

Annual Pollution Report

Minnesota Pollution Control Agency
April 2003

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Foreword

The Annual Pollution Report statute requires the Minnesota Pollution Control Agency (MPCA) to estimate to the best of its ability the total amounts of air and water pollution emitted in the state during the most recent calendar year for which data are available. The statute further directs the MPCA to estimate the percentage increase or decrease over the previous calendar year, and to estimate the relative contributions of the various sources of these emissions and discharges to the environment.

The MPCA has prepared this report since 1996. It has evolved to include new kinds of information, such as discharges of toxic air pollutants, greenhouse gas emissions, and emerging contaminants of concern as these kinds of data have become available. The following observations of some strengths and shortcomings of the current reporting process are presented for interested parties to help determine if and how the report should be changed.

Strengths

- The Annual Pollution Report is the only MPCA report that specifically asks for an accounting of emissions and discharges. Such inventories are inherently important, as understanding emission amounts and sources is fundamental in protecting the environment and human health.
- The report attempts to track trends year to year, which is valuable if data are reliable.
- The report covers both air and water pollutants in one document, instead of separate reports, reminding readers of the potential for cross-media impacts.
- The report shows relative contributions of various pollution sources to the total.

Minn. Statutes 116.011 Annual pollution report.

A goal of the pollution control agency is to reduce the amount of pollution that is emitted in the state. By April 1 of each year, the pollution control agency shall report the best estimate of the agency of the total volume of water and air pollution that was emitted in the state in the previous calendar year for which data are available. The agency shall report its findings for both water and air pollution:

(1) in gross amounts, including the percentage increase or decrease over the previous calendar year; and

(2) in a manner which will demonstrate the magnitude of the various sources of water and air pollution.

HIST: 1995 c 247 art 1 s 36; 2001 c 187 s 3

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Shortcomings

- Aggregating data into total volumes lacks the important context of relative risk. Pollutants emitted in smaller volumes can have a greater impact than some emitted in tremendously larger volumes. The volume figures also do not convey whether such emissions and discharges are acceptable or unacceptable.
- The most current pollutant emissions and discharge data is usually at least two years behind real time, sometimes more depending on the type of pollutants. Air emission estimates are frequently revised by the EPA as industrial output models and factors used to estimate emissions are refined to better reflect economic activity. The April 1 annual deadline, which the MPCA suggested for the 2001 amendments, turns out to be problematic with respect to getting EPA air pollutant emission figures needed for the report.

Shortcomings, cont.

- Year-to-year comparisons are not always reliable, as air and water databases are “moving targets,” updated periodically with information that becomes available long after the calendar year in which the pollutants were discharged.
- There is currently no reliable way to quantify the volumes of water pollutants released by nonpoint sources in the form of polluted runoff, such as city streets, construction sites and farm fields. This is a major gap in inventorying pollutants discharged, for a category highly culpable for water quality impairments.

The examples noted above are presented to help the reader get a sense for the dilemmas the MPCA faces in attempting to deliver accurate, timely and useful information about what is discharged into Minnesota’s air and water. The MPCA welcomes suggestions for upgrading the current reporting process to better meet its intended purposes envisioned in the statute.

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Introduction and Summary

The Minnesota Pollution Control Agency (MPCA) is required by Minnesota Statutes, Chapter 116.011 to submit to the Legislature an annual report of the volume of pollution emitted or discharged to the state's air and water resources. In addition to gross amounts, the MPCA must report the annual percentage increase or decrease of pollutants for the most recent year for which data are available. The report must also demonstrate the magnitude of the various sources of air and water pollution. The basis of the MPCA's 2003 Annual Pollution Report is the U. S. Environmental Protection Agency's (EPA) Air Emissions Inventory for 2000, the 1999 Minnesota Air Toxics Emissions Inventory and the 2001 Water Quality National Pollutant Discharge Elimination System (NPDES) Discharge Monitoring Reports, which are part of the EPA's Permit Compliance System.

Annual emissions and discharge estimates are one important component of tracking progress on air and water pollution, and for tracking performance and relative contributions of pollution sources. The MPCA also regularly prepares reports on the physical, chemical and biological conditions measured in the environment, and on pollutants of special concern to human health and the environment. These reports and others are available on the Internet and are referenced throughout this document for readers who would like additional context and information.

The MPCA is continually seeking to improve its reporting of environmental data and information, and welcomes comments and suggestions from readers for future reports of this nature.

Air Emissions

The EPA estimates annual emissions of major air pollutants for every state in order to assess historic trends. The major air pollutants summarized in this report include carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO₂), volatile organic compounds (VOCs), particulate matter (PM₁₀ and PM_{2.5}) and ammonia (NH₃). The most recent emissions data for the major air pollutants is from 2000.

Global climate change is a continuing concern worldwide. Therefore, Minnesota emissions of the principal greenhouse gas, carbon dioxide (CO₂), are included again for 2001. The statewide emissions were calculated using a variety of fuel use data sources.

The Minnesota Air Toxics Emission Inventory estimates emissions of air toxics including compounds such as benzene, formaldehyde and mercury. There may be some overlap between the Minnesota Air Toxics Emission Inventory and the EPA emission estimates for VOCs because many air toxics are also VOCs. Air toxics emission inventories are not generated for every year. The most recent complete inventory of air toxic emissions is from 1999.

Table 1 lists the total statewide emissions of the major air pollutants from 1996 to 2000. The percent change from 1999 to 2000 is given in the final column. It is possible to look at emission trends between these years. However, it is important not to place undue emphasis on a yearly change. Trends should be viewed over several years of data. In addition, emission estimates fluctuate as a result of changes and improvements in the inventory.

An increase may result because new sources were added to the inventory, rather than as a result of actual increased emissions in Minnesota. The EPA releases a complete inventory every three years (e.g., 1996 and 1999). Therefore, the 2000 emissions reported are projected numbers based on available 1999 information, economic growth activity and historical trends.

**Table 1: Minnesota Air Pollution Emissions Estimates, 1996-2000
(thousand short tons)**

Pollutant	1996	1997	1998	1999	2000	1999 to 2000 % Change
Carbon monoxide (CO)	1,794	1,790	1,851	1,828	2,105	+15.0%
Sulfur dioxide (SO ₂)	157	164	159	165	190	+15.0%
Oxides of nitrogen (NO _x)	490	510	499	488	533	+9.2%
Volatile organic compounds (VOCs)	441	439	410	395	458	+16.0%
Particulate matter (PM ₁₀)	828	850	940	847	894	+5.5%
Particulate matter (PM _{2.5})	191	193	206	191	211	+10.0%
Ammonia (NH ₃)	188	192	195	199	196	-1.5%
Total*	3,898	3,945	4,054	3,922	4,376	+12.0%

*PM_{2.5} is already included in PM₁₀ and so is not included in the total. PM_{2.5} emissions represent only primary formation; secondary formation, which is the major contributor, is not included.

There may be differences in the total emission figures for a given year discussed in this report versus previous emission reports the MPCA has published. This is because the data are continually being updated in the EPA's air emissions inventory. In addition, it should be noted that despite the importance of the secondary formation of fine particulates, estimated air emissions data in this report are only based on direct releases from sources into the atmosphere. Secondary formation occurs when emissions of volatile gases, including SO₂, NO_x and VOCs, combine and form fine particulates. These particles are not directly emitted but are formed downwind of the emission source.

All of the pollutants except ammonia showed an increase from 1999 to 2000. Ammonia essentially remained constant. Overall, all of the pollutants have increased slightly from 1996 levels, with some fluctuation up and down through the years.

The total emissions of CO₂ in 2000 were 109 million short tons. This represents a 5.6 percent increase from 1999. The 1999 emissions of air toxics are given in the body of the report.

Water Discharges

Owners or operators of any wastewater disposal system, identified as a point source, are required by Minnesota Statutes, Chapter 115.03(7), through their NPDES permit, to maintain records and make reports of required monitoring for discharges to waters of the state. These self-monitoring reports submitted to MPCA are commonly referred to as Discharge Monitoring Reports (DMRs). These data, (maintained by MPCA data specialists), are used to generate Effluent Discharge Mass Loading Reports from EPA's Permit Compliance System, and are the basis for the point source discharge summary (Table 2) for the last five years for which data are available. These figures represent the combined loading from 58 municipal and 27 industrial discharges (85 major facilities each discharging more than one million gallons per day to waters of the state). These major facilities represent approximately 85% of the total volume of discharge to waters of the state from point sources. The remaining 15% comes from many smaller municipal and industrial facilities. Although discharges from these facilities are small, they can have significant impacts on individual lake and stream segments.

**Table 2: Minnesota Water Pollution Discharge Estimates
from Major Point Sources 1997-2001 (thousand kilograms)**

Pollutant	1997	1998	1999	2000	2001	2000 to 2001 % Change
Total suspended solids	10,076	8,000	6,069	5,119	8,552	+40.1%
Carbonaceous biological oxygen demand (CBOD) and Biological oxygen demand (BOD)	6,743	5,397	4,264	3,471	4,920	+29.5%
Phosphorus	1,171	1,652	1,405	1,441	1,374	-4.6%
Ammonia (NH ₃)	1,709	1,415	1,219	1,283	1,023	-20.2%
Nitrate (NO ₃)	4,123	4,703	4,701	4,684	4,276	-8.7%
Total	23,822	21,167	17,658	15,998	20,145	+20.6%

In 2001, major point source discharges of total suspended solids and biological oxygen demand showed significant increases, a departure from the steady downward trend shown by these parameters for the period 1996-2000 (see the April 2002 Annual Pollution Report—2000 Air Emissions and Water Discharges at http://www.pca.state.mn.us/hot/legislative_reports/2002/airwater.pdf. Statewide, total suspended solids increased by about 40 percent, while biological oxygen demand was up by nearly 30 percent in 2001.

Much of this increase was possibly due to rapid snowmelt, heavy spring rains and high runoff rates especially in the southern half of the state. Increased flows may have reduced treatment plant performance by decreasing residence time. For example, the Mississippi River at St. Paul crested at 23.4 feet on April 19, 2001, a level not exceeded since March 1969. The river was above flood stage for 33 straight days during the spring of 2001. The total suspended solids load from the Metropolitan Council's Metropolitan Wastewater Treatment Plant went from 1,490 thousand kilograms in 2000 to 3,892 thousand kilograms in 2001. (It is important to note that despite the increased flows and loadings the facility was in compliance with its permit limitations). That increase alone of 2,402 thousand kilograms accounts for much of the statewide increase in total suspended solids observed in 2001.

Statewide, a total of 16 of the 85 major treatment facilities more than doubled their discharge of total suspended solids to waters of the state in 2001 compared to 2000. A similar trend was noted for biological oxygen demand, also a possible reflection of high flows and decreased residence time.

Interestingly, phosphorus and ammonia discharges were down in 2001, reversing the slight upward trend for both parameters noted in 1999 and 2000. Treatment advances combined with continued progress in removal of phosphorus from the waste stream likely contributed to these declines. Dilution caused by high flows may also have been partly responsible for the declines. Nitrate discharges showed an 8.7 percent decline in 2001, continuing a trend begun in 1998. Statewide, nitrate discharges have declined 9.1 percent since 1998, from 4,703 thousand kilograms down to 4,276 kilograms in 2001. This is encouraging, since nitrate is a major contributor to the problem of hypoxia in the Gulf of Mexico.

However, point source contributions of nitrate and phosphorus to waters of the state are still small compared to nonpoint contributions of these pollutants from sources such as agricultural and urban runoff. Point sources tend to have greatest impact during periods of low precipitation and stream flow, while nonpoint sources are most significant during periods of high precipitation and stream flow, both of

which were a factor during the spring of 2001. Unfortunately, we are limited in our ability to measure the effects of nonpoint pollution on Minnesota's lakes, rivers and ground water. Although MPCA is investigating better ways to do this, nonpoint source monitoring is expensive and often requires a more complex, labor-intensive (and therefore more costly) monitoring network than measuring volume and quality of discharge from pipes.

Chapter 1: Air Pollutant Emissions Overview

Thousands of chemicals are emitted into the air. Many of these are air pollutants that can directly or indirectly affect human health, reduce visibility, cause property damage and harm the environment. For this reason, the EPA and the MPCA attempt to reduce the amount of air pollutants released into the air. In order to understand how much pollution is released and to track the success of reduction strategies, these agencies estimate the emissions of certain air pollutants released in Minnesota.

Criteria Pollutants

The 1970 Clean Air Act identified six major air pollutants that were present in high concentrations throughout the United States called “criteria pollutants.” These air pollutants are particulate matter (PM₁₀), sulfur dioxide (SO₂), nitrogen oxides (NO_x), ozone (O₃), carbon monoxide (CO) and lead (Pb). Fine particulate matter (PM_{2.5}) was later added as an additional criteria pollutant. The National Emissions Trends (NET) database inventories emissions of five criteria pollutants (PM₁₀, PM_{2.5}, SO₂, NO_x, and CO). Ozone is not directly emitted, so a group of ozone precursors called volatile organic compounds (VOCs) is included instead. Lead is inventoried with the hazardous air pollutants.

Greenhouse Gases

Another group of air pollutants has risen in importance. Although greenhouse gases do not necessarily directly harm human health, their increase in concentration can lead to global climate change. Global climate change poses risks to human health and to ecosystems. Important economic resources such as agriculture, forestry, fisheries, and water resources also may be affected. The principal greenhouse gas is carbon dioxide (CO₂). MPCA tracks the emissions of CO₂ in Minnesota.

Air Toxics

Many other chemicals are released in smaller amounts than the criteria pollutants, but are still toxic. EPA refers to chemicals that cause serious health and environmental hazards as hazardous air pollutants or air toxics. Air toxics include chemicals such as benzene, formaldehyde, acrolein, mercury and polycyclic organic matter (POMs). EPA tracks emissions of these chemicals in the National Toxics Inventory (NTI) database. Minnesota values come from the 1999 Minnesota Air Toxics Emission Inventory.

This report is limited to a summary and discussion of emissions of various air pollutants in Minnesota. However, the MPCA has prepared several other reports that discuss air pollution trends and emissions in more detail. Please reference the following reports for more information regarding air pollution.

Air Quality in Minnesota: Into the Future—2003 Legislative Report
<http://www.pca.state.mn.us/hot/legislature/reports/index/html>

Air Quality in Minnesota: Problems and Approaches—2001 Legislative Report
<http://www.pca.state.mn.us/hot/legislature/reports/2001/airquality.html>

Minnesota Environment 2000
<http://www.pca.state.mn.us/about/pubs/mnereport/index.html>

Criteria Air Pollutant Emissions

EPA prepares estimates of annual national emissions of criteria pollutants for every state to assess historic trends in emissions. This emissions inventory, the National Emissions Trends (NET) database, includes five criteria pollutants (PM₁₀, PM_{2.5}, SO₂, NO_x, and CO). Ozone is not directly emitted, so a group of ozone precursors called volatile organic compounds (VOCs) is included instead. Ammonia is also inventoried in the NET database because of its importance in particle formation. Lead is inventoried with the air toxics.

The NET database is released every three years (e.g., 1996 and 1999). EPA calculates aggregate emissions for each year between the inventory releases based on economic growth activity. Therefore, 2000 emissions reported are projected based on available 1999 information and historical trends. Each pollutant's emissions are estimated for many source categories, which collectively account for all manmade emissions. Air pollutant emissions in this report are discussed by pollutant based on the following three classes of pollutant sources as defined in the Clean Air Act:

- Point source - a stationary source of emissions, such as an electric power plant, that can be identified by name and location. A "major" source emits a threshold amount (or more) of at least one criteria pollutant, and must be inventoried and reported.
- Area source - a small point source such as a home or commercial building, or a diffuse stationary source, such as wildfires or agricultural tilling. These sources do not individually produce sufficient emissions to qualify as point sources. For example, a single dry cleaner typically will not qualify as a point source, but collectively the emissions from many dry cleaning facilities may be significant.
- Mobile source - any kind of vehicle or equipment with a gasoline or diesel engine. Mobile sources are broken up into two categories; highway sources which include gasoline and diesel cars and trucks and off-highway sources which include non-highway vehicles such as lawnmowers, construction equipment, snowmobiles, aircraft, marine vessels, railroads, etc.

This report presents trend data from 1996-2000 when available. The emission trends are the net effect of many factors, including changes in the nation's economy and in industrial activity, technology, consumption of fuels, traffic, and other activities that cause air pollution. The trends also reflect changes in emissions as a result of air pollution regulations and emission controls. In addition, the emissions reported are estimates. Changes in the way emissions are calculated may also affect trends, even if there was no real increase or decrease in emissions.

The reader may note differences in the total emission figures for a given year discussed in this report versus previous MPCA emission reports. This is because the data are continually being updated in the NET database. Furthermore, despite the importance of the secondary formation of some pollutants (e.g. PM_{2.5}), estimated air emissions data in this report are only based on direct releases from sources into the atmosphere. Secondary formation of pollutants is not included in the estimates.

Find more information on the NET database in the following EPA web site:

<http://www.epa.gov/air/data/netdb.html>

See the EPA AIRData web site to download criteria pollutant emissions data:

<http://www.epa.gov/air/data/index.html>

Find more information on criteria air pollutants in the following EPA web site:

<http://www.epa.gov/air/urbanair/6poll.html>

Carbon Monoxide

Carbon monoxide (CO) is a colorless and odorless toxic gas formed in high concentrations when carbon in fuels is not burned completely.

CO enters the bloodstream and reduces the delivery of oxygen to the body's organs and tissues. The health threat from CO is most serious for those who suffer from cardiovascular disease. At higher concentrations it also affects healthy individuals. Exposure to elevated CO levels is associated with impairment of visual perception, work capacity, manual dexterity, learning ability and performance of complex tasks. Prolonged exposure to high levels can lead to death.

At concentrations commonly found in the ambient air, CO does not appear to have adverse effects on plants, wildlife or materials. However, CO is oxidized to form carbon dioxide (CO₂), a contributor to global warming.

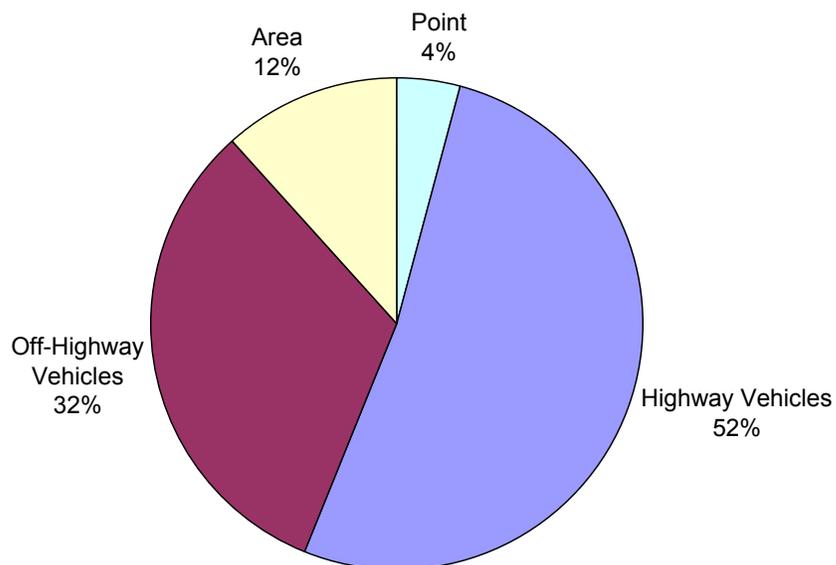
Emissions Data and Sources

The EPA estimate for statewide emissions of CO in 2000 is 2,104,632 tons.

The figure below shows sources of 2000 CO emissions. The majority of CO emissions come from the transportation sector, which consists of highway and off-highway vehicles. Highway vehicles contribute 52 percent of total statewide CO emissions, while off-highway vehicles and engines contribute 32 percent of total CO emissions. Off-highway emissions come primarily from gasoline consumption by lawn and garden, industrial and recreational engines.

The remaining 16 percent of emissions come from point and area sources. Area source emissions are primarily from residential wood burning, waste disposal through open burning and other combustion sources such as wildfires. Point sources include electric utilities and other industries that contribute to CO emissions through fuel combustion. Petroleum refineries are the primary industrial point source that contributes to CO emissions.

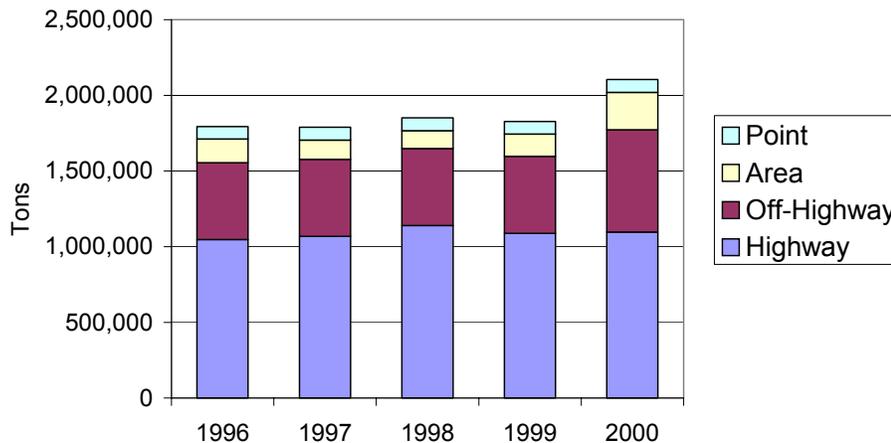
Sources of Carbon Monoxide Emissions in Minnesota, 2000



Trends

Nationally, CO emissions have decreased 18 percent over the last 20 years. However, in Minnesota from 1996-2000, CO emissions have generally remained constant except for the estimated 2000 emissions, which represent a 15 percent increase from 1999 values. The EPA inventory attributes this increase to an increase in residential wood burning, non-highway gasoline engine emissions and miscellaneous combustion including wildfires. It is unlikely that actual emissions increased this much over one year, based on trends from years past.

**Carbon Monoxide Trends in Minnesota,
1996-2000**



References/Web Links

For more information on carbon monoxide, see the following web sites:

<http://www.epa.gov/air/urbanair/co/index.html>

<http://www.epa.gov/airtrends/>

<http://www.pca.state.mn.us/air/emissions/co.html>

Nitrogen Oxides

Nitrogen oxides (NO_x) is the generic term for a group of highly reactive gases, all of which contain nitrogen and oxygen in varying amounts. The two primary constituents are nitric oxide (NO) and nitrogen dioxide (NO₂). NO is a colorless, odorless gas that is readily oxidized in the atmosphere to NO₂. NO₂ exists as a brown gas that gives photochemical smog its yellowish-brown color. NO_x is reported because NO and NO₂ continuously cycle between the two species. NO_x form when fuel is burned at high temperatures. NO is the principal oxide of nitrogen produced in combustion processes.

NO_x contributes to a wide range of human health effects. NO₂ can irritate the lungs and lower resistance to respiratory infection (such as influenza). However, more importantly, NO_x are a major precursor both to ozone and to particulate matter (PM). As discussed in the ozone and PM sections of this report, exposure to both PM and ozone is associated with serious adverse health effects.

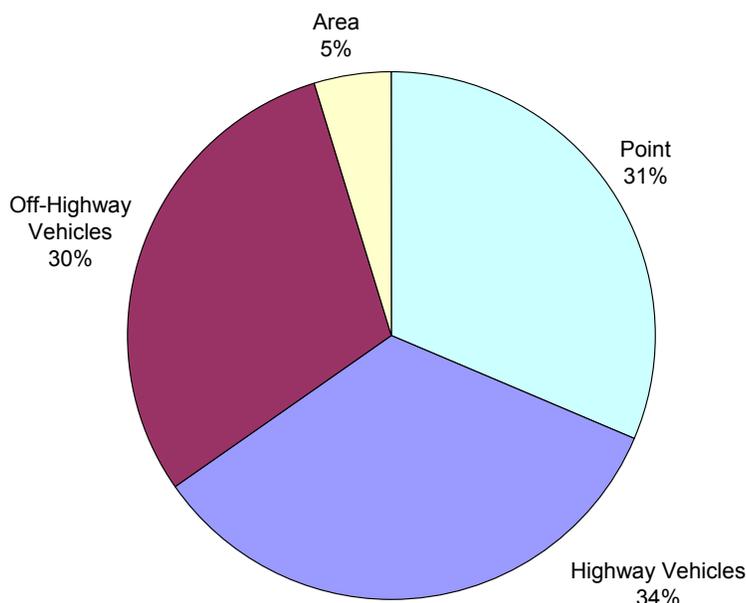
High NO_x concentrations also cause serious environmental impacts. Deposition of nitrogen can lead to fertilization, eutrophication, or acidification of terrestrial, wetland and aquatic systems. This can result in changes in species number and composition such as the reduction of fish and shellfish populations. In addition, nitrous oxide (N₂O), another component of NO_x, is a greenhouse gas that contributes to global warming.

Emissions Data and Sources

The EPA estimate for statewide emissions of NO_x in 2000 is 532,853 tons.

The figure below shows sources of 2000 NO_x emissions. The majority of NO_x emissions come from the transportation sector, which consists of highway and off-highway vehicles. Highway vehicles contribute 34 percent of total statewide NO_x emissions, while off-highway vehicles and engines contribute 30 percent of total NO_x emissions. Gasoline and diesel engines contribute the majority of emissions from the

Sources of Nitrogen Oxide Emissions in Minnesota, 2000

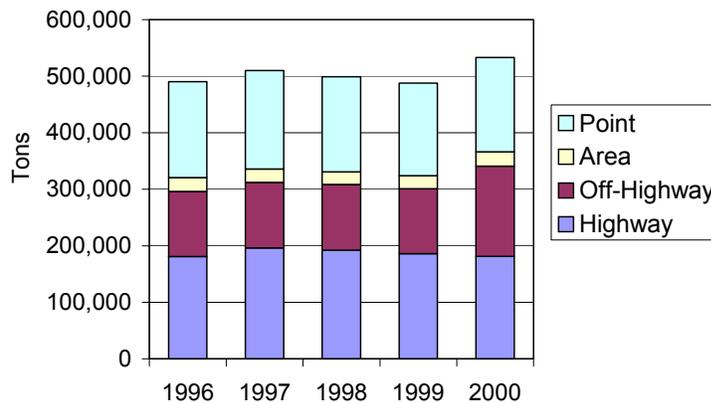


transportation sector. Thirty-one percent of NO_x emissions come from point sources as electric utilities and industrial facilities emit NO_x during coal and gas combustion. Area sources are responsible for the remaining 5 percent of NO_x emissions. Residential and small industrial combustion makes up the majority of area source emissions.

Trends

Nationally, NO_x emissions have increased 4 percent over the last 20 years. In Minnesota, from 1996-2000, NO_x emissions have generally remained constant while the estimated 2000 emissions represent a 9 percent increase from 1999 values. The increase in 2000 estimated emissions is primarily a result of increased off-highway emissions including a 10-fold increase in marine vessel emissions and a doubling of emissions from railroads. Increases from these source categories are surprising and it is likely that they result from a methodology change or error in the EPA inventory. There was also an increase in residential combustion under area sources.

Nitrogen Oxide Emission Trends in Minnesota, 1996-2000



References/Web Links

For more information on nitrogen oxides, see the following web sites:

<http://www.epa.gov/air/urbanair/nox/index.html>

<http://www.epa.gov/airtrends/>

<http://www.pca.state.mn.us/air/emissions/no2.html>

Volatile Organic Compounds

Volatile organic compounds (VOCs) are compounds containing the elements carbon and hydrogen that exist in the atmosphere primarily as gases because of their low vapor pressure. VOCs are defined in federal rules as chemicals that participate in forming ozone. Therefore, only gaseous hydrocarbons that are photochemically reactive and participate in the chemical and physical atmospheric reactions that form ozone and other photochemical oxidants are considered VOCs.

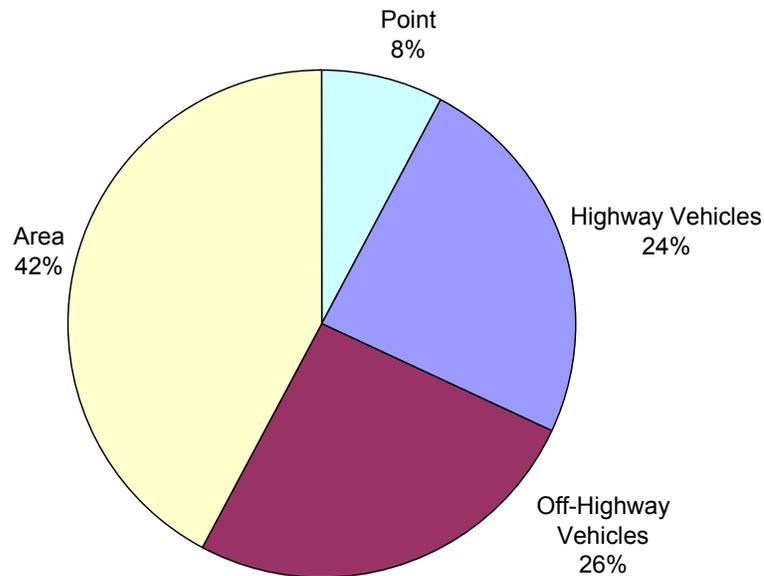
Many VOCs are also air toxics and can have harmful effects on human health and the environment. However, VOCs are regulated as a criteria pollutant because they are precursors to ozone. See the sections on ozone and air toxics for related human health and environmental effects.

Emissions Data and Sources

The EPA estimate for statewide emissions of VOCs in 2000 is 458,306 tons.

VOCs are emitted from a variety of sources, including industrial sources, motor vehicles, consumer products and natural sources such as lightning and biological processes in soil. The figure below shows manmade Minnesota sources of VOCs in 2000. Half of the emissions come from the transportation sector, which consists of highway and off-highway vehicles. Twenty-four percent of emissions come from highway vehicles and 26 percent come from off-highway vehicles.

Sources of Volatile Organic Compounds in Minnesota, 2000

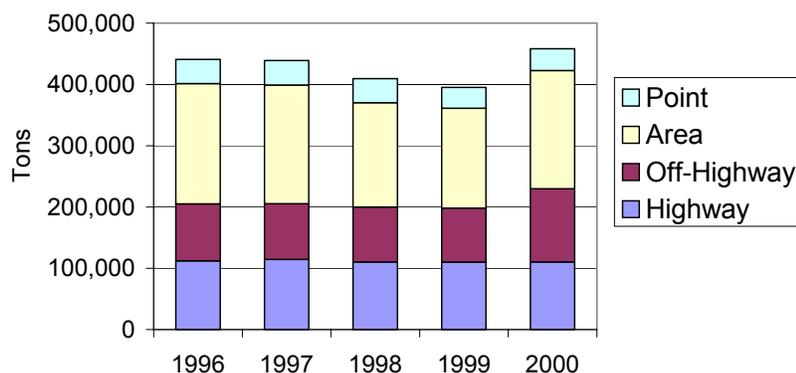


Area sources contribute 42 percent of VOC emissions, primarily from solvent utilization, residential wood combustion, and storage and transport of fuels and chemicals. The final 8 percent of emissions come from point source combustion, solvent utilization and storage and transport of fuels and chemicals.

Trends

Nationally, VOC emissions have decreased 32 percent over the last 20 years. In Minnesota, VOC emissions were slightly higher in 1996, 1997 and 2000 and slightly lower in 1998 and 1999. These differences may not be statistically significant. The estimated 2000 emissions represent a 16 percent increase from 1999 values. According to the EPA inventory, the increase is primarily a result of increased residential wood combustion, emissions from off-highway gasoline engines and miscellaneous combustion such as wildfires.

Volatile Organic Compounds Emission Trends in Minnesota, 1996-2000



References/Web Links

For more information on volatile organic compounds, see the following web sites:

<http://www.epa.gov/airtrends/>

<http://www.pca.state.mn.us/air/emissions/voc.html>

Sulfur Dioxide

Sulfur dioxide (SO₂) belongs to the family of sulfur oxide gases. It is a colorless gas that can be detected by taste and odor at concentrations as low as 0.3 ppm. Sulfur oxide gases are formed when fuel containing sulfur (mainly coal and oil) is burned and during metal smelting and other industrial processes.

SO₂ reacts with other chemicals in the air to form tiny sulfate particles. In fact, sulfate aerosols make up the largest single component of fine particulate matter. It is difficult to distinguish between health effects due to SO₂ exposure and those due to fine particulate exposure. The major health effects of concern associated with exposures to high concentrations of SO₂, sulfate aerosols and fine particulates include impaired breathing, respiratory illness, alterations in the lung's defenses, aggravation of existing respiratory and cardiovascular disease, and mortality. Children, asthmatics and the elderly may be particularly sensitive.

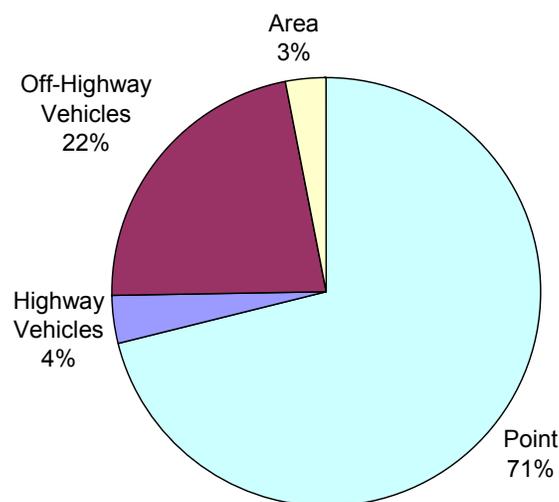
SO₂ also causes significant environmental damage. SO₂ reacts with other substances in the air to form acids, which fall to earth as rain, fog, snow, or dry particles. Acid rain damages forests and crops, changes the makeup of soil, and makes lakes and streams acidic and unsuitable for fish. Continued exposure changes the number and variety of plants and animals in an ecosystem. In addition, SO₂ accelerates the decay of buildings and monuments and is a major cause of reduced visibility due to haze in Minnesota.

Emissions Data and Sources

The EPA estimate for statewide emissions of SO₂ in 2000 is 189,636 tons.

The figure below shows sources of 2000 SO₂ emissions. Over 70 percent of SO₂ emissions come from point sources. Electric utilities and industrial facilities burning coal emit the majority (>85 percent) of SO₂ attributed to point sources.

Sources of Sulfur Dioxide Emissions in Minnesota, 2000



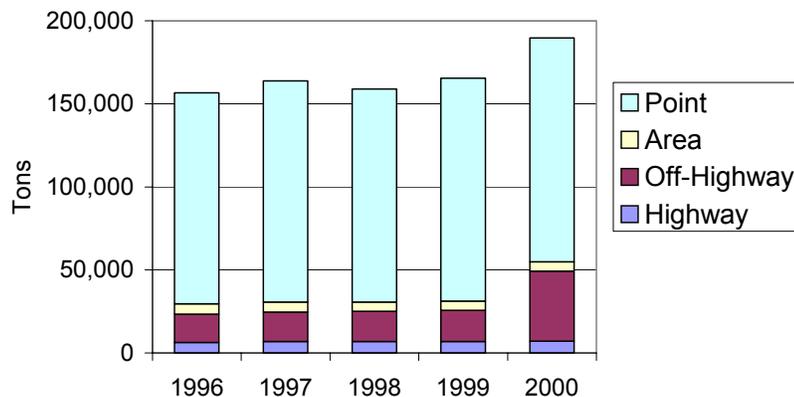
Off-highway vehicles and engines emit 22 percent of SO₂. Off-highway emissions come primarily from non-road diesel engines and marine vessels. Highway vehicles contribute 4 percent of the emissions. These emissions are divided between gasoline-powered cars, trucks and motorcycles and diesel vehicles.

The remaining three percent of area emissions of SO₂ result from fuel combustion by small industrial and commercial facilities and residences.

Trends

Nationally, SO₂ emissions have decreased 31 percent over the last 20 years. Nationally and in Minnesota emissions have remained essentially level in recent years. The estimated Minnesota 2000 emissions represent a 15 percent increase from 1999 values. The increase is primarily a result of an increase in off-highway emissions from marine vessels. Estimated marine vessel emission increased from 225 tons in 1999 to 23,807 tons in 2000. Increases from this source category are surprising and likely due to a methodology change or error in the EPA inventory.

Sulfur Dioxide Emission Trends in Minnesota, 1996-2000



References/Web Links

For more information on sulfur dioxide, see the following web sites:

<http://www.epa.gov/oar/urbanair/so2/index.html>

<http://www.epa.gov/airtrends/>

<http://www.pca.state.mn.us/air/emissions/so2.html>

Ammonia

Ammonia (NH₃) is a colorless gas with a very sharp odor. It dissolves easily in water and evaporates quickly. Ammonia reacts with sulfates and nitrates in the presence of water to create ammonium sulfate and ammonium nitrate, both of which are fine particles. Therefore, ammonia is an important precursor in PM_{2.5} formation.

Breathing low concentrations of ammonia may cause coughing and nose and throat irritation. However, ammonia in ambient air is a greater concern due to its role as a precursor to PM_{2.5} formation than from direct health effects. See the section on PM_{2.5} for related human health and environmental effects.

Emissions Data and Sources

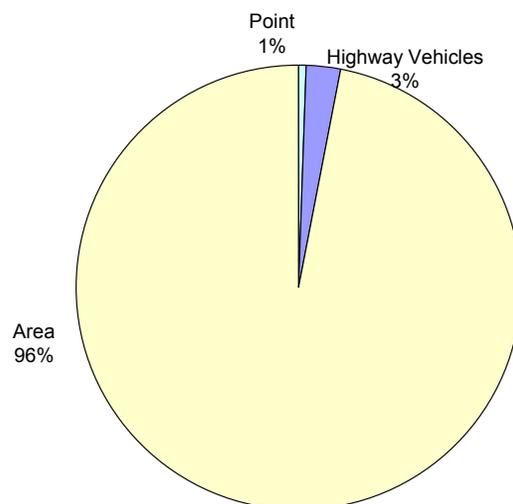
The EPA estimate for statewide emissions of NH₃ in 2000 is 195,729 tons.

The figure below shows sources of 2000 NH₃ emissions in Minnesota. The majority of NH₃ emissions (96 percent) come from area sources. According to the EPA inventory, agriculture and forestry contribute almost all of the NH₃ from area sources. Most of the ammonia emitted is generated from livestock waste management and fertilizer production.

Highway vehicles are responsible for 3 percent of ammonia emissions through the combustion of fuel. Ammonia is not emitted from the fuel combustion process itself, but from the control technology applied to control nitrogen oxide (NO_x) emissions. These methods reduce NO_x by injecting urea or ammonia into the exhaust gas to react with the nitrogen oxides. If the reaction is not complete, a portion of the ammonia may exit the system in the effluent.

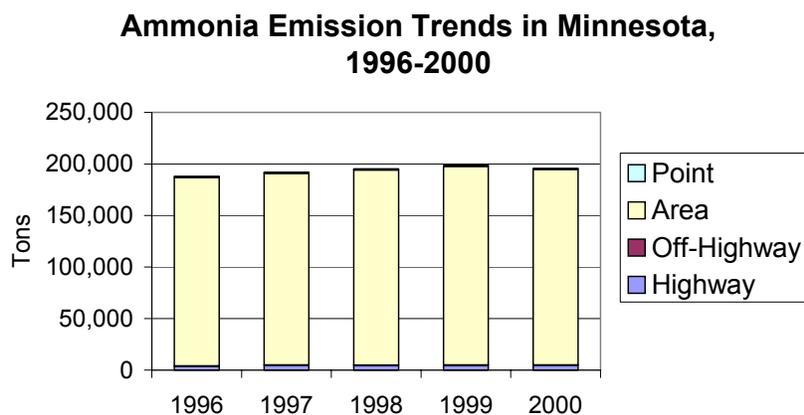
The remaining 1 percent of NH₃ comes from the petroleum industry and the manufacture of agricultural chemicals such as fertilizers. Currently, the United States Department of Agriculture and EPA are working to refine the NH₃ inventory for all source categories, including some natural sources that are not in the current inventory.

Sources of Ammonia Emissions in Minnesota, 2000



Trends

From 1996-2000 in Minnesota, NH₃ emission estimates have generally remained constant. The estimated 2000 emissions represent a 1.5 percent decrease from 1999 values. This decrease may not be statistically significant.



References/Web Links

For more information on ammonia, see the following web sites:

<http://www.atsdr.cdc.gov/tfacts126.html>

<http://www.epa.gov/airtrends/>

Particulate Matter

Particulate matter is the general term for particles found in the air, including dust, dirt, soot, smoke, and liquid droplets. Some particles are seen as soot or smoke. Others are so small that they can only be detected with an electron microscope. Particles less than or equal to 2.5 micrometers (μm) in diameter, or $\text{PM}_{2.5}$, are known as “fine” particles. Those larger than 2.5 μm but less than or equal to 10 μm are known as “coarse” particles. PM_{10} refers to all particles less than or equal to 10 μm in diameter.

PM₁₀

Coarse particles are generally emitted from sources such as vehicles traveling on unpaved roads, materials handling, and crushing and grinding operations, and windblown dust. Coarse particles can settle rapidly from the atmosphere within hours, and their spatial impact is typically limited because they tend to fall out of the air in the downwind area near their emissions point.

Both coarse and fine particles can be inhaled into the lungs. These particles then accumulate in the respiratory system and are associated with numerous adverse health effects. Exposure to coarse particles is primarily associated with the aggravation of respiratory conditions such as asthma.

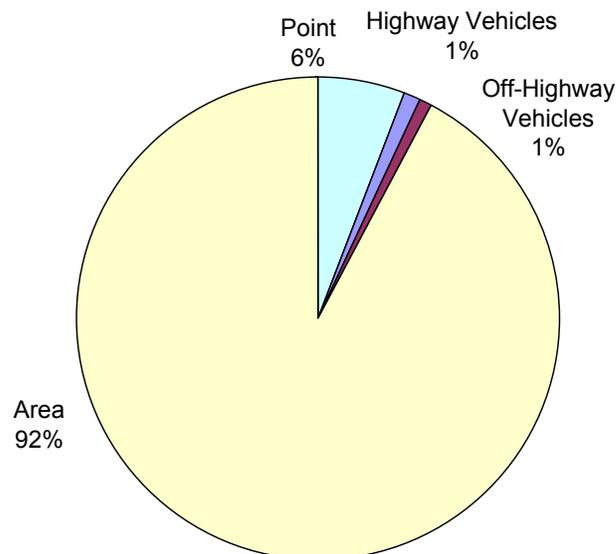
Particulate matter also causes adverse impacts to the environment. When particles containing nitrogen and sulfur deposit onto land or water bodies, they may affect nutrient balances and acidity. This can result in the depletion of nutrients in the soil, damage to sensitive forests and farm crops, and diversity changes in ecosystems. Particulate matter also causes soiling and erosion damage to materials and buildings.

Emissions Data and Sources

The EPA estimate for statewide direct emissions of PM_{10} in 2000 is 894,093 tons.

The figure below shows estimated sources of 2000 PM_{10} direct emissions. Emissions of secondarily formed PM_{10} are not accounted for in these emission graphs. Area sources contribute 92 percent of PM_{10}

Sources of PM_{10} Emissions in Minnesota, 2000



emissions. The area sources consist of fugitive dust (63 percent) and agriculture and forestry (33 percent) according to the EPA inventory. The remainder of the area source contribution is from combustion. Fugitive dust sources include unpaved roads, paved roads, construction and other sources.

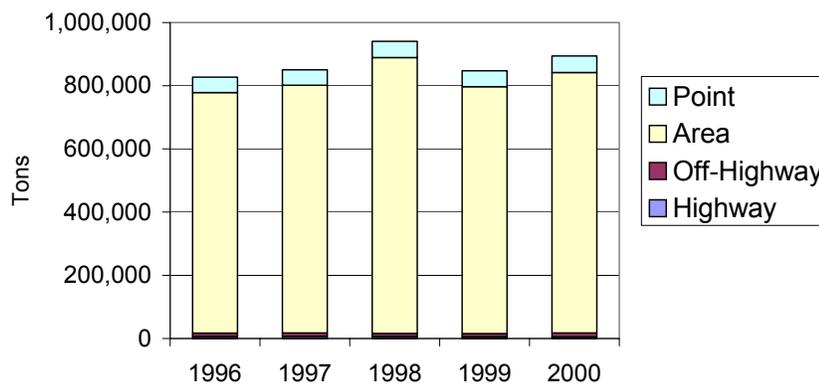
Industrial sources including metal processing, storage and transport, electric utilities, and other industrial processing account for 6 percent of PM₁₀ emissions. Metal processing accounts for 45 percent of the industrial portion of PM₁₀. Highway and off-highway sources make up about 2 percent of total PM₁₀.

Fugitive dust sources tend to be located away from people and tend to be coarser particles, which are of less concern from a human health perspective. Particles emitted from non-fugitive dust sources such as cars and wood stoves are smaller, more toxic and more often released in populated areas.

Trends

Nationally, manmade direct PM₁₀ emissions have decreased 47 percent over the last 20 years. In Minnesota direct emissions have oscillated up and down from 1996-2000. The estimated Minnesota 2000 emissions represent a 5.5 percent increase from 1999 values. The increase is primarily a result of increased residential wood burning, agricultural and forestry, fugitive dust, and an increase in miscellaneous combustion including wildfires.

**PM₁₀ Emission Trends in Minnesota,
1996-2000**



References/Web Links

For more information on PM₁₀, see the following web sites:

<http://www.epa.gov/oar/urbanair/pm/index.html>

<http://www.epa.gov/airtrends/>

<http://www.pca.state.mn.us/air/emissions/pm10.html>

PM_{2.5}

Fine particles are both directly emitted during fuel combustion (from motor vehicles, power generation, industrial processes, residential fireplaces and wood stoves) and formed secondarily in the atmosphere from gases such as sulfur dioxide (SO₂), nitrogen oxides (NO_x), and volatile organic compounds (VOCs). Fine particles tend to remain suspended for long times and travel farther than coarse particles. Therefore, they are likely to be more uniformly dispersed at urban and regional scales than coarse particles.

Both coarse and fine particles can be inhaled into the lung. These particles then accumulate in the respiratory system and are associated with numerous adverse health effects. Fine particles are associated with decreased lung function, increased hospital admissions and emergency room visits, increased respiratory symptoms and disease, and premature death. Studies indicate that fine particles may also affect the cardiovascular system and contribute to lung cancer. For two days in 2002 levels of fine particulate matter were high enough in the Twin Cities area to lead to air alerts for people in sensitive groups. These groups include people with respiratory or heart disease, the elderly and children.

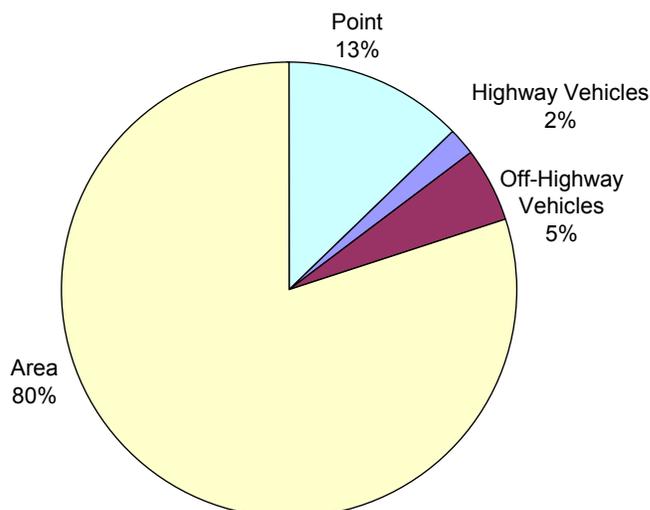
Particulate matter also causes adverse impacts to the environment. Fine particulates are the major cause of reduced visibility in parts of the United States. In addition, when particles containing nitrogen and sulfur deposit onto land or water bodies, they may affect nutrient balances and acidity, resulting in the depletion of nutrients in the soil, damage to sensitive forests and farm crops, and diversity changes in ecosystems. Particulate matter also causes soiling and erosion damage to materials and buildings.

Emissions Data and Sources

The EPA estimate for statewide direct emissions of PM_{2.5} in 2000 is 211,389 tons. However, this number only takes into account direct, manmade emissions of PM_{2.5}. Secondarily formed particles are not directly emitted, but are formed downwind of the emissions source. EPA is working to improve the PM_{2.5} emissions inventory since PM_{2.5} is predominantly comprised of secondary particles and directly emitted carbonaceous particles. The EPA emissions inventory shows PM_{2.5} emission sources mirroring PM₁₀ to a great extent. In fact, PM_{2.5} and PM₁₀ sources are markedly different because most crustal material particles are larger than 2.5 μm diameter while almost all of the secondary particles and directly emitted carbonaceous particles are smaller than 2.5 μm.

The figure below shows only directly emitted, manmade PM_{2.5} emissions. According to the EPA emissions inventory, 80 percent of direct PM_{2.5} emissions come from area sources such as fugitive dust (50 percent), agriculture/forestry (32 percent) and combustion (17 percent).

Sources of Direct PM_{2.5} Emissions in Minnesota, 2000



Industrial sources such as metals processing, storage and transport, electric utilities, fuel combustion and other industrial processes make up 13 percent of PM_{2.5} emissions. Highway and off-highway emissions make up only 7 percent of PM_{2.5} emissions.

Much of PM_{2.5} is the result of secondary formation. These sources are not represented in the figure provided. The principal types of secondary particles are ammonium sulfate and ammonium nitrate, formed in the air from gaseous emissions of SO₂ and NO_x reacting with ammonia. Some secondary particles are also formed from VOCs. Therefore, for a complete understanding of PM_{2.5} emissions, one should also consider the emissions of SO₂, NO_x, NH₃ and VOCs. See the sections on these other pollutants for a further understanding of the sources contributing to PM_{2.5}.

Overall, fuel combustion is a significant source of PM_{2.5}, while fugitive dust sources do not play a particularly important role.

Trends

Nationally, manmade direct PM_{2.5} emissions have decreased 5 percent over the last 10 years. The estimated Minnesota 2000 emissions (191,198 tons) represent a 10 percent increase from 1999 values (211,389 tons). Since the current 2000 emission estimates for PM_{2.5} are very incomplete, it would be misleading to attempt to present a trend chart.

References/Web Links

For more information on PM_{2.5}, see the following web sites:

<http://www.epa.gov/air/urbanair/pm/index.html>

<http://www.epa.gov/airtrends/>

<http://www.pca.state.mn.us/air/emissions/pm10.html>

Ozone

Ozone is an odorless, colorless gas composed of three atoms of oxygen. Naturally occurring ozone in the upper atmosphere helps protect the earth's surface from ultraviolet radiation. However, at elevated concentrations, ground-level ozone can irritate the respiratory system, reduce lung function, aggravate and potentially cause asthma, and cause other lung effects. Children, active adults, and people with respiratory diseases are particularly sensitive to ozone.

Ozone is an important criteria pollutant. In late June 2001, the Air Quality Index (AQI) for the Twin Cities reached some of its highest levels since the Clean Air Act took effect in the 1970s. On four days in 2001 the AQI reached a level considered unhealthy for sensitive groups. These high AQI readings were primarily a result of elevated ground-level ozone concentrations. The AQI also reached a level considered unhealthy for sensitive groups once in 2002.

Emissions of ozone are not reported because ozone is not normally emitted directly into the air. Instead, it is created when "ozone precursors" such as nitrogen dioxide (NO₂) and volatile organic compounds (VOCs) react in a hot stagnant atmosphere. Since heat and sunlight are needed for ozone to be produced, elevated levels of ozone in Minnesota are normally seen on very hot summer afternoons.

Ozone precursors come from a variety of sources. NO₂ can form when fuels are burned at high temperatures. The major NO₂ sources are combustion processes from automobiles and power plants. VOCs are emitted from a variety of sources, including industrial sources, motor vehicles, consumer products and natural sources such as lightning and biological processes in soil. See the NO_x and VOC sections of this report for more information regarding 2000 emissions of ozone precursors.

References/Web Links

For more information on ozone, see the following web sites:

<http://www.epa.gov/air/urbanair/ozone/index.html>

<http://www.epa.gov/airtrends/>

<http://bopp.pca.state.mn.us/aqi/>

Lead

Lead (Pb) is a metal found naturally in the environment as well as in manufactured products. In the past, the major sources of lead emissions were motor vehicles and industrial sources. Since lead in gasoline was phased out, metals processing (lead and other metals smelters) and aircraft using leaded fuel are the major source of lead emissions to the air today.

Lead causes damage to organs such as the kidneys and liver and may lead to high blood pressure and increased heart disease. In addition, exposure to lead may contribute to osteoporosis and reproductive disorders. Most importantly, lead exposure causes brain and nerve damage to fetuses and young children, resulting in seizures, behavioral disorders, memory problems, mood changes, learning deficits and lowered IQ.

Elevated lead levels are also detrimental to animals and to the environment. Wild and domestic animals experience the same kind of effects as people exposed to lead. Elevated levels of lead in the water can cause reproductive damage in some aquatic life and cause blood and neurological changes in fish.

Emissions Data and Sources

Annual lead emission data is not available through the NET database. However, the MPCA includes lead in the Minnesota Air Toxics Emission Inventory. The 1999 emissions inventory is the most recent complete inventory available. According to the inventory, 79084 lbs (55 tons) of lead was emitted in Minnesota in 1997. Of that, 72 percent was from point sources. Mobile sources contributed 22 percent of lead emissions and area sources contributed 7 percent of lead emissions. The area source contribution would be somewhat higher if prescribed burning and forest fires were included in the inventory. A table containing the lead emission values is included on page 25 in the air toxics section of this report.

Trends

In Minnesota, lead in the air has dropped significantly. Between 1984 and 1994 average lead concentrations decreased 87% from 0.53 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) to $.06 \mu\text{g}/\text{m}^3$. The national ambient air quality standard is $1.5 \mu\text{g}/\text{m}^3$.

References/Web Links

<http://www.epa.gov/air/urbanair/lead/index.html>

<http://www.pca.state.mn.us/air/lead.html#tips>

<http://www.pca.state.mn.us/air/toxics.html>

<http://www.commerce.state.mn.us/pages/Energy/Policy/06-Appendix%20A%20.pdf>

Carbon Dioxide

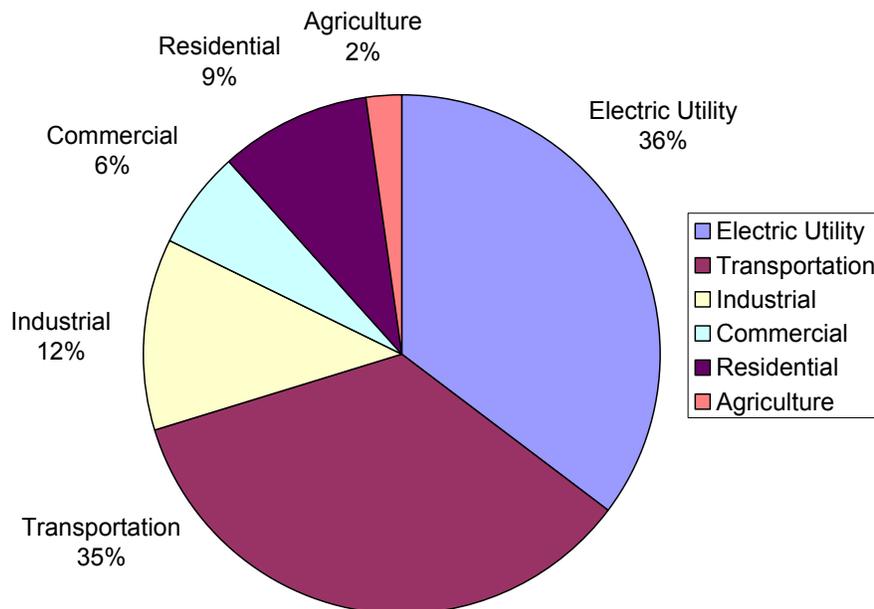
Carbon dioxide is a gas that is primarily formed from the combustion of fossil fuels such as oil, gas, and coal. It is a concern because it is the major greenhouse gas that contributes to accelerated warming of the earth's atmosphere. The earth's greenhouse effect is a natural phenomenon that helps regulate the temperature of our planet. Many greenhouse gases occur naturally, but fossil fuel burning and other human activities are adding gases to the natural mix at a substantial rate.

Emissions Data and Sources

The estimate for statewide emissions of carbon dioxide in 2001 is 106 million short tons.

The pie chart below shows the breakdown of carbon dioxide emissions from fossil fuel burning by sector. The majority of the carbon dioxide emissions come from the electric utility (36%) and transportation (35%) sectors. The remaining 29 percent of the emissions come from fossil fuel combustion in the industrial, commercial, residential and agriculture sectors.

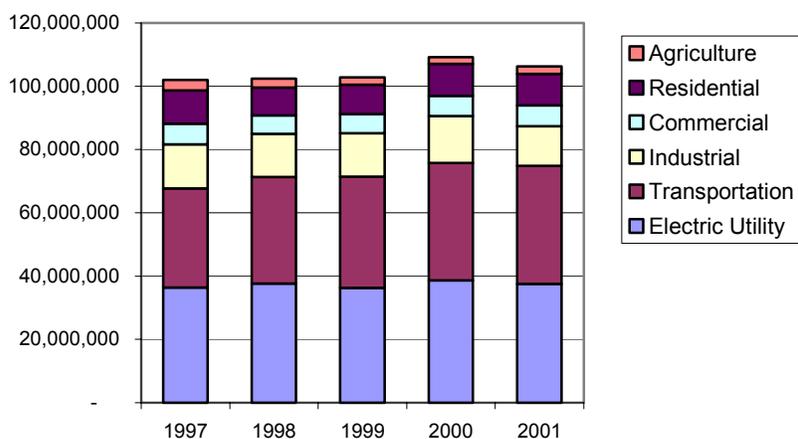
Sources of Carbon Dioxide Emissions from Fossil Fuel Burning in Minnesota, 2001



Trends

Carbon dioxide emissions from fossil fuel burning in Minnesota increased slightly from 1997 to 1999 with an increase of 5.6 percent from 2000 to 2001. From 2000 to 2001, carbon dioxide emissions decreased 2.6 percent.

Carbon Dioxide Emissions from Fossil Fuel Burning in Minnesota, 1997-2001



Source

The statewide emissions estimates for carbon dioxide were calculated in March, 2003 by Peter Ciborowski, MPCA senior pollution control specialist, using a variety of fuel use data sources.

Air Toxics

Through modeling and MPCA air toxics monitoring, several chemicals besides criteria pollutants have been identified at concentrations of potential concern in Minnesota air. These chemicals include compounds such as benzene, and formaldehyde. Chemicals of potential concern in Minnesota are identified in the MPCA's 2003 Legislative Report—Air Quality in Minnesota: Into the Future, <http://www.pca.state.mn.us/hot/legislature/reports/index.html>, and in the EPA's National Air Toxics Assessment (NATA), <http://www.epa.gov/ttn/atw/nata/>.

EPA refers to chemicals that cause serious health and environmental hazards as hazardous air pollutants or air toxics. EPA defines air toxics as pollutants that cause or may cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental and ecological effects.

The Minnesota Air Toxics Emission Inventory estimates emissions of air toxics. Air toxic emission inventories are generally compiled every three years. The most recent inventory for Minnesota is from 1999. The inventory includes three principal source categories: point, area, and mobile sources.

- Point source - a stationary source of emissions, such as an electric power plant, that can be identified by name and location. A "major" source emits a threshold amount (or more) of at least one criteria pollutant, and must be inventoried and reported.
- Area source - a small point source such as a home or commercial building, or a diffuse stationary source, such as wildfires or agricultural pesticide applications. These sources do not individually produce sufficient emissions to qualify as point sources. For example, a single gasoline station typically will not qualify as a point source, but collectively the emissions from many gas stations may be significant.
- Mobile source - any kind of vehicle or equipment with a gasoline or diesel engine. Mobile sources are broken up into two categories; highway sources which include gasoline and diesel cars and trucks and off-highway sources which include non-highway vehicles such as lawnmowers, construction equipment, snowmobiles, aircraft, marine vessels, locomotives, etc.

MPCA staff compiled the emissions estimates for the point and area sources in the 1999 inventory. The results for mobile sources were obtained from EPA's 1999 National Emission Inventory Version 3 for Hazardous Air Pollutants. Since mobile emission estimates are sensitive to many factors such as local fleet mix, climate conditions, and fuel programs, EPA's estimates may not match estimates made by states. MPCA will update the 1999 inventory when state-specific estimates of mobile sources become available.

Table 3 provides a summary of air toxics emissions from principal source categories taken from the 1999 Minnesota Air Toxics Emission Inventory. The table gives total statewide emissions of each chemical, along with the percent from point, area, highway, and off-highway sources. The inventory includes 156 chemicals: 17 polycyclic organic matters (POMs), 126 non-metal compounds (excluding POMs), and 13 metal compounds.

Table 3: 1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

Pollutant	Total (short tons)	Point (%)	Area (%)	Highway (%)	Off- Highway (%)
Polycyclic Organic Matter (POMs)					
Acenaphthene	41	90%	6%	1%	2%
Acenaphthylene	59		93%	4%	3%
Anthracene	8.9	2%	88%	6%	4%
Benz[a]Anthracene	11	1%	96%	2%	1%
Benzo[a]Pyrene	2.4		92%	4%	4%
Benzo[b]Fluoranthene	1.7		90%	6%	4%
Benzo[g,h,i]Perylene	5.7		91%	3%	6%
Benzo[k]Fluoranthene	2.8		94%	4%	2%
Chrysene	8.4		98%	1%	1%
Dibenzo[a,h]Anthracene	0.003	11%	5%	1%	84%
Fluoranthene	13	2%	86%	5%	8%
Fluorene	9.0	1%	70%	11%	18%
Indeno[1,2,3-c,d]Pyrene	3.0		95%	2%	3%
Naphthalene	468	12%	70%	14%	4%
Phenanthrene	30	1%	83%	5%	10%
Pyrene	16	1%	87%	5%	7%
Other POM not included above	171	8%	92%		
POM Total	850	13%	75%	9%	4%
Metal Compounds					
Antimony Compounds	1.4	85%	15%		
Arsenic Compounds	9.2	92%		4%	3%
Beryllium Compounds	0.21	85%	8%		7%
Cadmium Compounds	10	10%	89%		
Chromium Compounds	15	94%	5%	1%	
Chromium (VI)	0.28	55%	4%	36%	4%
Cobalt Compounds	2.7	91%	9%		
Copper Compounds	16	95%	5%		
Lead Compounds	55	72%	7%		22%
Manganese Compounds	107	97%	3%		
Mercury Compounds	2.6	68%	5%	18%	9%
Nickel Compounds	30	79%	17%	1%	3%
Selenium Compounds	2.0	95%	4%		
Metal Compound Total	250	85%	9%	1%	5%

1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

Pollutant	Total (short tons)	Point (%)	Area (%)	Highway (%)	Off- Highway (%)
Non-Metal Compounds (Excluding POMs)					
1,1,2,2-Tetrachloroethane	0.6	6%	94%		
1,1,2-Trichloroethane	0.05	100%			
1,2,4-Trichlorobenzene	3.7	100%			
1,2,4-Trimethylbenzene	78	88%	12%		
1,3,5-Trimethylbenzene	0.16	100%			
1,3-Butadiene	946		35%	41%	23%
1,3-Dichloropropene	382		100%		
1,4-Dichlorobenzene	186		100%		
2,2,4-Trimethylpentane	8315		2%	39%	59%
2,3,7,8-Tetrachlorodibenzo-p-Dioxin	0.000005	27%	73%		
2,3,7,8-Tetrachlorodibenzofuran	0.0002	6%	94%		
2,4-D (2,4-Dichlorophenoxyacetic Acid)(Including Salts)	84		100%		
2,4-Dinitrophenol	0.07	100%			
2,4-Dinitrotoluene	0.003	100%			
2,4-Toluene Diisocyanate	2.5	99%	1%		
2-Chloroacetophenone	0.07	100%			
2-Nitropropane	0.005		100%		
4,4'-Methylenedianiline	0.08	100%			
4,4'-Methylenediphenyl Diisocyanate (MDI)	32	99%	1%		
4-Nitrophenol	0.21	100%			
Acetaldehyde	2308	3%	30%	41%	25%
Acetamide	0.0003		100%		
Acetone	828	19%	81%		
Acetonitrile	6.1	100%			
Acetophenone	0.8	22%	78%		
Acrolein	508	2%	70%	14%	14%
Acrylamide	0.12	100%			
Acrylic Acid	6.9	100%			
Acrylonitrile	2.7	38%	62%		
Aldehydes	445	6%	94%		
Allyl Chloride	0.004	100%			
Aniline	0.0006	100%			
Atrazine	90		100%		
Benzaldehyde	0.7	100%			
Benzene	7035	1%	27%	46%	26%
Benzyl Chloride	6.0	100%			
Biphenyl	1.1	64%	36%		
Bis(2-Ethylhexyl)Phthalate (Dehp)	4.9	100%			
Bromoform	0.36	100%			
Butyraldehyde	0.08	100%			
Carbon Disulfide	1.4	84%	16%		

1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

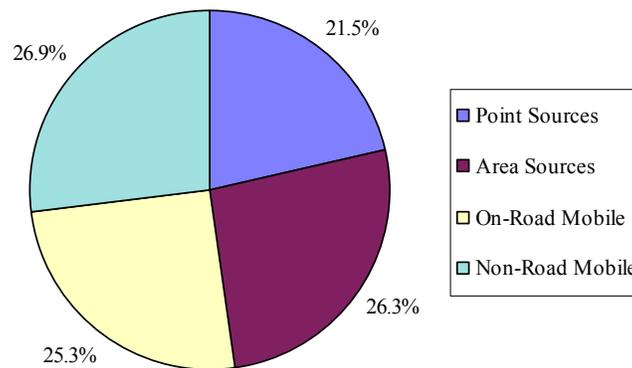
Pollutant	Total (short tons)	Point (%)	Area (%)	Highway (%)	Off- Highway (%)
Carbon Tetrachloride	0.8	47%	53%		
Carbonyl Sulfide	106	99%	1%		
Catechol	0.32	100%			
Chlorine	261	3%	97%		
Chloroacetic Acid	0.000	100%			
Chlorobenzene	172		100%		
Chloroform	27	80%	20%		
Chloroprene	0.0005	100%			
Cresol/Cresylic Acid (Mixed Isomers)	26	100%			
Crotonaldehyde	0.06	100%			
Cumene	23	72%	28%		
Cyanide Compounds	96	26%	74%		
Di-N-Octylphthalate	0.5	100%			
Dibenzofuran	0.02	10%	90%		
Dibutyl Phthalate	1.3	94%	7%		
Dichlorobenzenes	0.03	100%			
Diethanolamine	0.09	82%	18%		
Diethyl Sulfate	0.003	100%			
Dimethyl Phthalate	1.8	99%	1%		
Dimethyl Sulfate	0.45	100%			
Ethyl Acrylate	2.3	100%			
Ethyl Chloride	27	22%	78%		
Ethylbenzene	2750	5%	2%	50%	44%
Ethylene Dibromide (Dibromoethane)	0.28	99%	1%		
Ethylene Dichloride (1,2-Dichloroethane)	1.3	60%	40%		
Ethylene Glycol	101	23%	77%		
Ethylene Oxide	57	10%	90%		
Ethylidene Dichloride (1,1-Dichloroethane)	0.49	2%	98%		
Formaldehyde	5916	7%	43%	25%	25%
Glycol Ethers	1616	30%	70%		
Hexamethylene Diisocyanate	1.8	100%			
Hexane	4964	24%	34%	24%	17%
Hydrazine	0.0005	100%			
Hydrochloric Acid (Hydrogen Chloride [Gas Only])	12938	100%			
Hydrogen Fluoride (Hydrofluoric Acid)	1365	100%			
Hydroquinone	3.3	36%	64%		
Isophorone	13	42%	58%		
Lindane, (All Isomers)	0.002	100%	0		
M-Dichlorobenzene	0.7	7%	93%		
Maleic Anhydride	0.32	100%			
Methanol	2513	31%	69%		
Methyl Bromide (Bromomethane)	537	1%	99%		
Methyl Chloride (Chloromethane)	173	29%	71%		
Methyl Chloroform (1,1,1-Trichloroethane)	866		100%		

1999 Minnesota Air Toxics Emissions Inventory Statewide Summary

Pollutant	Total (short tons)	Point (%)	Area (%)	Highway (%)	Off- Highway (%)
Methyl Ethyl Ketone (2-Butanone)	2367	25%	75%		
Methyl Iodide (Iodomethane)	0.003	100%			
Methyl Isobutyl Ketone (Hexone)	1074	16%	84%		
Methyl Methacrylate	41	100%			
Methyl Tert-Butyl Ether	8.6	26%	1%	73%	
Methylene Chloride (Dichloromethane)	379	24%	76%		
Methylhydrazine	1.6	100%			
N,N-Dimethylformamide	29	18%	82%		
Nitrobenzene	0.24	100%			
O-Dichlorobenzene	202		100%		
Pentachlorophenol	0.000005	100%			
Phenol	108	100%			
Phosphine	0.43	51%	49%		
Phosphorus Compounds	38	55%	45%		
Phthalic Anhydride	0.38	100%			
Polychlorinated Biphenyls (Aroclors)	0.0006	91%	9%		
Polychlorinated Dibenzo-P-Dioxins And Furans, Total	0.00001	100%			
Polychlorinated Dibenzodioxins, Total	0.009	8%	92%		
Propionaldehyde	218	2%		37%	61%
Propylene Dichloride (1,2-Dichloropropane)	0.10	3%	97%		
Propylene Oxide	0.32	100%			
Quinoline	0.0001	100%			
Quinone (p-Benzoquinone)	0.9	100%			
Styrene	1418	73%		20%	8%
Tetrachloroethylene (Perchloroethylene)	202	19%	81%		
Toluene	27872	4%	19%	33%	44%
Trichloroethylene	213	93%	7%		
Trichlorofluoromethane (CFC-11, R-11)	20	1%	99%		
Trichlorotrifluoromethane (CFC-113, R-113)	277		100%		
Triethylamine	2.3	13%	87%		
Trifluralin	42		100%		
Trimethylbenzene	44	18%	82%		
Vinyl Acetate	21	70%	30%		
Vinyl Chloride	6.7	6%	94%		
Vinylidene Chloride (1,1-Dichloroethylene)	1.2	9%	91%		
Xylenes (Mixed Isomers)	14797	7%	24%	35%	34%
m-Xylene	1.7	9%	91%		
o-Xylene	104	4%	96%		
p-Dioxane	6.2	99%	1%		
p-Phenylenediamine	0.05	100%			
p-Xylene	0.07	100%			
Non-Metal Compound Total	105336	21%	26%	25%	27%
Grand Total	106436	22%	26%	25%	27%

The following pie chart summarizes air toxics pollutant emissions in Minnesota from 1999. Each principal source category is responsible for approximately a quarter of total emissions with slightly more from non-road mobile sources (26.9%) and slightly less from point sources (21.5%).

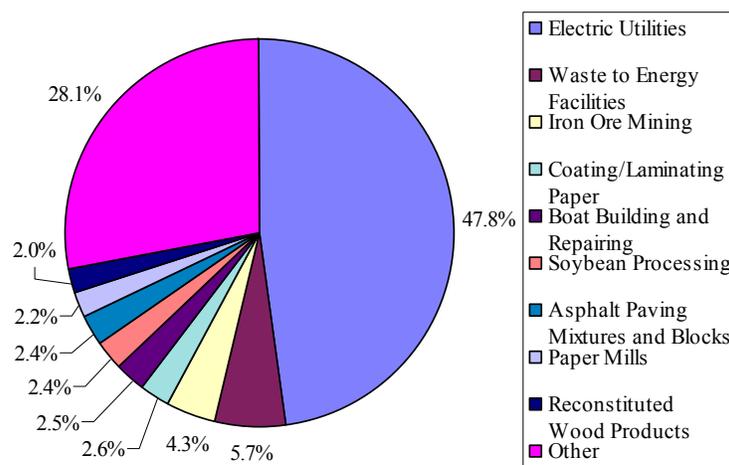
Contribution of Principal Source Categories to 1999 Air Toxics Emissions in Minnesota



Total air toxics emissions in 1999: 212,872,544 pounds

A more detailed breakdown of emissions for each principal source category is shown in the following three pie charts. For point sources, there are nine categories that collectively account for about 72% of the total point source emissions. The largest source category is Electric Utilities, which accounts for 47.8% of point source emissions.

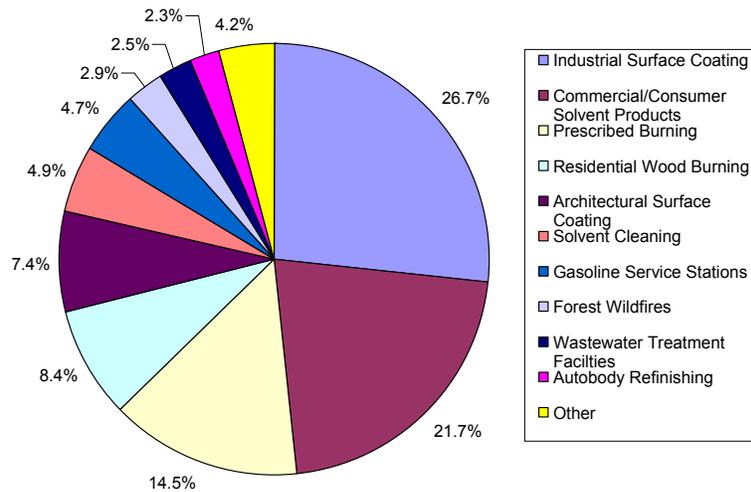
Contribution of Major Categories to 1999 Point Source Air Toxic Emissions in Minnesota



Total air toxics point source emissions: 45,774,769 pounds

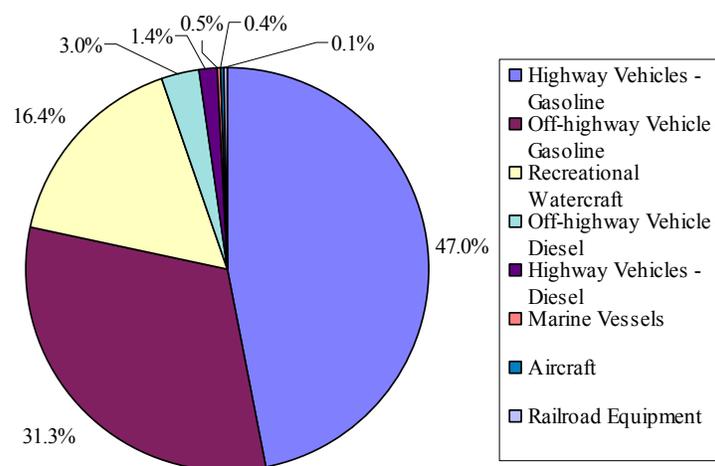
For area sources, the major contributors of emissions are Industrial Surface Coating and Commercial/Consumer Solvent Products. About half of the area source emissions are attributed to these two source categories.

Contribution of Major Categories to 1999 Area Source Emissions of Air Toxics in Minnesota



For mobile sources, the largest emission contributor is Highway Vehicles – Gasoline, which accounted for 47% of total mobile source emissions in 1999. The second largest contributor of mobile source emissions is Off-highway Vehicle – Gasoline, mainly Recreational Equipment. Snowmobiles contribute a significant fraction (70%) of emissions from Recreational Equipment.

Contribution of Major Categories to 1999 Mobile Source Emissions of Air Toxics in Minnesota



Total emissions from mobile sources of air toxics in 1999: 111,106,673 pounds

For more information on air toxics, the Minnesota Air Toxics Emission Inventory and the Great Lakes Air Emissions Inventory, see the following web sites:

<http://www.pca.state.mn.us/air/toxics.html>

<http://www.epa.gov/ttn/atw/index.html>

<http://www.glc.org/air/inventory/>

Chapter 2: Water Pollutant Discharges Overview

Minnesota's rivers, streams and lakes provide great natural beauty, and supply the water necessary for recreation, industry, agriculture and aquatic life. The MPCA is the state agency responsible for protecting Minnesota's water quality. The major goal of the MPCA's water-quality program is to protect and improve Minnesota's rivers, lakes, wetlands and ground water so that they meet designated public uses such as fishing, swimming and drinking water and support healthy aquatic communities. The key strategies for accomplishing this goal include regulating point-source discharges, controlling nonpoint sources of pollution, and assessing water quality to provide information and data for sound environmental management decisions.

Point sources consist mainly of municipal and industrial wastewater discharges, the vast majority of which enter streams and rivers. Point sources are most significant during periods of low precipitation and stream flow. Nonpoint sources include runoff from agricultural fields, feedlots, urban areas, and on-site sewage treatment systems. Nonpoint sources are most significant during periods of high precipitation and stream flow.

Minnesota has been successful in controlling end-of-pipe discharges from wastewater treatment plants and industries to our state's waters. But at the same time, the challenges posed by nonpoint sources of pollution, for example, runoff from cities and agricultural areas, are increasing in proportion with changing land uses and expanding population and development.

The federal Clean Water Act requires states to adopt water quality standards to protect the nation's waters. These standards define how much of a pollutant can be in a surface or ground water supply while still allowing it to meet its designated uses, such as for drinking water, fishing, swimming, irrigation or industrial purposes.

For each pollutant that causes a water resource to fail to meet state water quality standards, the federal Clean Water Act requires the MPCA to conduct a Total Maximum Daily Load (TMDL) study. A TMDL study identifies both point and nonpoint sources of each pollutant that fails to meet water quality standards. Rivers and streams may have several TMDLs, each one determining the limit for a different pollutant. Many of Minnesota's water resources cannot currently meet their designated uses because of pollution from a combination of point and nonpoint sources.

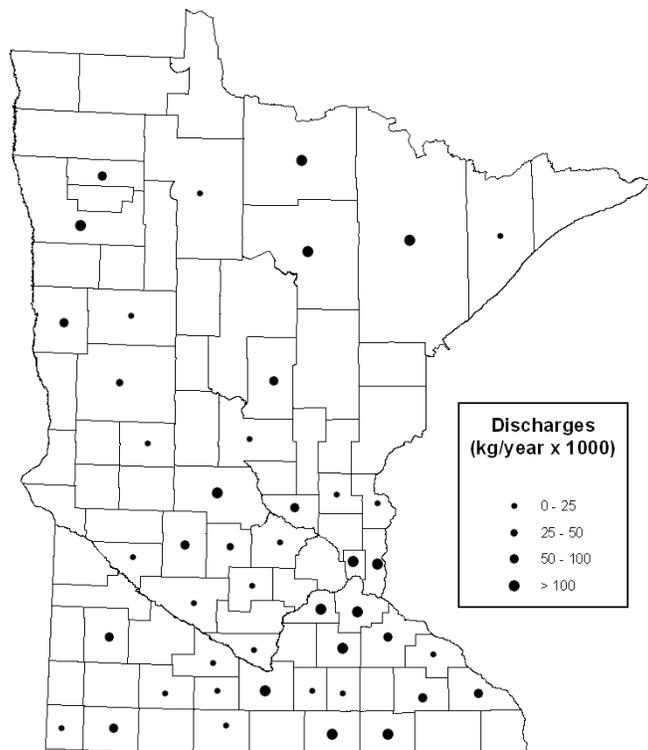
Major Water Discharge Parameters and Trends

This section presents the following water pollutants that are released by major facilities (point sources) into Minnesota's waters: total suspended solids (TSS); biochemical oxygen demand (BOD); total phosphorus (TP); nitrate (NO₃); and ammonia (NH₃). The MPCA continues to investigate ways to effectively measure and report water pollution from nonpoint sources. A summary table of the data from 1997-2001 (the most recent years for which data are available) and an analysis of trends for these pollutants are found on page 3 of this report.

Total Suspended Solids

Total suspended solids (TSS) is a measure of the material suspended in water or wastewater. Total suspended solids cause interference with light penetration, buildup of sediment and potential degradation of aquatic habitat. Suspended solids also carry nutrients that cause algal blooms that are harmful to fish and other aquatic organisms. Based on results of Discharge Monitoring Reports for 85 major treatment facilities, the estimated discharge of TSS to waters of the state for the year 2001 was 8,552,000 kilograms. This was an increase of just over 40 percent from the 5,119,000 kilograms reported in 2000. Much of this increase was likely due to rapid snowmelt, heavy spring rains and high runoff rates, especially in southern Minnesota. The state map below shows the 2001 TSS discharges to surface waters by major point sources of water pollutants, aggregated by county.

Total Suspended Solids Discharges from Major Point Sources, 2001

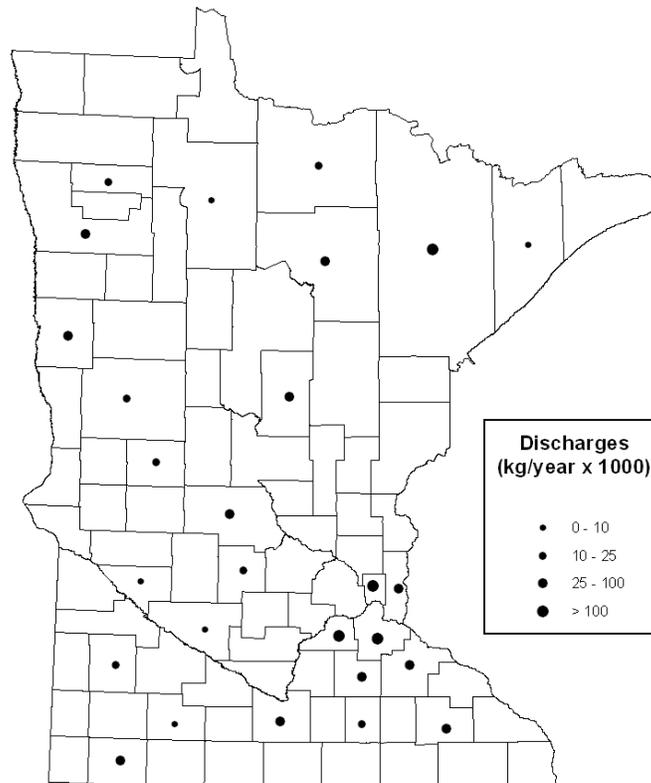


Biological Oxygen Demand and Carbonaceous Biological Oxygen Demand

When organic wastes are introduced into water, they require oxygen to break down. High concentrations of organic materials characterize untreated domestic wastes and many industrial wastes. The amount of oxygen required for decomposition of organic wastes by microorganisms is known as biological oxygen demand (BOD). The carbonaceous biological oxygen demand (CBOD) is the amount of oxygen required for microorganisms to decompose carbonaceous waste materials. Both BOD and CBOD are indicators of the strength of waste effluent and the effectiveness of treatment. A high demand for oxygen (the higher the value for BOD or CBOD) causes reduction in the concentration of dissolved oxygen in the receiving waters. Depletion of oxygen deteriorates water quality and impacts aquatic life, including fish and other organisms. Since their effects on receiving waters are similar, discharge data for BOD and CBOD have been combined in Table 2 of this report.

Based on results of Discharge Monitoring Reports for 85 major treatment facilities, the estimated discharge of the combined total of BOD and CBOD to waters of the state for the year 2001 was 4,920,000 kilograms. As with total suspended solids, the combined discharge of BOD and CBOD showed a significant increase, about 30 percent, over the year 2000. As with TSS, rapid snowmelt, heavy spring rains and high runoff rates likely contributed to this increase. The state map below shows the 2001 CBOD discharges to surface waters by major point sources of water pollutants, aggregated by county. Distribution of discharges for BOD is similar.

Carbonaceous Biological Oxygen Demand Discharges from Major Point Sources, 2001

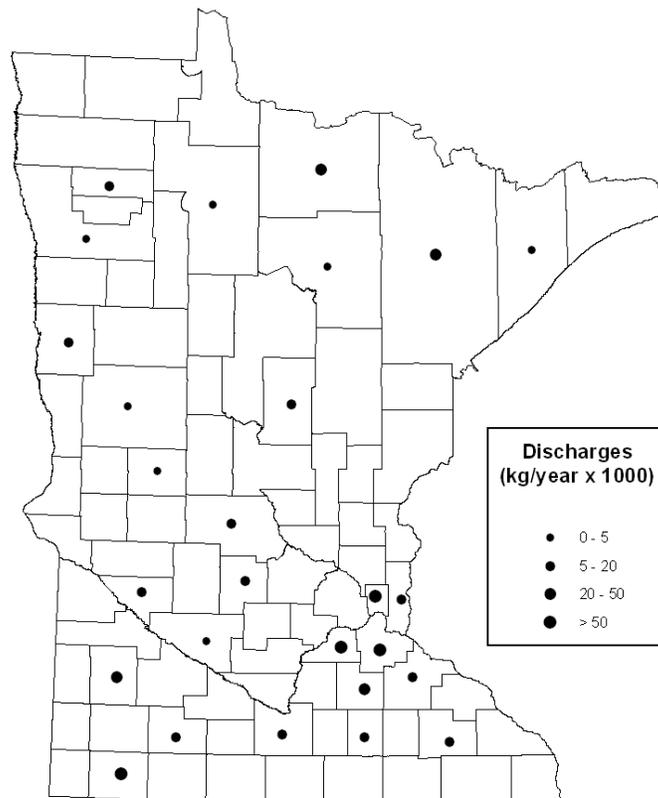


Total Phosphorus

Total phosphorus (TP) is the primary pollutant associated with the eutrophication of surface water from anthropogenic sources (sources that result from human activities). Excess phosphorus causes algae blooms and reduced water transparency, making water unsuitable for swimming and other activities. Phosphorus is released from both point and nonpoint sources of pollution. Minnesota has had point source effluent limitations for phosphorus since the early 1970s. According to Minn. Rule 7050.0211 subp. 1a, “Where the discharge of effluent is directly to or affects a lake or reservoir, phosphorus removal to one milligram per liter shall be required. In addition, removal of nutrients from all wastes shall be provided to the fullest practicable extent whenever sources of nutrients are considered to be actually or potentially detrimental to the preservation or enhancement of designated waters.”

Based on results of Discharge Monitoring Reports for 85 major treatment facilities, the estimated discharge of TP to waters of the state for the year 2001 was 1,374,000 kilograms, a decrease of 4.6 percent from 2000. Treatment advances combined with continued progress in removal of phosphorus from the waste stream likely contributed to the decline. Dilution due to high spring flow rates may also have been a factor. The state map below shows the 2001 TP discharges to surface waters by major point sources, aggregated by county.

Total Phosphorus Discharges from Major Point Sources, 2001

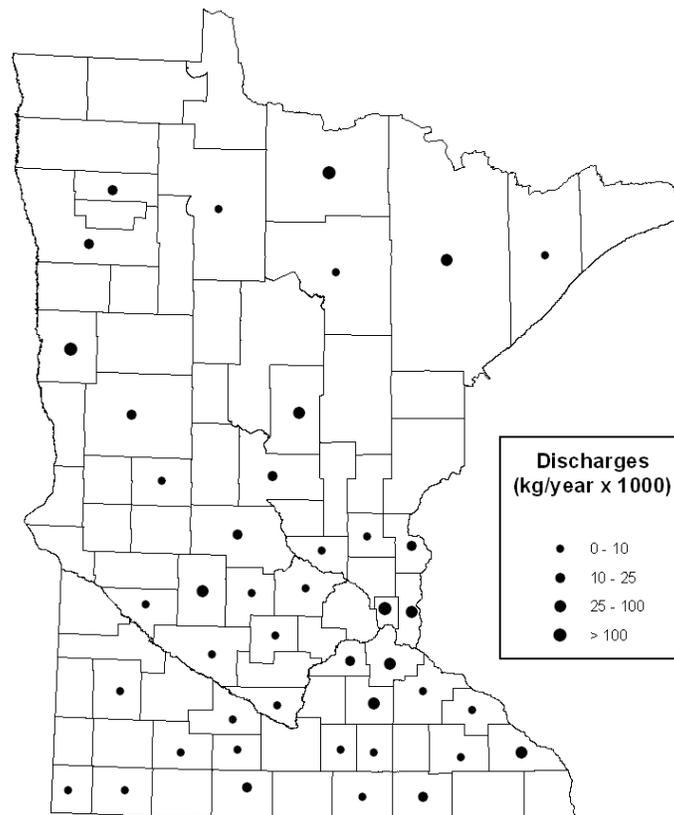


Nitrogen

Nitrogen, generally occurring as nitrate (NO_3) or ammonia (NH_3), is present in a wide variety of effluents including sewage (wastewater treatment plants and on-site sewage facilities), food processing wastes, mining effluents, landfill leachate, and agricultural and urban runoff. Nitrate and/or ammonia concentrations in most of these sources are monitored under permit requirements. Nitrogen as ammonia can be toxic to aquatic life and nitrogen in the form of nitrate can be a significant problem in ground water supplies. Nonpoint sources of nitrogen from agricultural and urban runoff are an important source of loading to waters of the state, although very little of this contribution is captured through Discharge Monitoring Reports required by permit.

Based on the results of Discharge Monitoring Reports for 85 major treatment facilities, the estimated discharges for the year 2001 were 1,023,000 kilograms of ammonia and 4,276,000 kilograms of nitrate, a decrease of 20.2 percent and 8.7 percent respectively. For nitrate, the decrease continues a trend that began in 1998. After increasing somewhat from 1999-2000, ammonia discharges decreased significantly in 2001. The state map below shows the 2001 ammonia discharges to surface waters by major point sources of water pollutants. Distribution of discharges for nitrate is similar.

Ammonia Discharges from Major Point Sources, 2001



Nonpoint Source Pollution

Minnesota has made significant progress in cleaning up point sources of water pollution as measured by discharges of major pollutants in municipal and industrial wastewater. An indicator of this success is shown by the fact that the 85 major treatment facilities discharging more than one million gallons per day have cut their total volume of discharge to waters of the state by over 3,000,000 kilograms since 1997, even accounting for the high flow conditions observed during the spring and summer of 2001.

It is the nonpoint sources of pollution from rainfall or snow melt moving over or through the ground carrying natural and human-made pollutants into lakes, rivers, wetlands and ground water that now pose the greater challenge for cleanup. Both point and nonpoint sources of pollution must be controlled to reach the Clean Water Act goal of fishable, swimmable waters in the state. Too much phosphorus and nitrogen continue to reach our lakes, rivers and shallow ground water aquifers, carried in soil erosion and runoff from roads, yards, farms and septic systems.

Many of the stresses from nonpoint sources of pollution that affect our surface and ground water resources are the result of choices that individuals make every day in their homes, in their yards and on their farms. The daily decisions that homemakers, developers, farmers and businesses make regarding land use are crucial to protecting water resources from the effects of nonpoint source pollution. Once a water resource declines in quality, recovery is costly and can take many years. Clearly, prevention is the key when it comes to nonpoint source pollution. What happens to Minnesota's water resources in the next 10 years will help determine the quality of those resources for the next 100 years.

The effects of nonpoint source pollution on a water resource are difficult and expensive to measure. The best long-term data about Minnesota streams comes from measuring six key pollutants at 80 stream locations over the past 40 years. These locations are chosen to not be unduly influenced by the effects of point source pollution, although the results certainly reflect the contribution of all discharges upstream of the monitoring point. The results agree well with those shown by point source discharges from Discharge Monitoring Reports in that significant reductions in ammonia and phosphorus have been observed. Nitrogen (NO₃), which is generally associated with nonpoint sources of pollution, increased over the same period, although as shown in Table 2, recent improvements have been made in removing nitrate from point source discharges. Ground water data collected by MPCA from 1992-1996 show that in aquifers that are sensitive to nitrate contamination, 60 percent of the wells monitored had nitrate levels above one part per million (ppm), suggesting some possible anthropomorphic impacts to the aquifer that the well taps. Of these, 18 percent contained nitrates above the drinking water standard of 10 ppm. Again, much of this is likely due to the effects of land use practices at the surface and the effects of nonpoint source pollution.

For a further discussion of the effects of nonpoint source pollution on Minnesota's water resources see:

<http://www.pca.state.mn.us/about/pubs/mnereport/>

Appendix A

Emerging Contaminants of Concern*

One of the greatest challenges of recent decades in protecting the environment is that the mix of chemicals used by society is continually changing. New compounds, or their by-products, eventually find their way into the waste stream, and can ultimately become part of what we inhale, eat, and drink. How do local and national agencies keep up with continuous change? This summary explores contaminants, unknown or practically unnoticed just a few years ago, that are emerging as a concern today and the research being undertaken and supported by the MPCA to understand the issues surrounding these contaminants.

Increasing knowledge of the environmental occurrence or toxicological behavior of emerging contaminants has resulted in concern for potential adverse environmental and human health effects. The lack of knowledge of the processes controlling contaminant transport and fate in the environment, and of the magnitude of exposure to ecological species and humans, has increased the need to study the presence of these contaminants in the environment. Public health experts have an incomplete understanding of toxicological effects of these contaminants, including the significance of long-term exposure.

But even with incomplete knowledge, science and policy must continue to evolve to speed the process of identifying and preventing problems, to ensure protection of human health and the environment. The MPCA has been tracking and contributing to information on emerging contaminants being identified by researchers in academia, government, and private industry. Polybrominated diphenyl ethers (PBDEs), brominated dioxins and furans, perfluorooctane sulfonate (PFOS), pharmaceuticals and industrial and household wastewater products, including personal care products, are contaminants under investigation as environmental contaminants of concern.

Polybrominated Diphenyl Ethers (PBDEs)

In recent years, unexpected and undesirable consequences from the widespread use of polybrominated diphenyl ethers (PBDEs) have been observed. PBDEs are used as additive flame retardants in plastics, textiles, coatings, and electrical components in products such as computers, TVs, electrical appliances, furniture, building materials, carpets, and automobiles¹. These chemicals have been found to persist in the environment and bioaccumulate in humans and wildlife^{2,3}. Concerns about PBDEs stem from their similarities in structure and properties to polychlorinated biphenyls (PCBs), chemicals with known bioaccumulative and toxic properties.

The toxicological profile of PBDEs suggests that exposure may interfere with development, behavior, and reproduction^{5,6}. Experimental animal studies have shown that prenatal exposure to PBDEs can affect neurodevelopment, resulting in decreased motor function⁷. Skeletal abnormalities were also observed in rodents exposed prenatally to mixtures of PBDE congeners. Adult animals exposed to PBDEs have exhibited decreased reproductive success and impaired immune function. PBDEs can affect the normal functioning of endocrine or hormone systems and neurotransmitters in the central nervous system, both

** Fardin Oliaei and Angela Preimesberger from the MPCA's Outcomes Division summarized the information in the appendix on emerging contaminants of concern.*

possible mechanisms of action behind the observed health effects in experimental animals. Thyroid disruption was one of the most common and sensitive endpoints observed in animal studies⁷. Thyroid and neurological effects have also been observed in workers exposed to PBDEs and other brominated chemicals.

PBDEs have been detected globally in developed and remote environments. Monitoring studies have measured PBDEs in sediment, air, wildlife, fish, human blood, and human milk^{2,3,8,9}. A human-milk monitoring program in Sweden indicates that PBDE concentrations in breast milk are doubling every five years¹⁰. Similar studies of breast milk conducted in other countries support the findings that human exposure to PBDEs is increasing^{11,12}. Monitoring and assessment of PBDEs in North America has only begun recently. In the Great Lakes, PBDE concentrations were measured in lake trout and salmon from Lakes Erie, Huron, Superior, and Ontario. When concentrations were compared on a fat basis, the fish from Lake Ontario had the highest concentrations of PBDEs, followed by Superior, Huron, and Erie^{13,14,15,16}. The relatively high level of PBDEs in Lake Superior fish is surprising due to the more pristine character of this lake.

Recently, the MPCA conducted a study titled “Occurrence and Concentrations of Polybrominated Diphenyl Ethers (PBDEs) in Minnesota Environment.” The study focused on areas where PBDEs were most likely to be present with the assumption that if PBDEs are not found in these targeted areas, PBDEs are not likely to be a problem in more ambient locations in Minnesota. The targeted systems were landfill leachates, wastewater treatment plant (WWTP) sludges and effluents, as well as, fish and sediment collected from rivers below WWTP effluent discharges. Collecting fish and sediment samples from the major river basins in Minnesota (Mississippi, St. Louis, Red, Rainy, Minnesota and St. Croix) ensured geographical representation. PBDEs were detected in all sample categories at all sites.

The data from the investigation indicated that PBDEs are an environmental contaminant in Minnesota. The MPCA will begin creating a database of PBDE concentrations in Minnesota. Models designed to predict the transport and fate of PBDEs in aquatic ecosystems will use the data collected in the PBDE study. Measuring fish PBDE contamination helps to explain the movement and bioaccumulation of PBDEs in the aquatic food chain and predict potential exposure to humans from eating fish. The results of this study will help the MPCA to better understand the environmental impacts of PBDEs as an emerging contaminant in Minnesota; knowing the levels of background PBDE contamination will help establish benchmarks to guide future monitoring efforts and to track environmental trends.

Polybrominated Dioxins and Furans

The term PBDDs/PBDFs refers to a group of toxic chemicals, consisting of polybrominated dibenzo dioxins and polybrominated dibenzo furans. These compounds have similar chemical structures and mode-of-action biological characteristics to polychlorinated dibenzo dioxins and polychlorinated dibenzo furans. Chlorinated and brominated dioxins are by-product of a number of human activities. Major contributors of chlorinated dioxin to the environment include: municipal solid waste and medical incinerators, backyard trash burning, cement kilns, pulp and paper bleaching plants, herbicide manufacture, copper smelters and iron sintering plants. Incineration of products containing brominated compounds and flame retardants (plastics and electrical appliances) results in emissions of brominated dioxins³. Brominated and chlorinated dioxin may also have natural sources, but they are small compared to emissions arising from human activities.

Brominated and chlorinated dioxins are persistent, accumulate in biological tissues and enter the human body through consumption of contaminated fish, meat and dairy products. As a result, most people have detectable chlorinated dioxin levels in their tissues, because of a lifetime of exposure and bioaccumulation. This “background exposure” may result in an increased risk of cancer and is close to

levels that can cause adverse non-cancer effects in humans and animals (U.S. EPA, Persistent, Bioaccumulative, and Toxic Initiative, 2000). Public health and environmental concerns about dioxin stem from studies linking exposure with a broad spectrum of adverse effects, including reproductive and developmental abnormalities, suppression of the immune system, and cancer. (U.S. EPA, Summary of Dioxin Reassessment Science, 2000).

Chlorinated dioxins are contaminants of concern in Lake Superior and it is important to assess the environmental prevalence of both chlorinated and brominated dioxins and furans in the Western Lake Superior watershed and St. Louis River Area of Concern. The MPCA plans to have the same fish and sediment composites collected from six major rivers in Minnesota for PBDE analyses in 2001 analyzed for brominated dioxins. There are also plans to have wastewater treatment plant sludges, landfill leachates and landfill sludges, also sampled for the PBDE study, analyzed for these chemicals.

Pharmaceuticals and Household and Industrial Wastewater Products

A new area of environmental research is focusing on pharmaceuticals and household and industrial wastewater contaminants, including personal care products detected in the environment. Human and veterinary antibiotics and other prescription and non-prescription drugs, natural and synthetic hormones, detergents, disinfectants, plasticizers, fire retardants, insecticides, and antioxidants are all examples of pharmaceutical and wastewater contaminants¹⁷. Sources of these contaminants, many of which originate in common medications and household products, include wastewater treatment facilities, septic systems, animal feedlots, and medical industry discharges.

A recent study by the Toxic Substances Hydrology Program of the US Geological Survey (USGS) shows that a broad range of pharmaceuticals and household and industrial wastewater products, also called organic wastewater contaminants (OWCs), are found in mixtures at low concentrations downstream from areas of intense urbanization and animal production¹⁷. Eighty percent of the streams sampled had one or more OWCs. The most abundant substances were insect repellents, non-prescription drugs, detergents, antibiotics, caffeine, and cotinine, a byproduct of tobacco. Difficulties measuring pharmaceuticals and personal care products occur, because many of the degradation products are unknown, drug compositions constantly change, and little data exists on environmental contamination. Implications of these substances being in the environment range from human and ecosystem health effects, possible cumulative and synergistic toxicity, and increased antibiotic resistance¹⁷. The toxicity and environmental chemistry of most OWCs are not well known. Future research in this area should seek to improve analytical methods and determine concentrations in sediments and tissue.

During 2001, the MPCA began a cooperative study with USGS to assess the presence of several classes of pharmaceuticals, hormones, and industrial and household wastewater products in Minnesota waters (Table 4). The objective was to determine whether selected Minnesota streams and groundwater resources contain measurable amounts of these biologically-active chemicals. The study included water sampled from the main rivers of the state (Minnesota, Mississippi, Red, Rainy, St. Croix, and St. Louis) below WWTPs and at several smaller streams that have relatively high contributions from WWTP effluents (low dilution streams). We have also sampled groundwater near septic systems, urban areas, and feedlots that may be contaminated by these chemicals. The study also assessed the presence of these chemicals in the waste stream by sampling wastewater treatment plant effluents and landfill leachates. USGS is in the process of analyzing samples and compiling results. USGS is also working with the Minnesota Department of Health (MDH) to evaluate the presence of these chemicals in ambient waters that serve as sources of drinking water in Minnesota.

Table 4: Pharmaceuticals and Household and Industrial Wastewater Products

Veterinary and Human Antibiotics	
<p><u>Tetracyclines</u></p> <ul style="list-style-type: none"> Chlortetracycline Doxycycline Oxytetracycline Tetracycline <p><u>Fluoroquinolones</u></p> <ul style="list-style-type: none"> Ciprofloxacin Enrofloxacin Norfloxacin Sarafloxacin <p><u>Macrolides</u></p> <ul style="list-style-type: none"> Erythromycin-H₂O (metabolite) Tylosin Roxithromycin 	<p><u>Sulfonamides</u></p> <ul style="list-style-type: none"> Sulfachlorpyridazine Sulfamerazine Sulfamethazine Sulfathiazole Sulfadimethoxine Sulfamethiazole Sulfamethoxazole <p><u>Others</u></p> <ul style="list-style-type: none"> Lincomycin Trimethoprim Carbadox Virginiamycin

Human Drugs	
<p><u>Prescription</u></p> <ul style="list-style-type: none"> Metformin (antidiabetic agent) Cimetidine (antacid) Ranitidine (antacid) Enalaprilat (antihypertensive) Digoxin Diltiazem (antihypertensive) Fluoxetine (antidepressant) Paroxetine (antidepressant, antianxiety) Warfarin (anticoagulant) Salbutamol (asthmatic) Gemfibrozil (antihyperlipidemic) Dehydronifedipine (antianginal metabolite) Digoxigenin (digoxin metabolite) 	<p><u>Non-Prescription</u></p> <ul style="list-style-type: none"> Acetaminophen (analgesic) Ibuprofen (anti-inflammatory, analgesic) Codeine (analgesic) Caffeine (stimulant) 1,7-Dimethylxanthine (caffeine metabolite) Cotinine (nicotine metabolite)

Table 4: Pharmaceuticals and Household and Industrial Wastewater Products cont.

<p><u><i>Insecticides</i></u> Diazinon Carbaryl Chlorpyrifos <i>cis</i>-Chlordane N,N-diethyltoluamide (DEET) Lindane Methyl parathion Dieldrin</p> <p><u><i>Plasticizers</i></u> <i>bis</i>(2-Ethylhexyl)adipate Ethanol-2-butoxy-phosphate <i>bis</i>(2-Ethylhexyl)phthalate Diethylphthalate Triphenyl phosphate</p> <p><u><i>Detergent metabolites</i></u> <i>p</i>-Nonylphenol Nonylphenol monoethoxylate (NPEO1) Nonylphenol diethoxylate (NPEO2) Octylphenol monoethoxylate (OPEO1) Octylphenol diethoxylate (OPEO2)</p> <p><u><i>Fire retardants</i></u> Tri(2-chloroethyl)phosphate Tri(dichlorisopropyl)phosphate</p>	<p><u><i>Polycyclic aromatic hydrocarbons (fossil fuel and fuel combustion indicators)</i></u> Naphthalene Phenanthrene Anthracene Fluoranthene Pyrene Benzo(<i>a</i>)pyrene</p> <p><u><i>Antioxidants</i></u> 2,6-di-<i>tert</i>-Butylphenol 5-Methyl-1H-benzotriazole Butylatedhydroxyanisole (BHA) Butylatedhydroxytoluene (BHT) 2,6-di-<i>tert</i>-Butyl-<i>p</i>-benzoquinone</p> <p><u><i>Others</i></u> Tetrachloroethylene (solvent) Phenol (disinfectant) 1,4-Dichlorobenzene (fumigant) Acetophenone (fragrance) <i>p</i>-Cresol (wood preservative) Phthalic anhydride (used in plastics) Bisphenol A (used in polymers) Triclosan (antimicrobial disinfectant)</p>
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Sex and Steroidal Hormones	
<p><u><i>Pharmaceuticals</i></u> 17<i>a</i>-Ethinylestradiol (ovulation inhibitor) Mestranol (ovulation inhibitor) 19-Norethisterone (ovulation inhibitor) Equilenin (hormone replacement therapy) Equilin (hormone replacement therapy)</p>	<p><u><i>Biogenics</i></u> 17<i>b</i>-Estradiol 17<i>a</i>-Estradiol Estrone Estriol Testosterone Progesterone <i>cis</i>-Androsterone</p> <p><u><i>Sterols</i></u> Cholesterol (fecal indicator) 3<i>b</i>-Coprostanol (carnivore fecal indicator) Stigmastanol (plant sterol)</p>

Perfluorooctane Sulfonate (PFOS)

Another class of chemicals generating concern is fluorinated surfactants, particularly perfluorooctane sulfonate (PFOS)¹⁸. PFOS is used in the manufacture of numerous products, and is thought to be a metabolite of several fluorinated surfactants. The uses of fluorinated surfactants are numerous and diverse: fabric and leather protectors, fire fighting foams, adhesives, pesticide formulations, and paper coatings. 3M primarily produced PFOS as a key ingredient in the fabric protector, Scotchgard, and for paper coating¹⁸. In spring 2000, 3M announced the elimination of their line of PFOS-related products by 2002.

Extremely resistant to environmental breakdown, PFOS is now a ubiquitous contaminant found in reptiles, amphibians, fish, and fish-eating mammals and birds across North America and in people from the United States^{19,20}. Traditional methods for analyzing persistent pollutants missed PFOS exposure for a long time, because unlike most persistent, bioaccumulative toxic chemicals, PFOS doesn't accumulate in fatty tissue¹⁹. Instead, the properties of PFOS result in protein binding, and accumulation in blood and liver tissue. According to EPA (2000), PFOS persists in humans and animals, with an estimated half-life of 4 years in humans. Experimental animal studies have found nervous system, liver, and developmental toxicity after PFOS exposure¹⁸.

Future research is needed on PFOS to assess its presence and persistence in the environment, humans, and ecological species. The MPCA is working with the Duluth Environmental Protection Agency (EPA) to have carp collected below WWTP discharges analyzed for PFOS. This data will provide preliminary information on PFOS contamination in Minnesota's resources.

Supporting References

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