Again, this is to be expected given the time-varying nature of the weather in between the source and the receptor.

Another example of such simulation results is shown in Figure II-7. Here, the total 20-week deposition flux at a series of receptors arising from 20 weeks of eight-hour-per day emissions of three grams per hour from a hypothetical source in north-eastern Nebraska is shown. The magnitude of the predicted flux and the relative proportion of wet and dry deposition vary considerably from receptor to receptor. Each of these variations is, of course, a reflection of the fact that the weather is very complex, and that, therefore, over any time period, a given source will affect each receptor differently.

The overall set of the 20-week-total atrazine deposition fluxes estimated at each of the receptors from each of the 27 general standard source locations are presented in the Appendix. As already noted, the data summarize the overall effect of the individual weekly contributions.

4. <u>The method of interpolating the depositions due to actual sources from the depositions due to the hypothetical standard source points</u>:

Because it would be impractical to run the HYSPLIT model from each of the many thousands of source locations, an interpolation procedure was used to estimate the source-receptor relationships for sources at locations that were not explicitly simulated by HYSPLIT. This interpolation procedure was performed with the

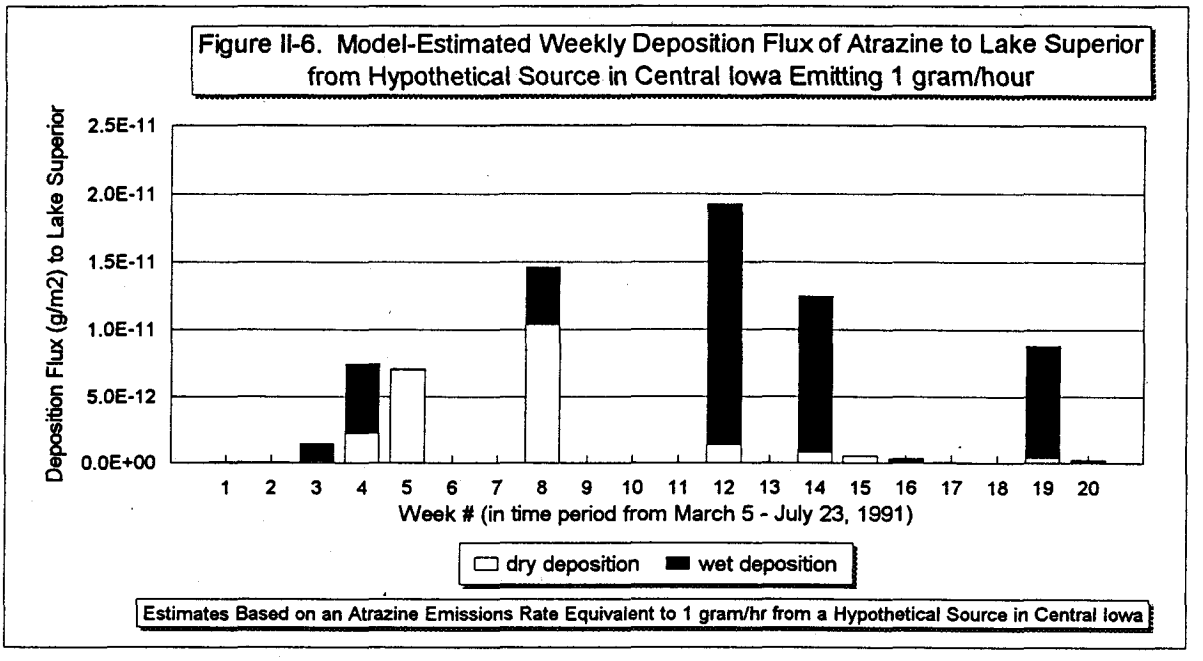


Figure II-6. Model-Estimated Weekly Deposition Flux of Atrazine to Lake Superior from Hypothetical Source in Central Iowa Emitting 1 gram/hour
Deposition Flux (g/m2) to Lake Superior
2.5E-11
2.0E-11
1.5E-11
1.0E-11
5.0E-12
0.0E+00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20
Week # (in time period from March 5 - July 23, 1991)
dry deposition
wet deposition
Estimates Based on an Atrazine Emissions Rate Equivalent to 1 gram/hr from a Hypothetical Source in Central Iowa

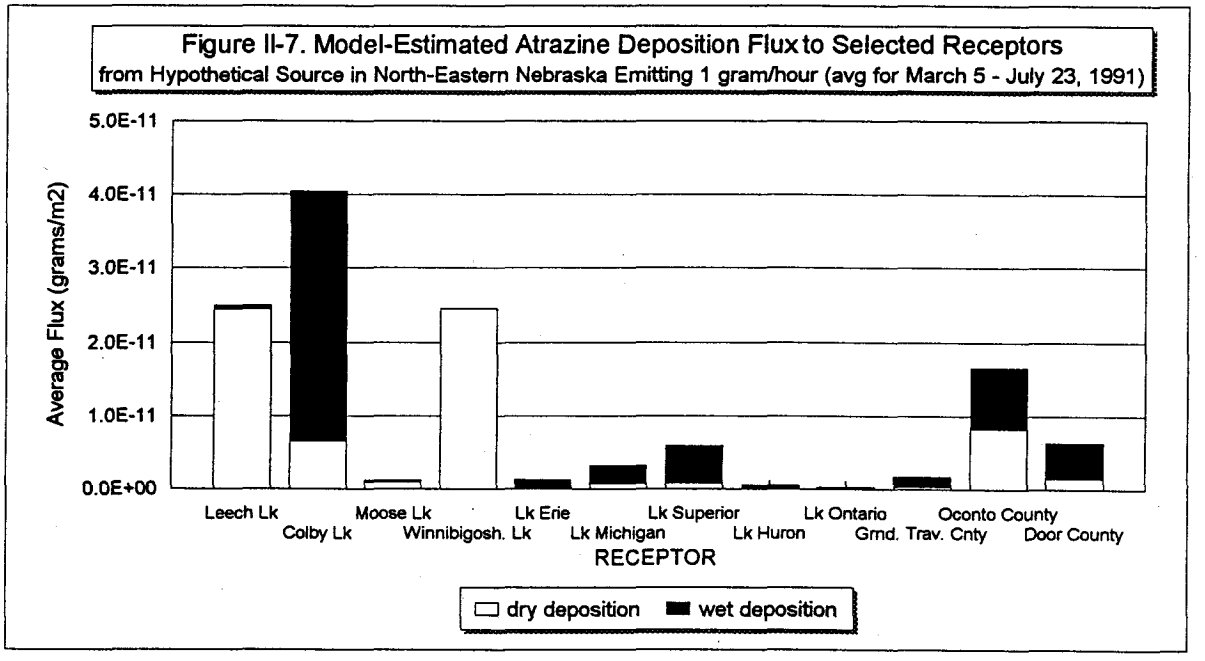


Figure II-7. Model-Estimated Atrazine Deposition Flux to Selected Receptors
from Hypothetical Source in North-Eastern Nebraska Emitting 1 gram/hour (avg for March 5 - July 23, 1991)
Average Flux (grams/m2)
5.0E-11
4.0E-11
3.0E-11
2.0E-11
1.0E-11
0.0E+00
Leech Lk
Colby Lk
Moose Lk
Winnibigosh. Lk
Lk Erie
Lk Michigan
Lk Superior
Lk Huron
Lk Ontario
Grnd. Trav. Cnty
Oconto County
Door County
RECEPTOR
dry deposition
wet deposition

TRANSCO computer program developed at CBNS. The interpolation procedure works in the following way.

First, for a given source location, the four closest standard source locations were identified. Then, the impact of the given source on each receptor (i.e., the amount of atrazine deposited) was estimated as the weighted average of the impacts of each of these four closest standard points. The weighting factors were based on the relative proximities of the four points to the actual source location (closer points counted more) and the degree to which the angular orientation of the actual source to the receptor matched the corresponding orientation of each of the four closest standard points. In other words, all things being equal, it was hypothesized that source-receptor relationships would be more similar for closely matched source-receptor directional orientations. This interpolation procedure had been thoroughly tested in previous work (Cohen *et al.*, 1995) and found to allow reasonable approximations of the actual source-receptor relationships. The net result of the interpolation procedure is the predicted dry and wet flux at each of the receptors of interest that would arise from a "unit" emissions of 1 gram/hr from the given actual source.

A basic assumption of this methodology is that a sufficient number of standard source locations have been chosen to capture the major features of the geographical distribution of the actual source-receptor relationships. If an insufficient number of standard source locations were selected, so that they were spaced too widely, the interpolation procedure might yield inaccurate results. As discussed below, we found that our original set of 27 standard source locations was indeed insufficient to provide accurate estimates for all sources for all weeks to all receptors, although it appeared to do reasonably well in most instances. To remedy this situation, additional, more closely spaced standard source locations were simulated with HYSPLIT; as discussed below, these were included in the interpolation algorithms resulting in an improved set of estimates.

In future applications of this methodology, two refinements to this interpolation methodology will be practiced. First, a finer grid of standard source points will be run, as a matter of course, with additional attention paid to the areas of intense emissions. The size of the grid required for accurate interpolations depends on the area of the receptors (smaller receptors require a finer grid), the length scale of atmospheric transport of the pollutant of interest (all things being equal, a coarser grid will work better for a pollutant with a long atmospheric lifetime than one with a shorter lifetime), and the temporal resolution required of the results (a finer grid is required to produced more highly time-resolved results).

Our earlier experience with modeling PCDD/F and HCB transport to the Great Lakes was at one end of this spectrum: the receptors themselves were very large, the pollutants had relatively long atmospheric lifetimes, and generally only annual estimates were used (i.e., the temporal resolution "required" of the overall results was 1 year). The situation with atrazine is much different: we were considering USGS receptor sites

that were literally small buckets (much smaller than a Great Lake), and atrazine has a much shorter half-life than PCDD/F or HCB in the atmosphere. Moreover, we required a temporal resolution of one week in our results in order to compare our results with the amount of atrazine in rainfall at the USGS wet deposition measurement sites.

Second, the validity of the interpolation procedure will be rechecked for each model. To carry out such a check, a series of test source locations can be selected and simulated directly with HYSPLIT. Test locations might best be located in the areas of highest emissions. Then, TRANSCO can be used to estimate source-receptor relationships for each of the same test points. If the degree of matching between the explicitly simulated and interpolated results are acceptable, then this strongly suggests that the interpolation procedure — based on the grid of standard source locations — can provide reasonably accurate estimates. On the other hand, if these tests show that the interpolation procedure fails, then additional standard source locations can be simulated explicitly with HYSPLIT.

5. <u>The addition of the emissions data to the source-receptor relationships established by the model</u>:

This is the final step of the calculation and is performed within TRANSCO. It follows the model-generated estimates of the source-receptor relationships, expressed as deposition fluxes at each receptor arising from a "unit" emissions rate of 1 gram per hour for a given source (for a given week). The actual estimated emissions from the source (i.e., the "actual" number of grams emitted per hour) are simply multiplied by the unit-emissions flux to arrive at the flux that would result from the real source.

III. RESULTS

A. Model Evaluation:

The original HYSPLIT model has been successfully validated by comparing its predictions with the actual measurements of an experimental tracer substance, perfluorocarbon (Draxler, 1992). The model that we have modified, HYSPLIT/ TRANSCO, has also been validated by comparing the predicted and measured values of airborne dioxin at a site in Canada (Cohen *et al.*, 1995). The new modified model for atrazine has been evaluated by comparing measured values of the atrazine concentration in rainfall collected at a series of 20 test sites in the Midwest and Northeast (USGS, 1995) with the values predicted by the model for these sites. The USGS survey included measurements of the amount of atrazine deposited (as a flux: micrograms per square meter) in rainfall collected during successive week-long periods in 1991. As already noted above, we have produced an inventory of the amount of atrazine emitted into the air, during each week in the period March 5-July 23, 1991. With this inventory entered into the model, we were in a position to compare, in each of

these weeks, the measured values with those predicted by the model. The locations and designation of the USGS test sites are shown in Figure III-1.

This comparison was made at 20 of the 82 test sites studied by USGS. Sites chosen for comparison were those that were in areas of little or minimal use of atrazine, as the purpose of this study was to determine the extent to which atrazine emitted in areas of intense usage might deposit in areas of less intense usage.[9] As shown in Figure III-2, the comparison sites have deposition values in the mid to low range of values observed in the total list of sites, a not unexpected result, since we selected sites away from areas of the most intense use.

We compared the week-by-week model-predicted wet deposition with the measured week-by-week deposition at the 20 comparison sites over a period of 20 weeks (from March 5 through July 23, 1991). Thus, there were 400 data points of comparison. Except for 11 outliers, there was good agreement between the remaining 389 values. The standard deviation between the predicted and measured values for deposition over the entire 20-week study period was 42% of the mean measured value. Given that the measured values on which this standard deviation is based were spread over a hundred-fold range, this is a reasonably good agreement. The values of the weekly measurements themselves are spread over a considerably larger range. If the outliers are excluded, the standard deviation would be only 12% of the mean measured value.

In order to understand the significance of the outliers, we conducted a sensitivity analysis on six of them. The sensitivity of the predicted deposition values to variations in two key components of the model was evaluated. Variations in the vapor/particle partitioning calculations caused no significant changes in the predictions. In contrast, when the standard points used to estimate the transfer coefficient of the source that contributed most to the amount of atrazine deposited at the outlier test sites was shifted east or west by one degree longitude, the predicted values change by one to two orders of magnitude.

We concluded that when a source is located in an area where the transfer coefficients to a given receptor vary abruptly from place to place, over relatively short distances, standard points that are too widely spaced may lead to erroneous interpolation-predicted deposition values. Accordingly, it would appear that the outliers may be improved by using a more finely spaced set of standard points, especially in areas of intense emission.

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[9] It might be noted that the modeling methodology described and utilized in this analysis could be applied to estimate deposition in areas of intense usage. Such an analysis would require somewhat more computational resources, since more close-in standard source locations would have to be simulated.

Fig. III-1: Locations and Designations of the U.S.G.S Rainfall Measurement Sites Used for Model Evaluation

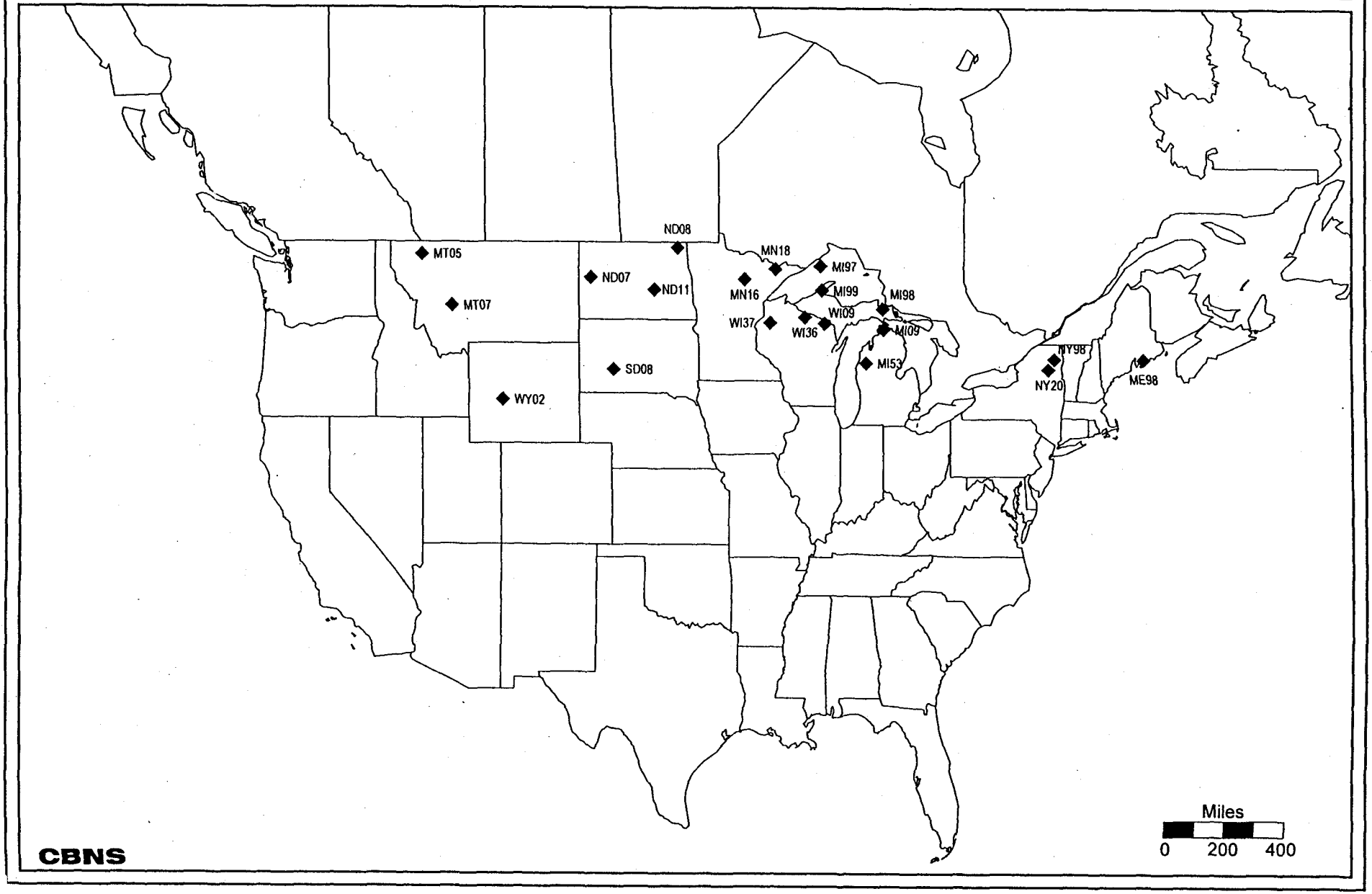
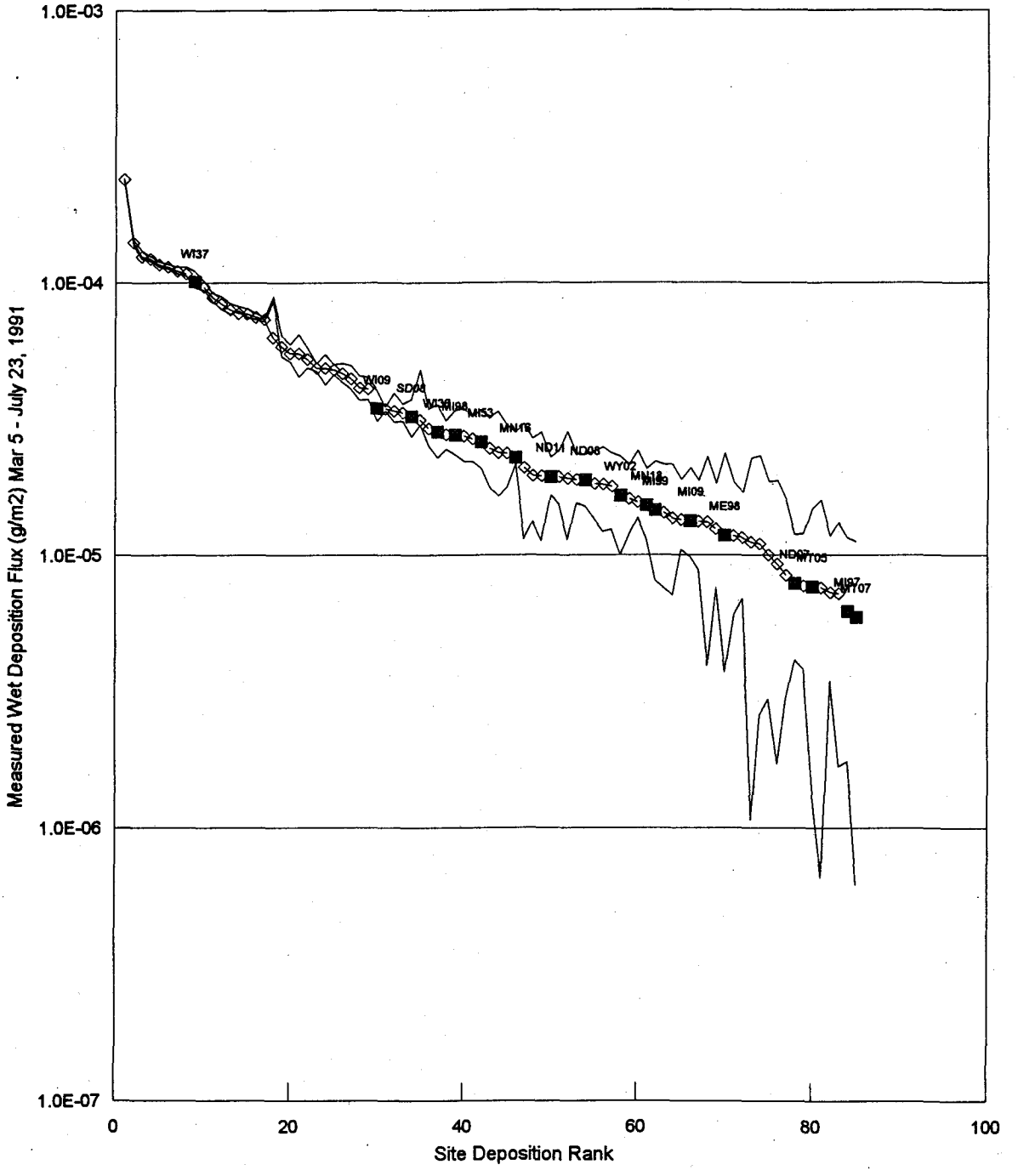


Figure III-2. Measured Wet Deposition of Atrazine at USGS Rainfall Deposition Sites

Total Wet Deposition Flux for the Period from March 5 - July 23, 1991



To test this hypothesis, additional standard source locations were selected and HYSPLIT simulations were performed from each of them. In all, a total of 88 additional source locations were simulated. Together with the original 27 locations, the calculation now included 115 standard source locations. In addition to the expanded standard source grid, improvements were made to the emissions inventory (based on additional information obtained), and, close-in model simulations were completed for the remainder of the test locations. New estimates based on this refined analysis were carried out. A summary of these new results are shown in Figure III-3, for all of the weekly values at the 20 comparison sites — a total of 400 values. The new analysis resulted in a significant improvement: the average error decreased from 42% to only 25%, and, there were only 6 outliers out of the 400 data points instead of the 11 which were found previously. With the 6 outliers removed, the average error was only 11%. These improved results were used in the analysis discussed in the remainder of this report.

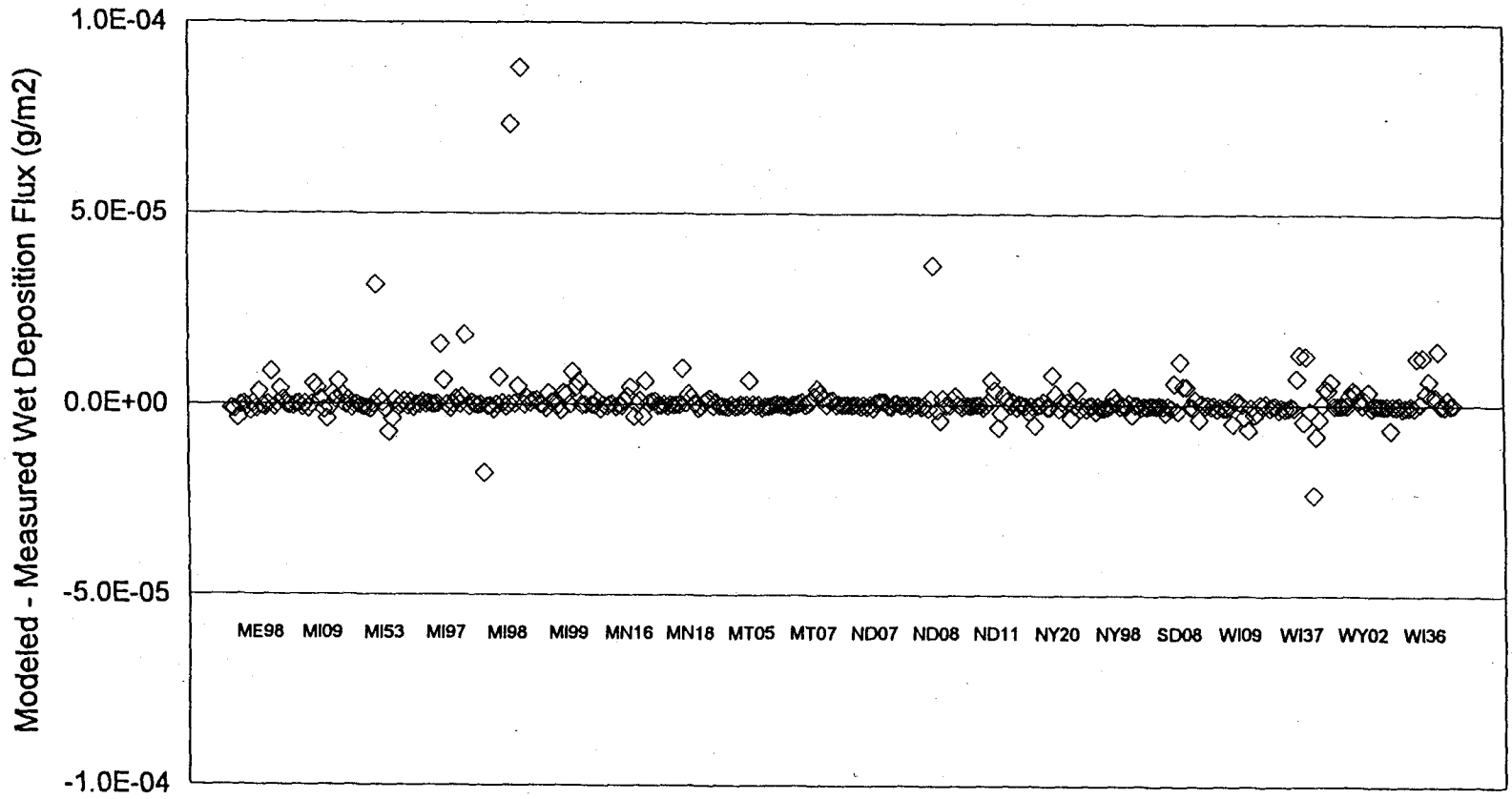
B. The Geographic Distribution of Atrazine Usage, Emission Factors, and Emissions:

The basic model input, which we have derived from the agricultural data, is the amount of atrazine emitted into the air by each of the 3,141 U.S. counties and the 855 Canadian zones (i.e., the sources). These values are the product of the amount of atrazine used in each source and the source emission factor — that is, the fraction of the applied atrazine that is volatilized and enters the air.

A series of color-coded maps show the geographic distribution of the levels of atrazine usage, the emission factors, and their product -- the amounts emitted. **Map 1** reflects the wide range of annual atrazine usage, which in 1991 varied from nearly 100 kg to more than 400,000 kg per county in certain Corn Belt counties. Atrazine is used in nearly every county in the eastern half of the United States and in the comparable regions of Canada. There is a sharp gradation in decreasing usage from the Corn Belt to northern Wisconsin, Minnesota and Michigan. There are also smaller highly localized areas of intense usage, for example several counties in south Florida, where atrazine is heavily used for weed control in sugarcane.

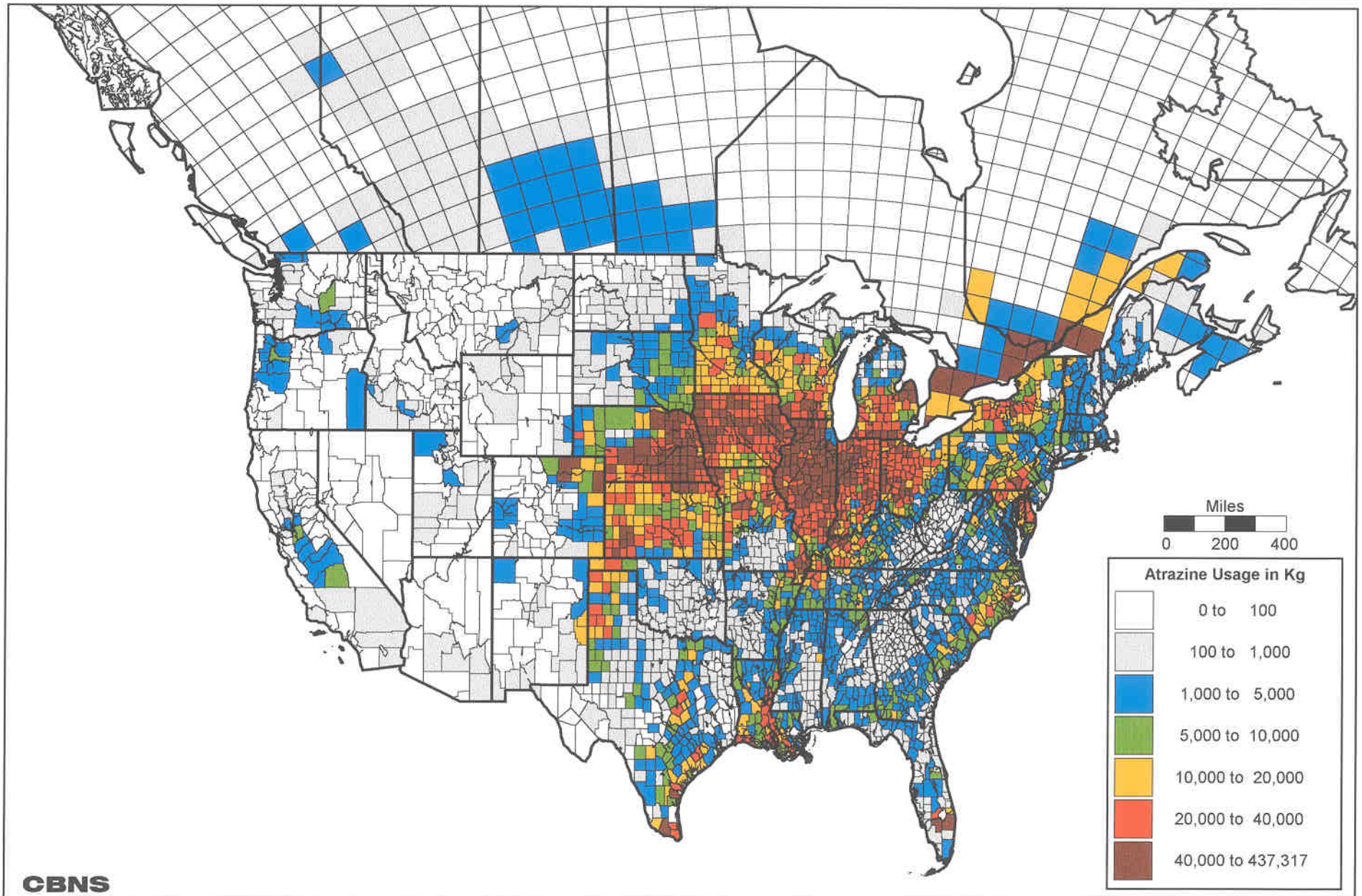
As shown in **Map 2**, the second factor that determines atrazine emission, the overall emissions factor, shows a very different geographic distribution. This factor varies considerably with soil structure, moisture, temperature and wind conditions, all of which influence the movement of soil moisture upward to the surface, where the atrazine dissolved in it can be volatilized and enter the air. For example, relatively hot, windy conditions contribute to high emission factors which occur in the western part of the Corn Belt — such as Nebraska and Kansas — where about a third of the applied atrazine is volatilized and enters the atmosphere. Eastward, in Iowa, Missouri, Illinois and Indiana, the emission factors are in the range of 0.124 to 0.15.

Figure III-3. Comparision of Measured and Predicted Week-by-Week Results for the 20 Studied USGS Rainfall Measurement Sites



The Weekly Deviations are Plotted in Series for Each Site, from Week 1 through Week 20

Map 1: GEOGRAPHIC DISTRIBUTION OF ANNUAL ATRAZINE USAGE IN U.S. COUNTIES AND CANADIAN ZONES (in kilograms)



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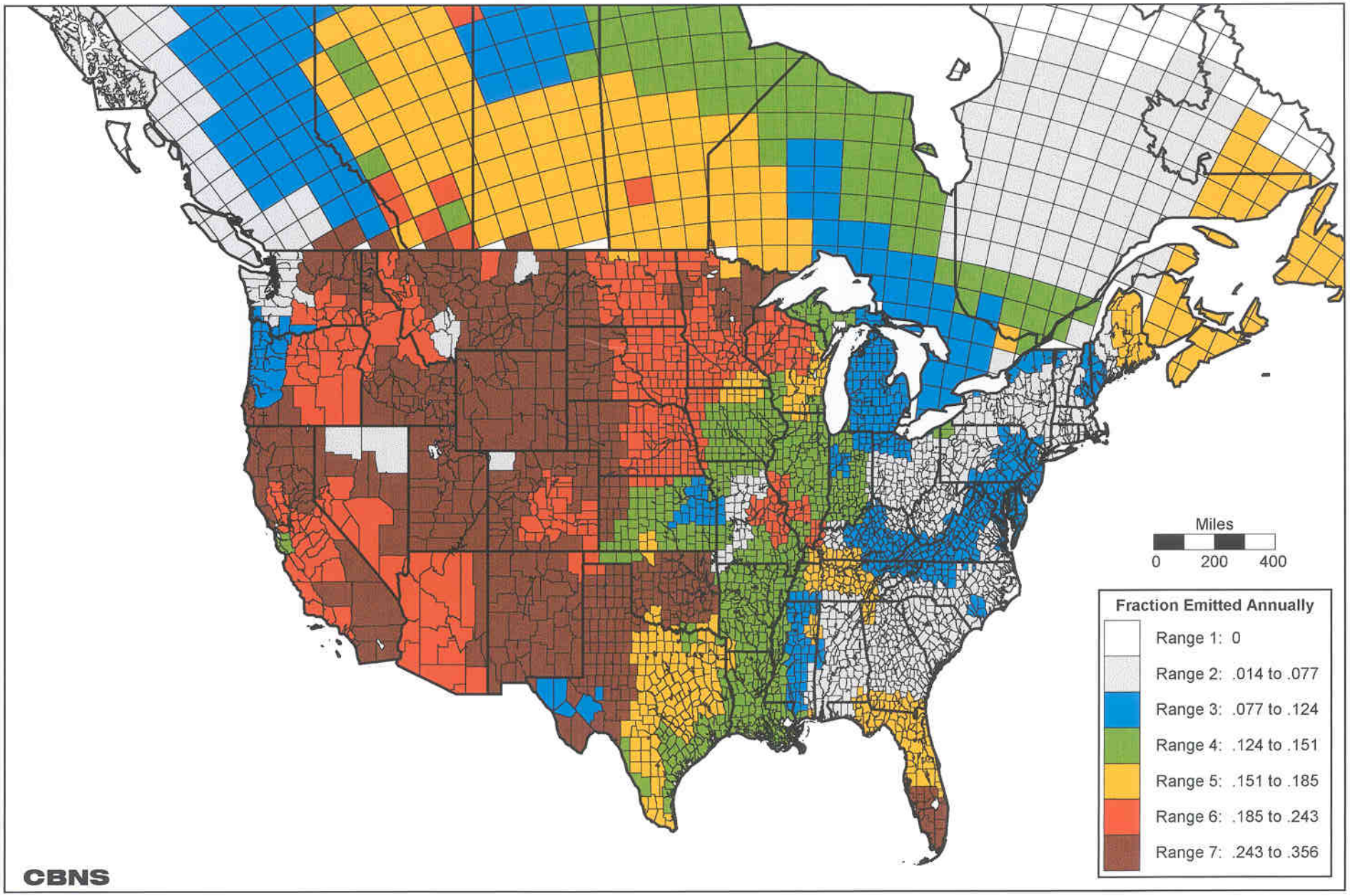
Map 2: GEOGRAPHIC DISTRIBUTION OF ATRAZINE EMISSION FACTORS FOR U.S. COUNTIES AND CANADIAN ZONES



CBNS

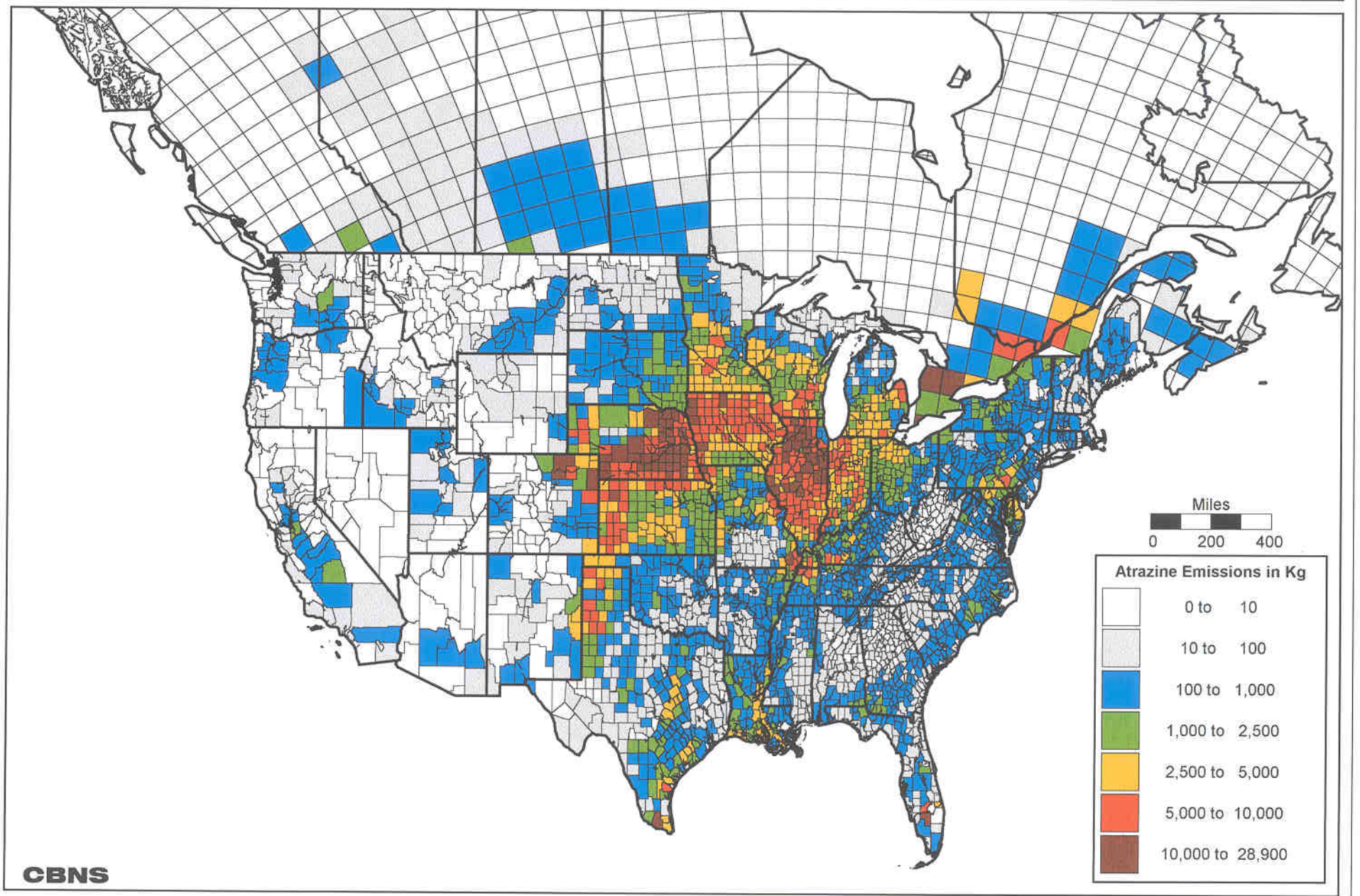
The resultant of the two preceding factors, the geographic distribution of the amount of atrazine emitted into the air annually, is shown in **Map 3**. The geographic distribution of emissions tends to be considerably more localized than the usage. Thus, relatively few counties in the Corn Belt states exhibit the highest emission levels (more than 15,000 kg per year). Similarly, only two adjacent counties in Florida are in the highest emission range, surrounded by counties in which there is little or no emission. A comparable situation exists on the western border of Texas, where 15 counties are characterized by emissions of 5,000-15,000 kg per year and nearby counties, especially to the west in New Mexico, exhibit little or no emissions.

C. The Relation Between Sources and Receptors:

The chief aim of this project has been the development of means of ranking the sources of atrazine (for example, individual counties) with respect to their contribution to the total amount of the airborne atrazine that is deposited on the receptors that are important avenues of exposure, for example drinking water supply reservoirs. For that purpose, it is necessary to enter into the model both the amount of atrazine emitted by the source and an air transfer coefficient which represents the efficiency with which atrazine emitted by the source is ultimately deposited at the receptor. The air transfer coefficient represents the quantitative relation between a specific receptor (for example, Lake Superior) and each of the sources that emit airborne atrazine. Hence, for any given receptor, a total of 3,996 air transfer coefficients must be computed, since the sources consist of 3,141 U.S. counties and 855 Canadian zones. In our computer system (Pentium PCs with 200 MHz processing speed), this would require several computer-hours for a single source. As described in the Methodology section, the interpolation model, TRANSCO, was developed to overcome this difficulty. It allows us to determine, for each receptor, the transfer coefficients for only a limited number of standard source locations. The standard source locations used in this analysis are shown in both Figures III-4 and III-5, together with the transfer coefficients, as examples, computed for Oconto County, MN (Fig. III-4) and those computed for Lake Superior (Fig. III-5). We then use an interpolation program that estimates the coefficient for a given source (e.g., a county).

In this way air transfer coefficients have been computed for each of the 27 standard source locations and 33 different receptors. It is then possible to estimate, using the TRANSCO interpolation program, the amount of deposited atrazine that a given receptor receives from each of the 3,996 sources. In turn, these values are used to compute the percentage of the total amount of atrazine deposited at the receptor that originates from each of the receptors. This is the **source/receptor coefficient**. This is a crucial policy-oriented value, for by signifying the degree to which the receptor's exposure to atrazine arises from each of the entire array of sources, it can direct remedial action to those sources most responsible for the receptor's environmental situation.

Map 3: GEOGRAPHIC DISTRIBUTION OF ANNUAL ATRAZINE EMISSIONS IN U.S. COUNTIES AND CANADIAN ZONES (in kilograms)



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Maps depicting the geographic distribution of these source/receptor coefficients have been prepared for a sample of the USGS test sites, for Lake Superior and for a series of Minnesota lakes and Wisconsin and Michigan farming counties. These provide a visual picture of the relative contributions of each of the numerous sources to the amounts of airborne atrazine deposited on these receptors.

Map 4 shows the geographic distribution of the source/receptor coefficients for the total deposition of atrazine to Lake Superior (the sum of atrazine deposited in rainfall and in dry conditions). The largest contributors to the airborne atrazine that the lake receives are counties in Wisconsin, Iowa and Illinois. Each of these counties contributes 0.5-6.1 percent of the airborne atrazine deposited on the receptor. A much larger number of counties contribute 0.1 to 0.5 percent each, many of which lie a few hundred miles closer to the lake. Only minor contributions arise in Canadian sources, except for two heavily contributing zones near Lake Ontario. A 100 mile band south of Lake Superior contributes relatively little atrazine deposition, since it is an area in which there is little or no atrazine usage.

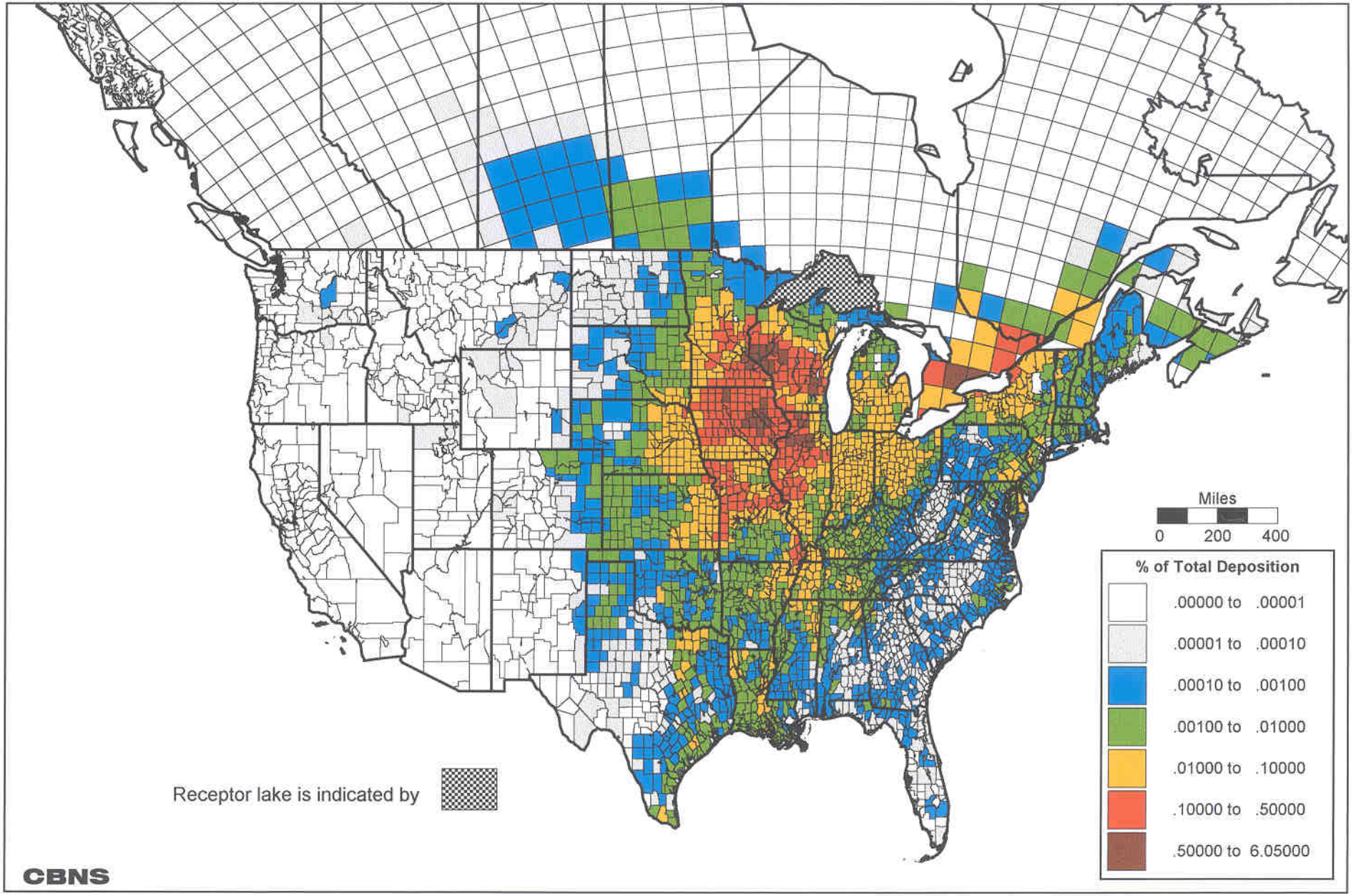
Map 5 depicts the geographic distribution of the Lake Superior source/receptor coefficients, this time based only on atrazine deposited in rainfall. The total amount deposited in the lake from rainfall is 1700 kg, in comparison with 2400 kg, the sum of atrazine deposited in rainfall and in dry conditions. The rainfall deposition comes most prominently from a smaller area than the total deposition. Rain is extremely efficient at removing atrazine from the atmosphere, so that where there is little rain, atrazine can travel further in the atmosphere. Thus, distant sources can then contribute more significantly to the deposition to the Lake. In this way, the geographical distribution of heavier source contributions for dry deposition is enlarged relative to that for wet deposition.

In **Map 6** the receptor is USGS test site MN18 at the northern boundary of Wisconsin, an area of little or no atrazine usage. The source/receptor coefficients shown here are those only for atrazine deposited in rainfall. A large part of the atrazine deposited in rainfall at MN18 originates in heavy usage areas in Iowa, Indiana, Minnesota and eastern Nebraska. The areas making the major contributions tend to be rather scattered. Areas that contribute little or no atrazine to the MN18 deposition also occur in areas of southern Wisconsin and Illinois, which nevertheless emit atrazine heavily. This phenomenon suggests that in these areas isolated rainstorms (which may be heavy in that season) have washed atrazine out of the area air, leaving little to be deposited when the air mass reached MN18.

It is also useful to visualize the source-receptor relationships in terms of distance. This is shown in Figure III-6, where the percent of the rainfall-deposited atrazine that originates from sources located in a series of concentric zones around the receptor, in this case MN18, is plotted. This plot shows that 80% of the atrazine deposited on MN18 was emitted from sources that lie in a zone 600-1,250 km from the

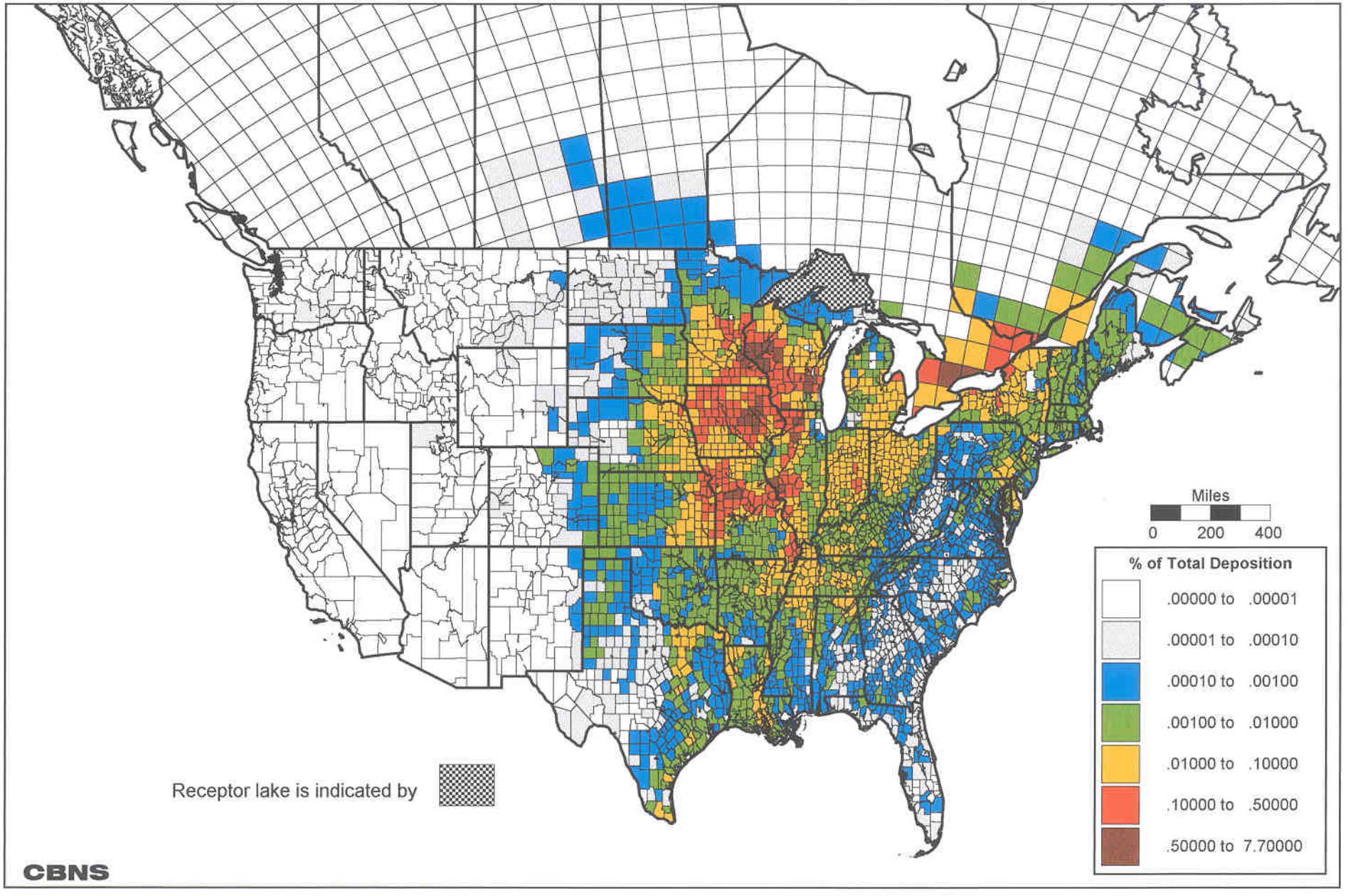
Map 4: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Lake Superior from Each Source



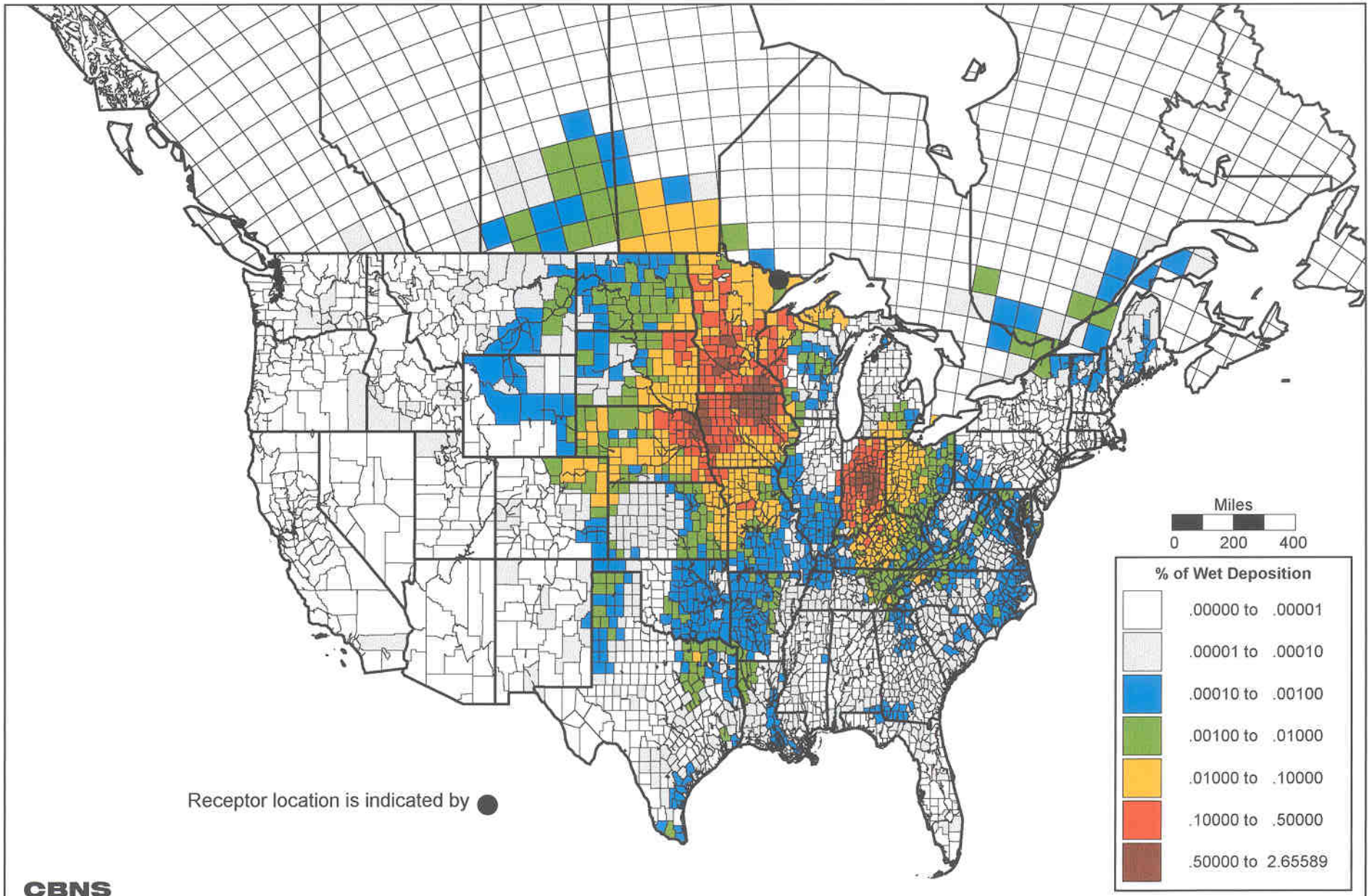
Map 5: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Lake Superior from Each Source (in rainfall only)



Map 6: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited at Receptor MN18 from Each Source (in rainfall only)



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receptor. These results coincide with the evidence in **Map 6** that most of the deposition originates in the heavy usage area in Iowa and Indiana. These observations are indicative of a generally south-to-north wind direction.

As shown in **Map 7**, the source-receptor relations for WI37 are dominated by the fact that this receptor is contained within a group of Wisconsin counties that are major contributors to the atrazine deposited at the receptor. Moderately heavy contributions arise from a large group of counties in southern Minnesota, northern Iowa and eastern Wisconsin, and lesser contributions are made by counties extending to southern Illinois. Thus, as shown in Figure III-6, significant contributions to deposition are made by sources that are 25 to 650 km distant from the receptor. The largest contribution arises from the zone only 25-50 km from the receptor, the location of the group of counties with high source/receptor coefficients surrounding the receptor. Here too the overall results are indicative of a northward wind direction.

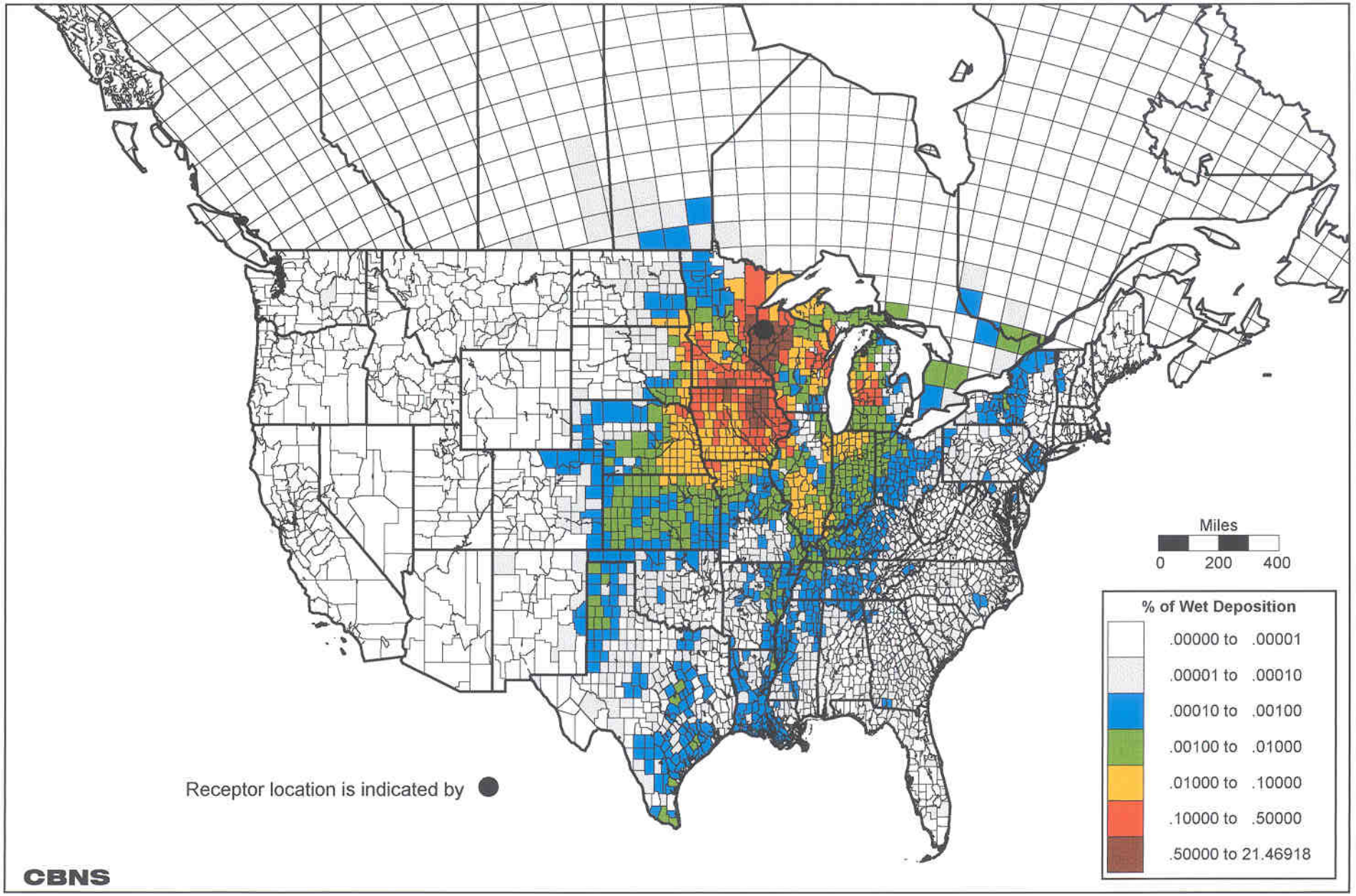
Source/receptor coefficient maps for regions other than the Midwest are shown in **Maps 8, 9**, and **10**. **Map 8** depicts the source contributions to atrazine deposited on USGS site NY20 from rainfall. This site is in northern New York about 100 miles northeast of a high-usage zone on the southern border of Lake Ontario. An additional high-usage area is in Canada west of NY20. The impact of these two high-usage areas on atrazine deposition at NY20 is evident from the map; they make the highest contribution to deposition, with the exception of central New York, New Jersey and southeast Pennsylvania, which are also high-usage areas. Another high-contribution area is in northern Ohio, which is also a high-usage area. In general, nearly all of the deposition originates in sources that are south/southwest of the receptor, within a radius of about 800 km. It is interesting to note that atrazine carried from New Jersey and southeast Pennsylvania to NY20 is likely to pass over the New York City water supply reservoirs in the Catskill Mountains, which are certain to receive part of it.

Map 9 describes the geographic distribution of the source/receptor coefficients for USGS test site SD08 in southwest South Dakota. A striking feature of this distribution is the sharp demarcation along the Mississippi River; sources east of the Mississippi contribute almost none of the atrazine deposited at this receptor. This is the natural consequence of the general west-to-east weather pattern across the country. Most of the contributing sources are directly south of SD08, with the largest amount originating in an area of Nebraska and Kansas — high-usage areas also affected by high emission coefficients — about 500 miles directly south of this receptor.

Map 10 describes the distribution of sources that deposit atrazine at test site MT07 in western Montana, which was measured by USGS to serve as a control for the sites in the Corn Belt states. Indeed, the total atrazine wet deposition flux at that site for the period from March 5-July 23, 1991, measured by USGS, was 5.9 micrograms per square meter, in comparison with a moderately high usage area, WI37, where the measured flux was 100.9 micrograms per square meter. Again, no sources in the

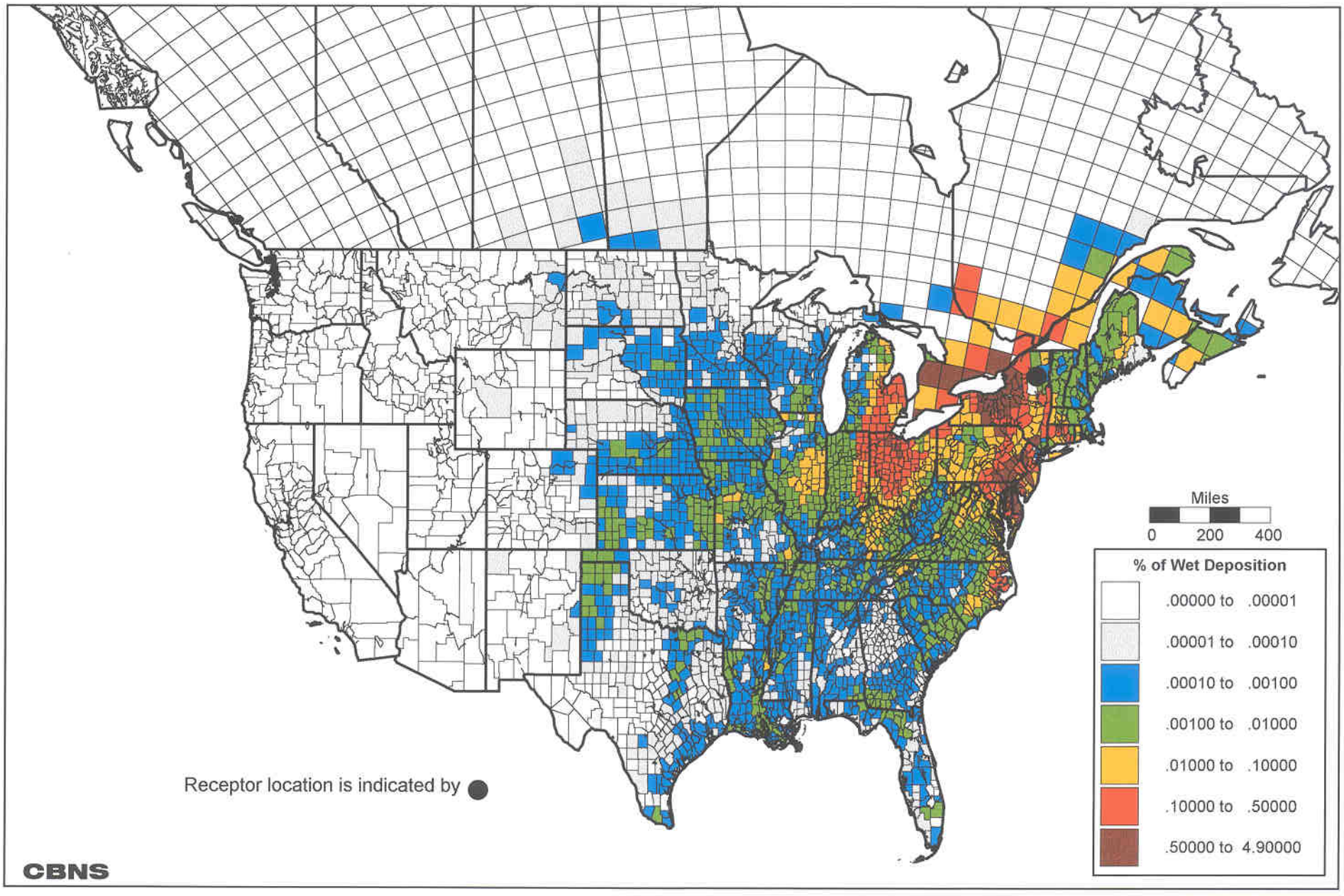
Map 7: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited at Receptor WI37 from Each Source (in rainfall only)



Map 8: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited at Receptor NY20 from Each Source (in rainfall only)



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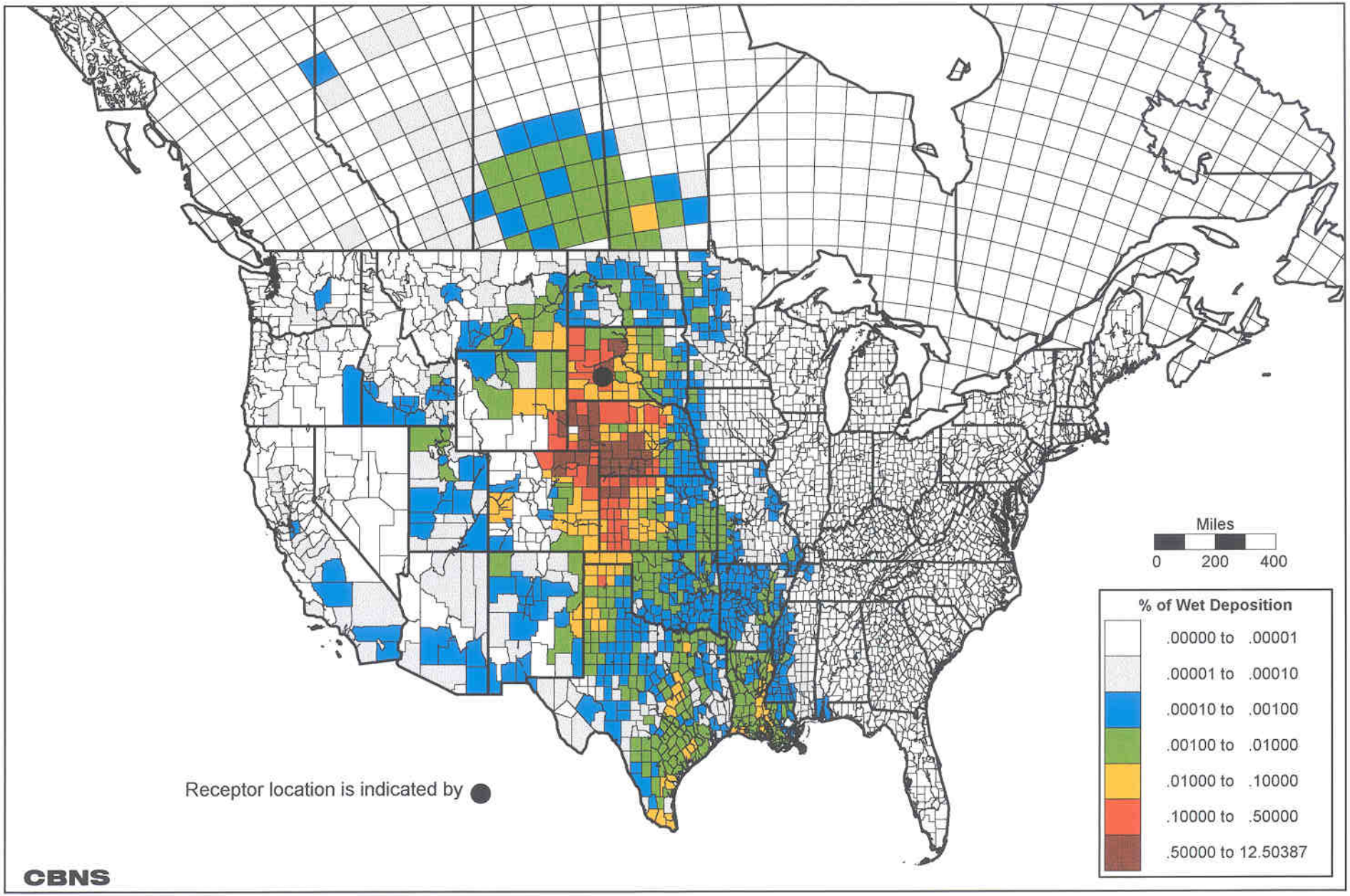
Map 9: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited at Receptor SD08 from Each Source (in rainfall only)



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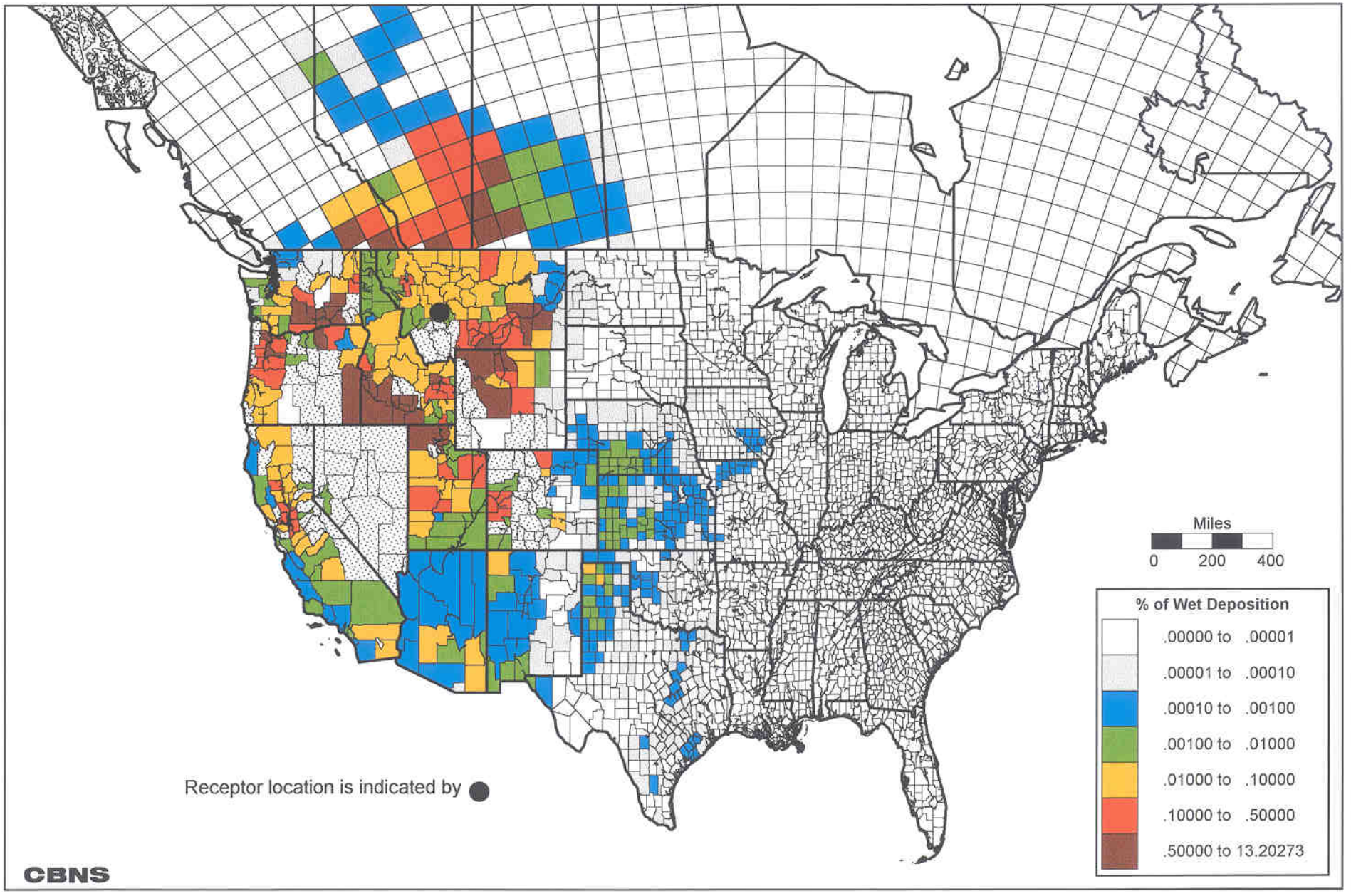
Map 10: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited at Receptor MT07 from Each Source (in rainfall only)



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eastern half of the country contribute to deposition at MT07, in keeping with the general weather pattern. The little airborne atrazine that reaches this receptor comes from scattered agricultural counties characterized by only moderate atrazine usage, generally situated to the south.

To illustrate the efficacy of the model as a means of ranking the sources responsible for the deposition of atrazine in receptors that can serve as avenues of exposure, we have computed the source/receptor coefficients for several lakes in Minnesota; two of these, Colby Lake and Moose Lake, serve as drinking water supplies for the local communities and resorts; the third, Leech Lake, is on the Leech Lake Reservation of the Chippewa Nation and is used for recreation. The Mississippi River -- close to its origin -- runs through the fourth, Lake Winnibigoshish, which lies in the Bowstring State Forest (see **Maps A-1**, **A-2** and **A-3**, Appendix).

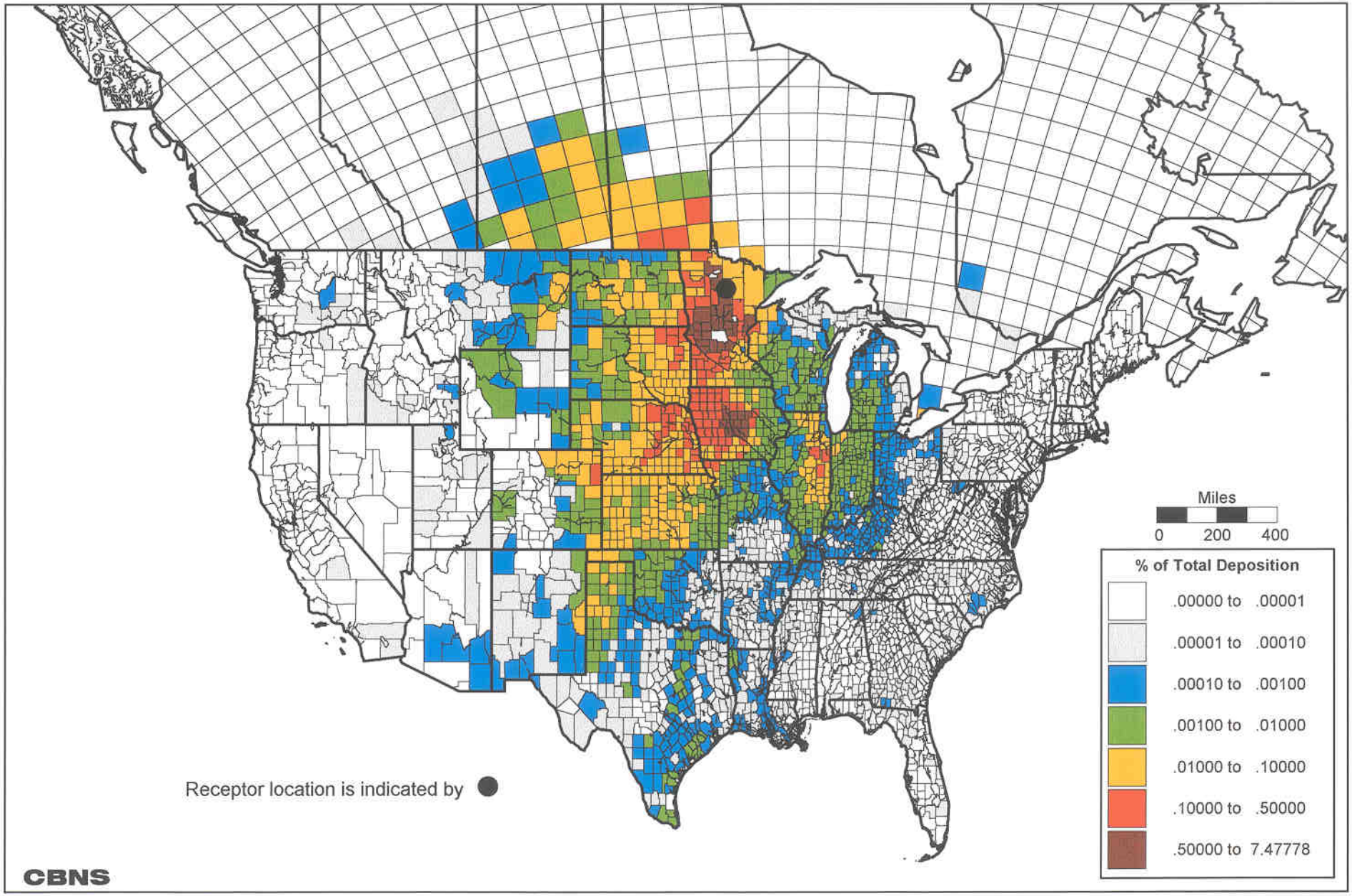
Maps 11 and 12 depict the geographic distribution of the sources responsible for the airborne atrazine deposited on two large adjacent lakes, Lake Winnibigoshish and Leech Lake. Most of the deposition is contributed by sources directly south of this receptor. Most northwest sources in Canada contribute moderately — at levels of 0.0001 to 0.1 percent per zone. The source-receptor distance plot (see Figure III-7) shows that 68.3% of the deposition originates in sources 100 to 300 km distant from Leech Lake. The agricultural area responsible for most of the airborne atrazine deposited in Lake Winnibigoshish and Leech Lake is in Minnesota, Iowa, some counties in Nebraska, and further away in a band in Illinois.

Colby Lake is in St. Louis County, the extreme northwest corner of Minnesota just south of the Canadian border and about 75 km from the eastern tip of Lake Superior. The geographic distribution of its source/receptor coefficients is shown in **Map 13**. It is useful to consider the source-receptor relations of Colby Lake in conjunction with those exhibited by Moose Lake (**Map 14**), since these receptors are within 50 miles of each other. There are important differences in the geographic distribution of the source/receptor coefficients. Moreover, Colby Lake receives a flux of 22 micrograms of atrazine per square meter, while at Moose Lake the figure is 35.9. The source-receptor distance plots (Fig. III-7) of the two lakes are similar except that the most distant sources, 1000-2500 km from the receptors, are relatively more important for Colby Lake.

In addition to drinking water, dietary sources of atrazine may include milk and vegetables. Of the latter, vegetables such as peas and snap beans that may be used in prepared baby food may be particularly important. Accordingly, it was of interest to test the feasibility of using the model to assess the exposure of farms that produce these foods to the deposition of airborne atrazine originating in distant sources. Three counties were selected for this purpose: Door and Oconto Counties in Wisconsin and Grand Traverse County in Michigan. In Door County there are about 12,500 dairy cattle and about 2000 acres planted to peas. Oconto County milks about 25,000 dairy cows.

MAP 11: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Lake Winnibigoshish from Each Source



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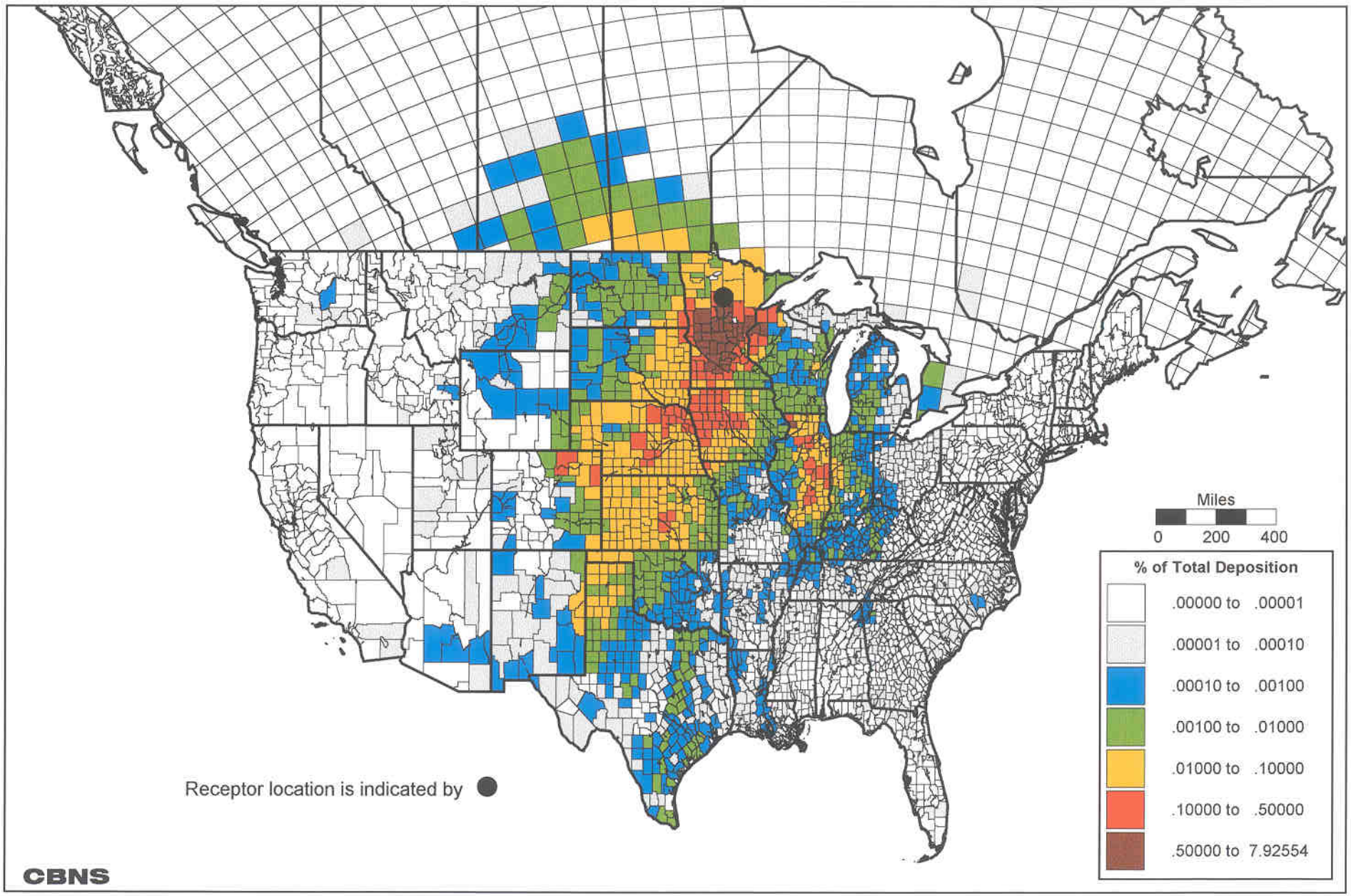
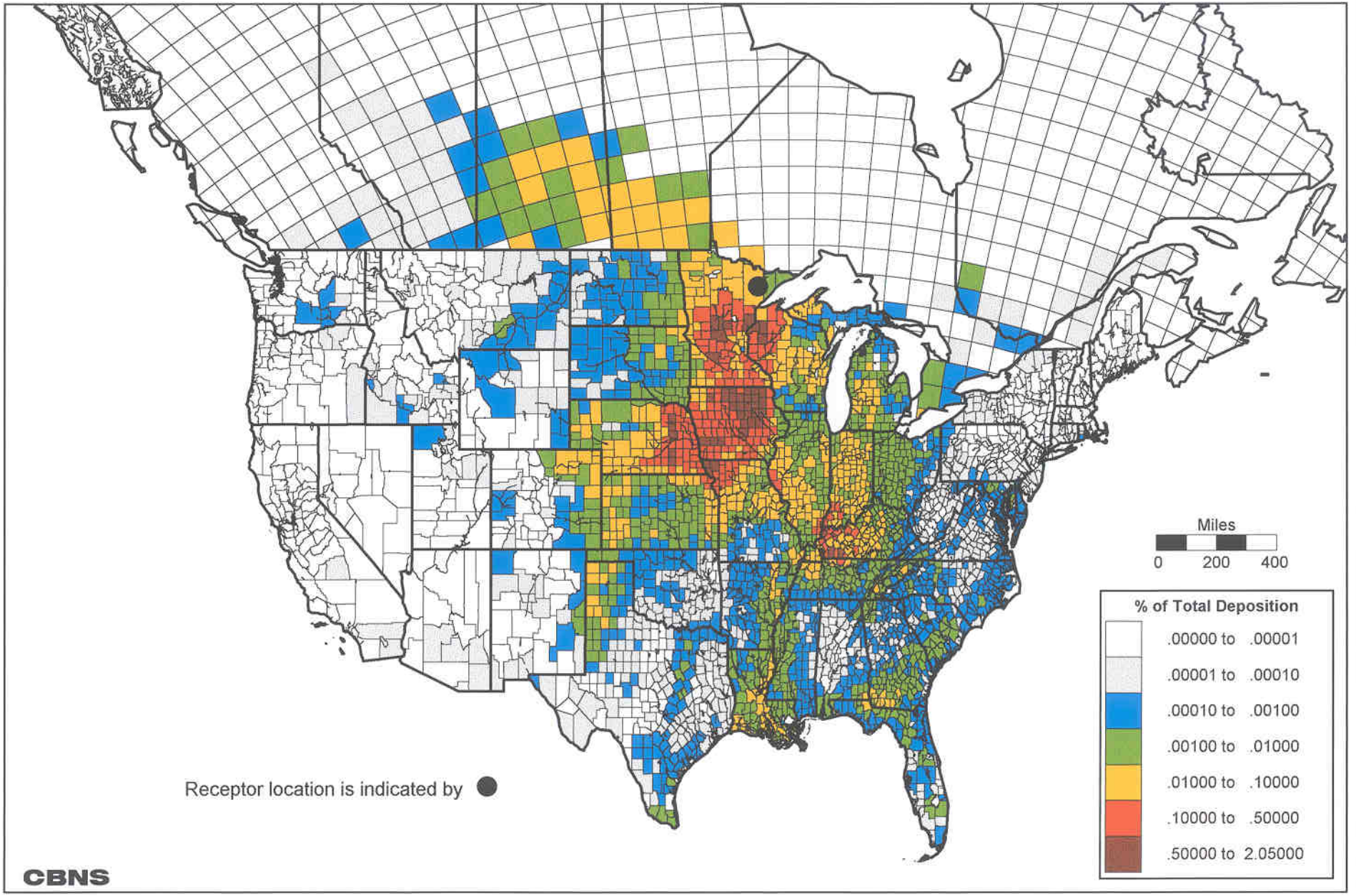
Map 12: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Leech Lake from Each Source



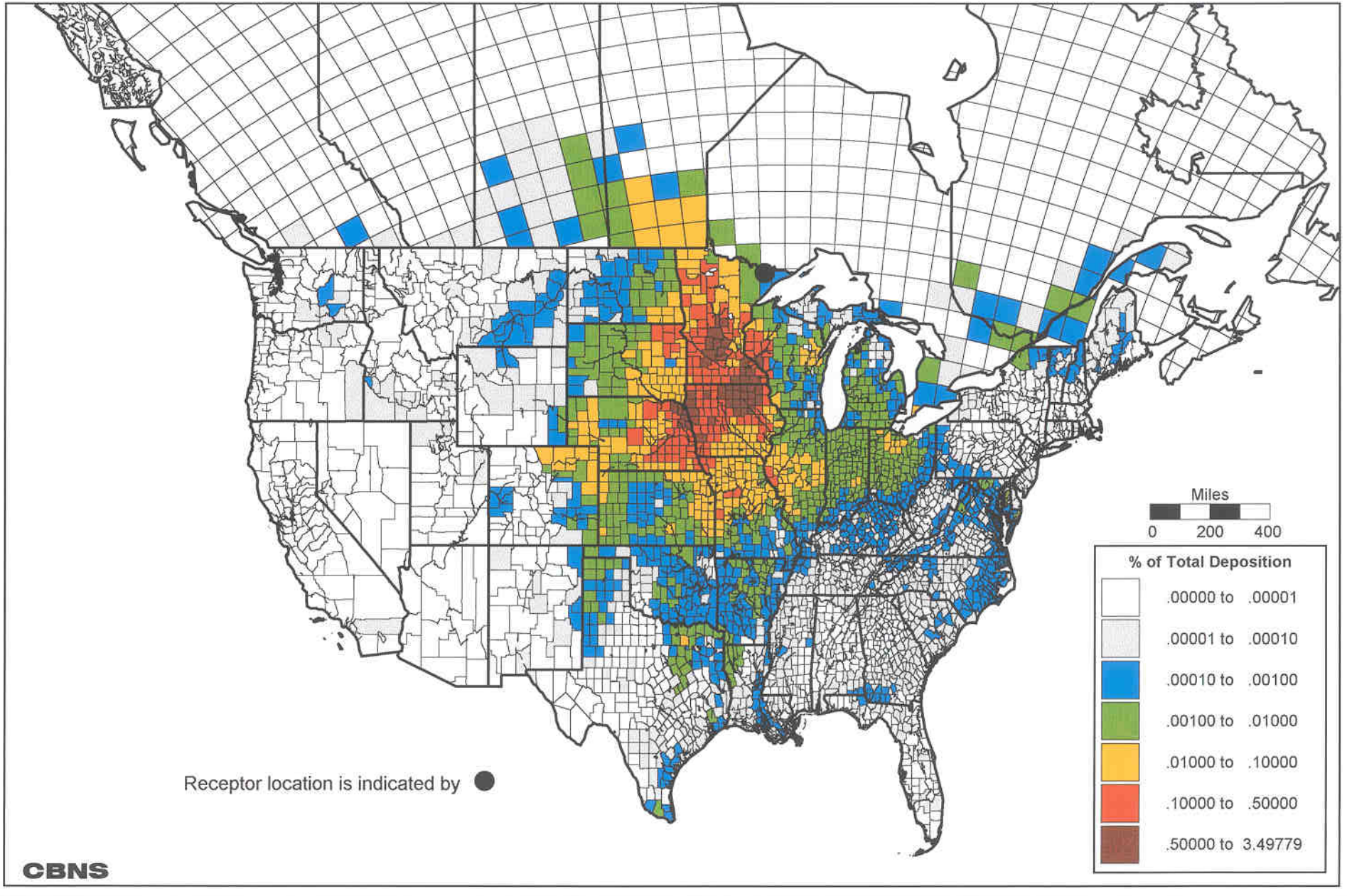
Map 13: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Colby Lake from Each Source



Map 14: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Moose Lake from Each Source



Grand Traverse County farms milk about 1500 dairy cows and has about 2000 acres in snap beans. The vegetable crops are mainly grown for processing, including possibly the production of baby food.

The model estimates the deposition of airborne atrazine to the total area of each county. The resultant geographic distribution of the source/receptor coefficients are shown in **Maps 15, 16**, and **17.** The sources that make the greatest contribution to atrazine deposition at Grand Traverse County are notably compact, while for Oconto and Door Counties, areas of highest contribution are extended further to the south. The sources that most affect atrazine deposition in Grand Traverse County are chiefly directly south of the receptor in Michigan. Oconto County's sources are heavily localized in areas in eastern Wisconsin, and northern Illinois and Michigan that surround Lake Michigan (**Map 16**). The bulk of the atrazine deposited on Door County (**Map 17**) originates in the heavy usage area in Illinois, Indiana, southeastern Wisconsin and Michigan.

IV. DISCUSSION

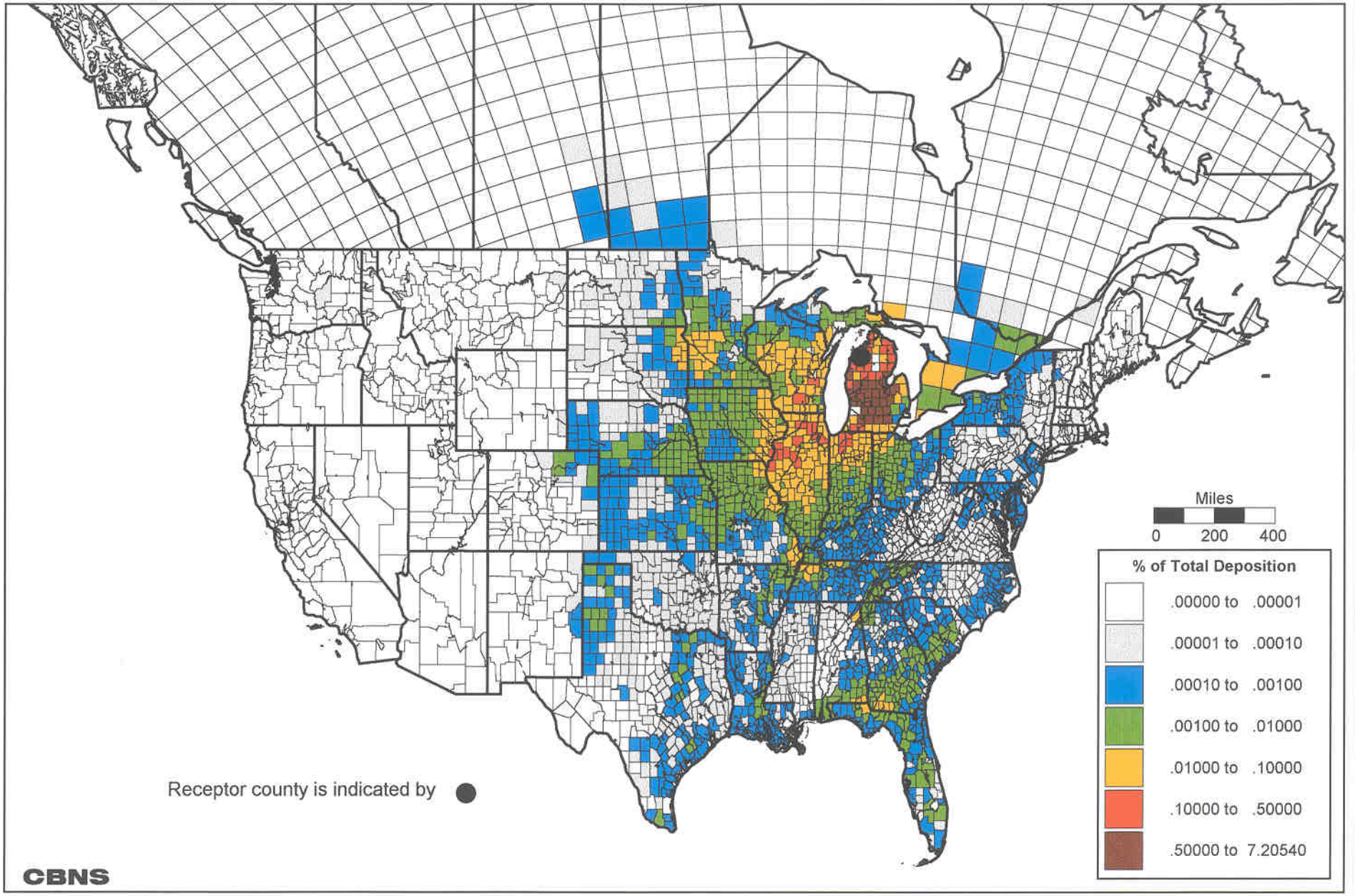
This project was designed to develop and assess the usefulness of a computer model to trace the atmospheric transport of a typical endocrine disrupter: atrazine, a heavily used herbicide that acts as an endocrine disrupter. In comparison with existing air transport models, this was an inherently complex task. The sources of airborne atrazine are, in effect, every acre of corn, sorghum or sugar cane that is treated with this weed killer. Their rates of emission will vary not only with the amount of atrazine applied, but will also reflect the method of application, the local soil structure, and the temperature, wind speed and precipitation shortly after application. All of these factors may vary considerably from region to region, county to county, and even farm to farm.

Consequently, as noted earlier, certain approximations and assumptions were needed to reduce the source variables to practical dimensions. In particular, it was necessary to define the sources in the United States as counties and as even larger areas in Canada, and to assume a certain uniformity of the method and timing of atrazine application by state and agricultural region. Thus, in contrast with, let us say, a source of dioxin such as an incinerator, the rates of emission of the atrazine sources depend on the inherently variable weather rather than the relatively fixed operational characteristics of the incinerator. Moreover, unlike the incinerator, the emissions of which are generally constant with time, the rate of atrazine emission from a given point of application will decline to very small levels four weeks after application. For that reason, it was necessary to estimate emissions and atrazine deposition at the receptor over successive one-week periods — rather than annually.

These circumstances will, of course, affect the characteristics of the model. The accuracy with which it can predict an actually measured value of deposition at the

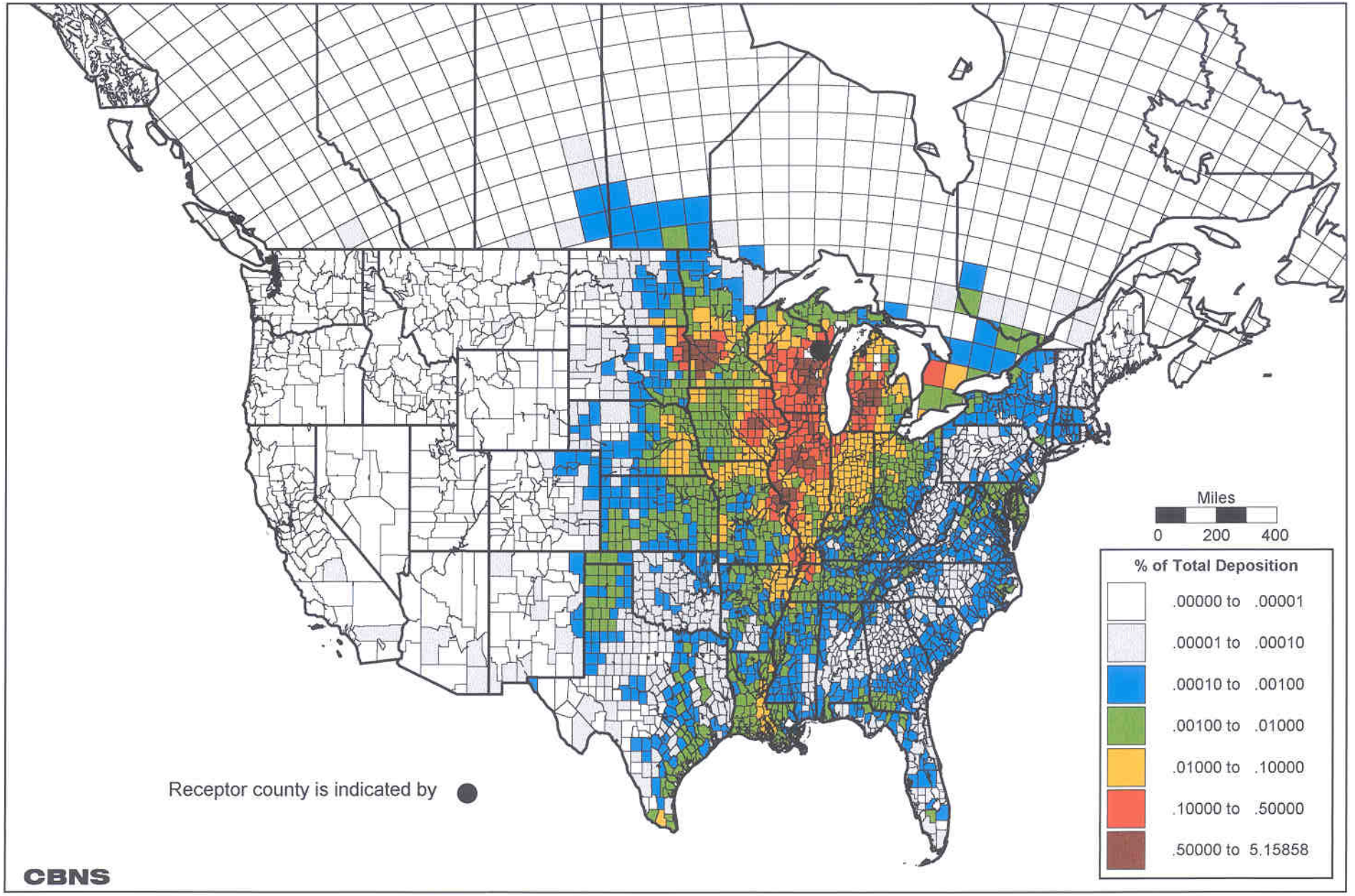
Map 15: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Grand Traverse County from Each Source



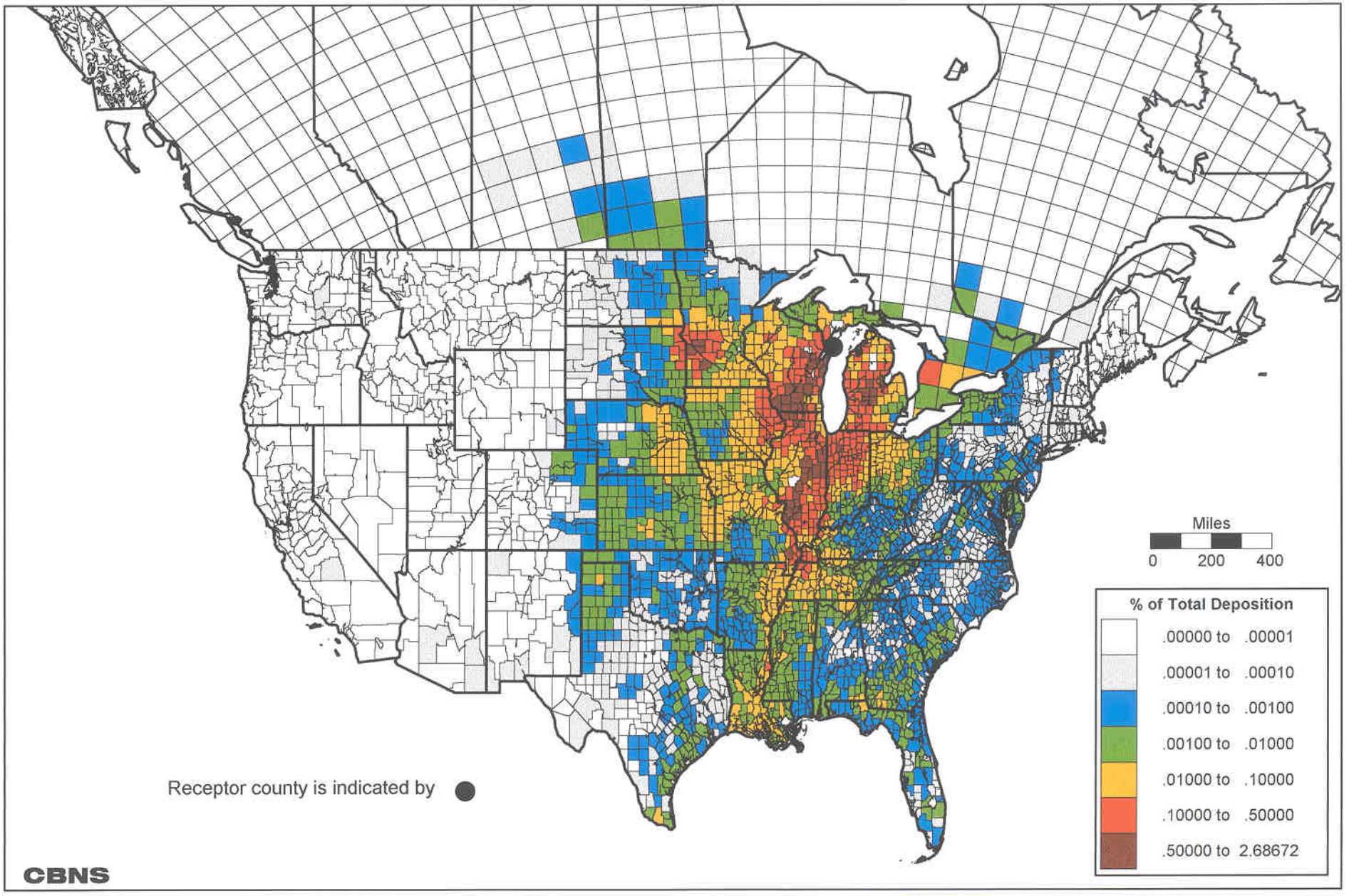
Map 16: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Oconto County from Each Source



Map 17: GEOGRAPHIC DISTRIBUTION OF SOURCE CONTRIBUTIONS TO ATRAZINE DEPOSITION

% of Atrazine Deposited onto Door County from Each Source



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receptor will reflect the sum of these effects. The model's robustness — that is, the degree to which source/receptor coefficient maps of very close receptors resemble each other — will reflect the validity of the assumed uniformity of the source units (counties). Finally, the model's spatial resolving power — that is, its ability to distinguish between the deposition at two receptors that are, in fact, subject to different weather patterns — will depend on the degree to which the model's weather data represent the actual conditions at the two sites.

In evaluating the model, we found that it is able to satisfactorily predict the amounts of airborne atrazine actually deposited in rainfall at a series of 20 USGS test sites. Accordingly, we believe that, in practice, the model can provide useful source/receptor coefficients for receptors, such as surface water supplies, that mediate environmental exposure to atrazine.

The atrazine air transport model can be regarded as reasonably robust if it yields reproducible results from very similar, but not identical, input data. An example of such evidence is provided by **Maps 11** and **12** for Lakes Winnibigoshish and Leech respectively, which are only five miles apart and therefore subject to very similar weather conditions. There are only minor differences in the two maps. They exhibit the same general pattern: the concentration of active counties in central Minnesota and Iowa.

Map 13, which describes the geographic distribution of the source contributions to the atrazine deposited on Colby Lake, provides evidence of the model's spatial resolution. This receptor is located about 100 miles east of Winnibigoshish and Leech, and its source pattern is different from theirs. The Colby map shows heavy atrazine contribution some 800 miles to the southeast in southern Illinois and Kentucky and significant atrazine contribution from the southeastern states. It would appear from these contrasting results that the model is capable of resolving differences in the weather pattern over a distance of about 100 miles.

Given their proximity to the Corn Belt, there has been considerable interest in the occurrence of herbicides, including atrazine, in the Great Lakes. Several recent studies provide important evidence about the processes that influence the atrazine content of the Lakes. The amounts deposited from the air are related to the lakes' areas and to their nearness to regions of heavy atrazine usage. As **Map 1** shows, Lake Superior is several hundred miles away from heavy usage areas, so that it receives very little atrazine in runoff from corn fields. A recent study (Goolsby *et al.*, 1997) estimates that 94% of the atrazine in Lake Superior is deposited from the air. In contrast, they found only 23% of the atrazine entering Lake Michigan is deposited from the air; the rest is runoff and drainage from the nearby heavy usage areas.

Schottler and Eisenreich (1997) have found that atrazine is accumulating in the Great Lakes. For example, they estimate the total amount of atrazine in Lake Superior

in 1991 at 36,000 kg; yet we estimate that only 2,404 kg of atrazine was deposited in Lake Superior in that year. Thus, the lake has apparently accumulated this atrazine inventory over at least the last 15 years. (U.S. atrazine usage increased rapidly to its current level of 70 million pounds per year between 1966 and 1976.) Atrazine accumulates in Lake Superior for two reasons: once in the water, as shown by Schottler and Eisenreich (1997) about 0.5% of the lake's volume is replaced annually (the "flushing rate").

It is of interest to consider our results on the deposition of airborne atrazine on small lakes in Minnesota in relation to the recent data on the Great Lakes. As shown in Table IV-1, the model estimated that the amounts deposited on Leech Lake and Winnibigoshish Lake were 48.2 kilograms and 13.5 kilograms respectively. The atrazine concentrations in Leech and Winnibigoshish were measured by the U.S. Geological Survey (1993) at intervals in 1992 and 1993; in both lakes concentrations were detected at 0.05-0.06 micrograms per liter. (No measurements were made in 1991.) Assuming that the airborne atrazine deposited on these lakes that we estimated for 1991 was about the same in 1991 and 1992, we can compare these results with values based on our fallout estimates. According to the USGS. measurements, the total amount of atrazine in Lake Winnibigoshish was equal to 0.05-0.06 micrograms per liter multiplied by the volume of the lake (1.29 trillion liters), which amounts to 65-78 kilograms of atrazine. Since the model estimated that 14 kilograms of atrazine entered Lake Winnibigoshish from the air in 1991, this may indicate that the lake has been accumulating atrazine, but that the accumulation has been counterbalanced by a significant flushing rate — much higher than the 0.5% rate characteristic of Lake Superior. An alternative explanation is that, because of rapid flushing, atrazine does not accumulate, so that annually about one-fifth of the atrazine enters from the air, with the rest derived from drainage and leaching. A similar calculation shows that, based on the measured concentration, Leech Lake contained about 100-120 kilograms of atrazine, twice the model's estimate of the airborne fallout in 1991: 48.2 kilograms. This may suggest that some atrazine accumulation had occurred that was balanced by a relatively high flushing rate or, alternatively, that fallout accounted for nearly half of the atrazine entering the lake in 1991, with the rest due to drainage from cornfields in the region.

From these observations it would appear that these lakes in northern Minnesota, where local atrazine usage is between one thousandth to one hundredth of the amounts used in many Corn Belt counties, are nevertheless vulnerable to atrazine pollution. The area is particularly susceptible to airborne atrazine because it is downwind of the high usage areas and — as can be seen in **Map A-1** (Appendix) — heavily covered with surface water, a medium in which atrazine tends to survive. The USGS measurements indicate that atrazine may occur in surface waters at a concentration that is 30-40% of the "acceptable" 0.15 parts per billion standard. Higher concentrations may occur where the flushing rate is low and atrazine accumulates — for example, in abandoned mine pits used as drinking water reservoirs. Closer to the Corn Belt, where moderate amounts of atrazine are used, the airborne fallout added to

the atrazine drained into water supplies from treated fields may be sufficient to raise concentrations above the standard.

A main purpose of the CBNS study was to help define the implications of airborne toxic pollution for remedial policy. Effective environmental policy prevents the production of the pollutant at the source, leading to zero emissions. The first task, then, is to identify the sources chiefly responsible for the receptor's exposure, for that is where preventive action must be directed. In this case, the people who drink water from a lake in Minnesota need to know which, among the thousands of U.S. counties and Canadian zones, are chiefly responsible for the airborne atrazine that falls in the lake. The atrazine air transport model provides an answer by ranking the numerous sources with respect to their contribution to the total amount of atrazine deposited on the lake. Thus, the rankings shown in **Maps 11 and 12** indicate that remedial action taken only by the states of Iowa and Minnesota would go a long way toward reducing the impact of airborne atrazine in Winnibigoshish and Leech Lakes. Minnesota and Iowa share a common boundary and could conceivably negotiate over the issue. Lake Winnibigoshish, Leech Lake and Moose Lake are resort areas popular among Iowans, and some of them might help this process when they discover they have been fishing in lakes contaminated with atrazine from their own farms. Nevertheless, there are formidable obstacles to such a course, which are particularly evident in the case of Colby Lake. Here interstate negotiations would engage Minnesota with not only Iowa, but Nebraska, Illinois, Indiana and Kentucky as well. It would appear that only a national policy that prevents the heavy agricultural use of atrazine could eliminate the widely disseminated hazard of airborne atrazine — and the more imminent hazard within the Corn Belt as well.

In sum, the results of this project support the conclusion that the massive amounts of atrazine used in agricultural operations generate emissions that can be carried hundreds of miles in the air and contribute to the exposure of human populations and wildlife far removed from the point of application. This result adds to the size and diversity of the populations that may be affected by exposure to atrazine. It broadens the scope of the necessary public discourse.

The project, we believe, has to a considerable degree accomplished the tasks it was designed to do: It has developed a model capable of tracking the atrazine emitted by numerous agricultural sources to receptors that serve as a route of human exposure. By ranking the sources with respect to their contribution to the amount of airborne atrazine deposited on the receptors, the model thereby facilitates preventive action at these sources. We recognize that, like any new model, the atrazine air transport model is still a work in progress, subject to further improvement as we gain more experience in using it. Finally, the project's results create opportunities for applying the model to receptors that play a critical role in mediating the exposure of human populations and wildlife not only to atrazine, but — with further model development — to other endocrine-disrupting herbicides as well.

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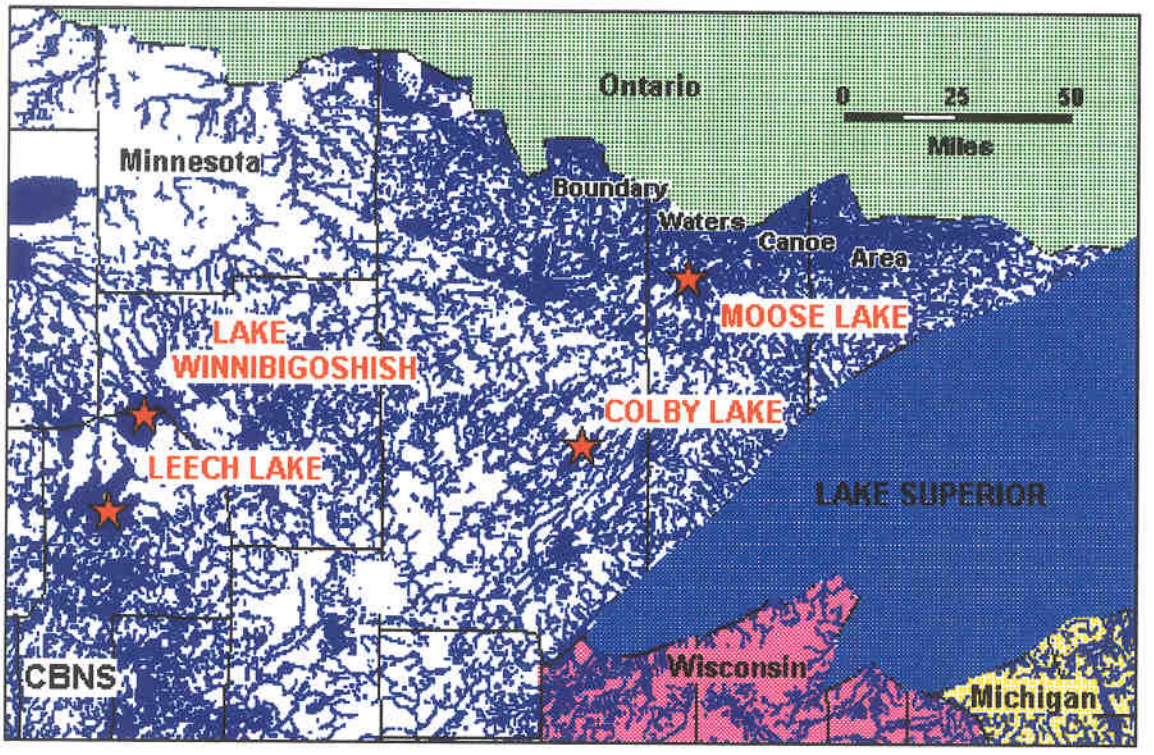
Table A1: Atrazine: Period of Application 1991

Data Source Crop Region	Quantity Applied ,000 Kgs*	Period of Application		
		Pre-Planting	Pre-Emergent**	Post-Emergent
Ortech Allocation Corn & Sorghum '89-90				
U.S. & Canada		40	45	5
USDA 1991 Survey				
Field Corn				
Georgia	224	19	9	72
Illinois	4,687	51	7	42
Indiana	2,891	39	29	33
Iowa	3,175	41	5	54
Kansas	686	43	15	41
Kentucky	906	59	26	15
Michigan	1,121	20	23	57
Minnesota	760	5	11	84
Missouri	1,200	41	18	41
Nebraska	2,606	34	38	28
North Carolina	459	21	22	58
Ohio	1,875	21	19	61
Pennsylvania	603	8	11	81
South Carolina	116	9	37	54
South Dakota	226	18	3	80
Texas	415	45	28	27
Wisconsin	911	11	2	87
17 Major States	22,862	36	17	47
Sorghum				
Kansas	1,198	45	14	40
Nebraska	506	38	40	21
Texas	634	19	24	56
3 Major States	2,338	37	23	41
Novartis Canada (3)				
Corn				
Canada	1,165***	-	20****	80****

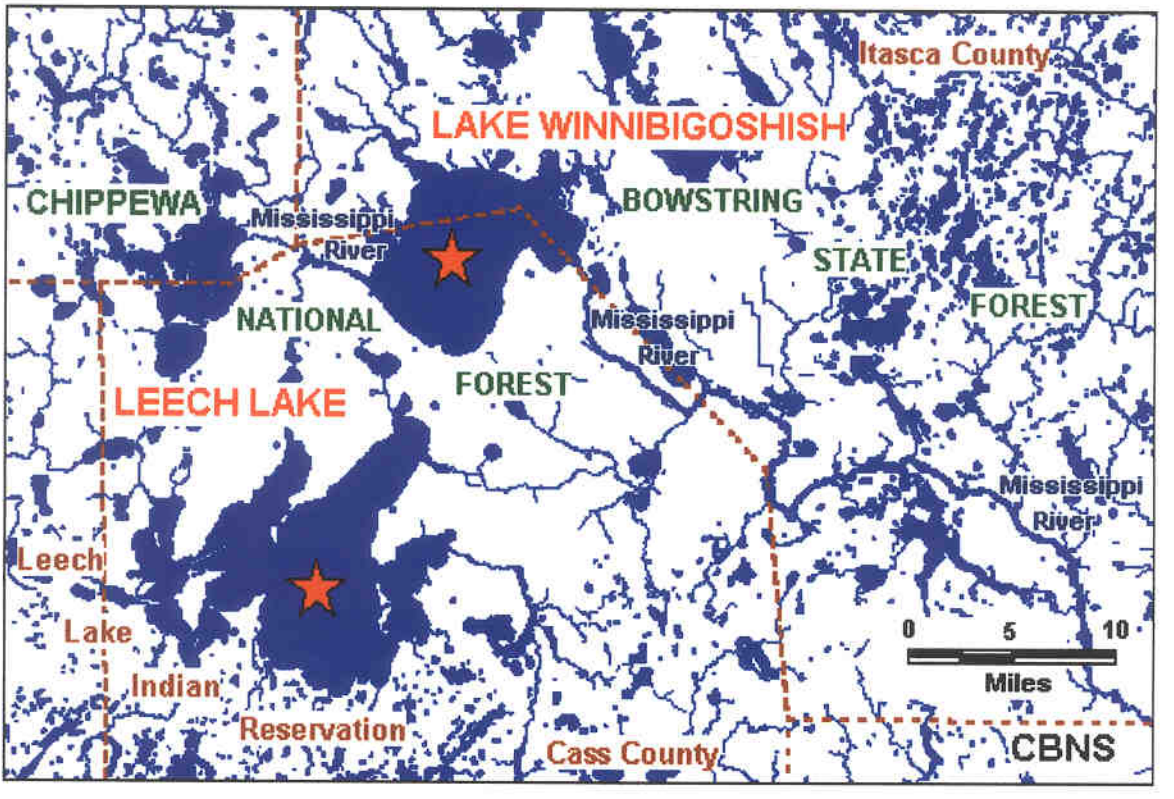
Sources: 1) *Pesticide Emissions Modelling* (1997), Trevor Scholtz, et al., Ortech Corporation, Mississauga, Ontario, page 67. Citing *Qualititative Use Assessment of Atrazine*, 1988, Szuhay, D., USEPA and Ortech estimations from other sources.
2) Calculated from the "1991 Cropping Practices Survey," Unpublished Data file, ERS and NASS, USDA.
3) Marketing survey data. Correspondence, August-September 1997, Judy Shaw, Novarti,sMississauga, Ontario.

Notes:
* Atrazine use totals are unadjusted for missing values in the USDA survey sample file.
** Pre-Emergent at time of planting
*** Novartis estimate of 1991 usage and CBNS estimate of % applied to corn.
**** Novartis estimate of 1997 allocation. There has been a shift towards more post-emergent since 1991, but they don't think there has ever been much pre-plant application.

Map A-1: Minnesota Lakes



Map A-2: Lake Winnibigoshish and Leech Lake



Map A-3: Colby Lake