

Air Toxics Monitoring in the Twin Cities Metropolitan Area

Preliminary Report

Minnesota Pollution Control Agency
January 2003

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Summary

The Minnesota Legislature appropriated \$250,000 for the fiscal year 2002-2003 biennium for increased monitoring of air pollutants by the Minnesota Pollution Control Agency (MPCA) in the Twin Cities metropolitan area. This appropriation was in response to MPCA reports on air quality and two Environmental Protection Agency (EPA) air modeling projects which highlighted potential air quality concerns in the Twin Cities. In addition, citizen groups have become increasingly concerned about the effects of air pollution on public health.

The funding was used to increase the number of monitors in the metropolitan air monitoring network by opening three new sites and adding monitors to two current monitoring locations. Each of the five sites now monitor for air toxics, including volatile organic compounds (VOCs) and carbonyls, total suspended particulate (TSP), and fine particulate matter (PM_{2.5}).

This report is considered preliminary since only three to nine months of data has been collected and analyzed, covering the period of January through September 2002. The concentration data for individual chemicals was compared to their respective health benchmarks or standards to get a general understanding of potential health effects from breathing ambient air. Differences between monitoring sites were also analyzed to determine if certain neighborhoods in the Twin Cities experience higher levels of air pollutants.

This preliminary analysis came to the following conclusions:

- According to MPCA air monitoring, average formaldehyde concentrations were above its health benchmark in the Twin Cities.
- Average benzene concentrations were above the lower range of its health benchmark at two monitoring locations.
- Of the remaining 44 compounds monitored by the MPCA, 21 were below the detection limit, 15 were detected but were below health benchmarks, and 6 did not have an available health benchmark.
- The majority of monitoring sites throughout the Twin Cities did not have significant differences in concentrations of the 44 pollutants monitored.
- Although PM_{2.5} concentrations are currently below the annual National Ambient Air Quality Standard, the MPCA should continue to track trends and follow ongoing scientific literature regarding health effects since effects may occur below the current standard.

In 2003, the MPCA plans to continue with the following steps:

- Complete at least a full year of data collection and analysis at all monitoring sites.
- Begin metal analysis of the particles captured on TSP filters for a better understanding of metal concentrations in the Twin Cities area.
- Complete seasonality and source apportionment for pollutants and sites of particular concern.
- Include a cumulative exposure analysis of pollutants, taking into account that exposures do not occur in isolation.

Although funds are not available for this work, the MPCA believes it would also be valuable to:

- Improve emissions inventories and regional air quality modeling of the Twin Cities to better identify hot spots; and
- Monitor for semi-volatile chemicals such as PAHs and dioxin to help better define the risks of air pollution in the Twin Cities metropolitan area

1. Introduction

This report fulfills the requirement (Minnesota Laws 2001, First Special Session, Chapter 2, Section 2, Subdivision 3) to submit to the Legislature a summary and analysis of the results of monitoring ambient air for hazardous pollutants in the metropolitan area by January 1, 2003. The Legislature appropriated \$250,000 for the fiscal year 2002-2003 biennium for increased monitoring of hazardous pollutants by the Minnesota Pollution Control Agency (MPCA) in the Twin Cities metropolitan area.

The MPCA has reported on the air quality in Minnesota and the metropolitan area in several reports including the *Staff Paper on Air Toxics*ⁱ in November 1999 and a January 2001 legislative report entitled *Air Quality in Minnesota: Problems and Approaches*ⁱⁱ. These reports have highlighted potential health concerns from hazardous air pollutants or air toxics. The reports summarized information from MPCA's air toxics monitoring network and from the Environmental Protection Agency's Cumulative Exposure Project (CEP) and the National-Scale Air Toxics Assessment (NATA)ⁱⁱⁱ. The CEP and NATA were projects that used computer models to estimate air pollutant concentrations nationwide from emissions data. The CEP used 1990 emissions data while NATA updated the CEP using 1996 emissions information.

The NATA analysis identified 10 pollutants in Minnesota above a health benchmark^{iv}. Of those 10, MPCA ambient air monitoring has confirmed that two of these pollutants (benzene and formaldehyde) are found at concentrations above levels of concern in the Twin Cities metropolitan area.

In addition, citizen groups in North, Northeast and Southeast Minneapolis have become increasingly concerned about the effects of air pollution on public health. Some Minneapolis neighborhoods are located near industrialized areas with emissions from industrial facilities, smaller area sources such as gas stations, and large amounts of vehicular traffic.

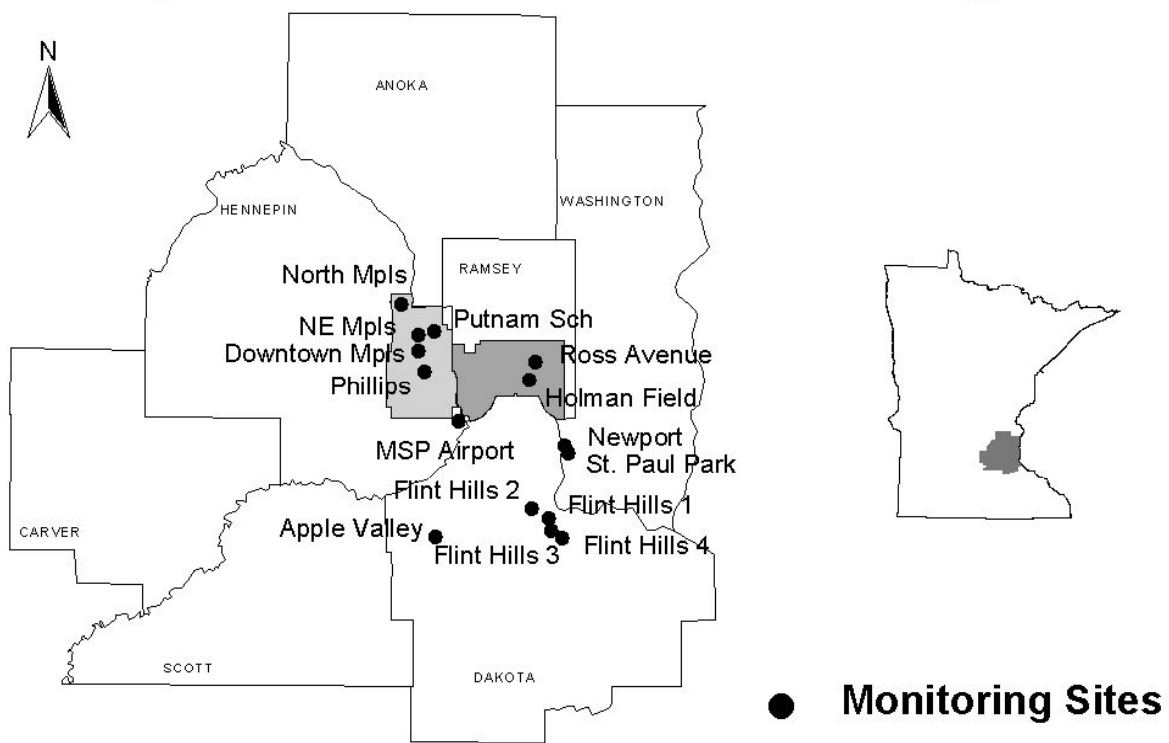
The MPCA currently has a metropolitan area ambient air monitoring network in place. In response to the legislative appropriation, the MPCA increased the number of monitors in the Twin Cities area by opening three new sites and adding monitors to two current monitoring locations. Each of the sites now monitor for fine particulate matter (PM_{2.5}), volatile organic compounds (VOCs), a subset of VOCs called carbonyls, and total suspended particulate (TSP). The appropriation is being used to operate and maintain the monitoring sites as well as to analyze and report the resulting data. The new sites are given in Table 1.1.

Table 1.1. Air Monitoring Sites Added for Metropolitan Area Special Study

MPCA Site ID	Site Name	Address	Status	Date Started /Augmented
907	North Mpls	4646 N Humboldt, Mpls	Added VOC and carbonyl monitors	1/14/02
940	NE Mpls	143 13 th Ave NE, Mpls	New monitoring site	2/1/02
963	Phillips	2727 10 th Ave S, Mpls	Added TSP monitor	5/8/02
964	MSP Airport	MSP Airport	New monitoring site	2/1/02
965	Putnam School	1616 Buchanan St, Mpls	New monitoring site	6/6/02

A complete list of MPCA air toxics, PM_{2.5} and TSP monitors can be found in Appendix A. Figure 1.1 shows the locations of MPCA air toxic monitors located in the Twin Cities metropolitan area in 2002.

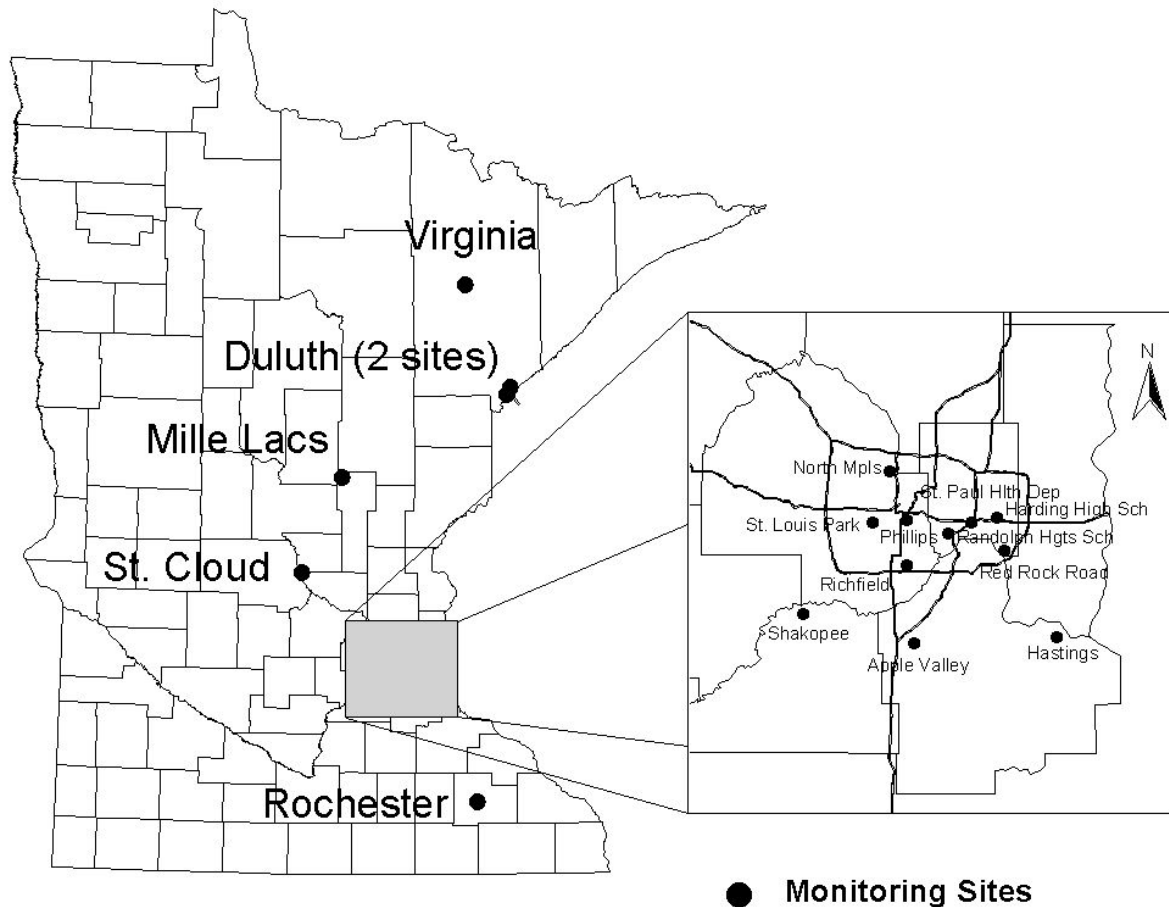
Figure 1.1. Metropolitan Air Toxics Monitoring Sites



MPCA, November 2002

Figure 1.2 shows the locations of MPCA PM_{2.5} monitors located in Minnesota in 2002. This analysis focuses on monitors in the Twin Cities metropolitan area.

Figure 1.2. PM_{2.5} Monitoring Sites



MPCA, November 2002

This special air monitoring study is funded through June 2003. The MPCA hopes to maintain the additional monitoring sites through the end of 2003 using a combination of state base and federal funding. This will provide at least a year of data at each site. This report is preliminary because less than a year of data has been collected at most of the new sites.

Air Pollutants of Concern

The MPCA focused on air toxics and fine particles for this study. Air toxics are substances that have the potential to cause cancer or other serious health problems at high enough exposure levels. Air toxics include VOCs, carbonyls and metals. Concern regarding health effects from fine particles has increased dramatically over the last few years and it is currently a pollutant of interest at the MPCA.

Volatile Organic Compounds (VOCs)

VOCs include pollutants such as benzene. They tend to remain in the air due to their chemical properties and are considered to be primarily a health concern due to people inhaling them when they breathe. Daily human activities in Minnesota emit thousands of different VOCs. Over 400,000 tons of VOCs are released in Minnesota every year. The MPCA has been able to calibrate and standardize the analysis for 37 of them at this time. Based on current available scientific evidence, these 37 compounds include those that are believed to be of greatest concern to human health such as benzene and 1,3-butadiene. By the end of 2003, the MPCA expects to increase the number of VOCs analyzed and reported to 65. Table 1.2 lists the VOCs currently reported by MPCA.

Table 1.2. VOCs Currently Monitored in Ambient Air by the MPCA

#	COMPOUND NAME	CAS # ^y	#	COMPOUND NAME	CAS #
1	(meta & para)-Xylene	108-38-3	20	cis-1,3-Dichloropropylene	10061-01-5
2	1,1,2,2-Tetrachloroethane	79-34-5	21	Dichlorodifluoromethane (Freon 12)	75-71-8
3	1,1,2,3,4,4-Hexachloro-1,3-butadiene	87-68-3	22	Dichloromethane (Methylene chloride)	75-09-2
4	1,1,2-Trichloroethane	79-00-5	23	Dichlorotetrafluoroethane (Freon 114)	76-14-2
5	1,1-Dichloroethane	75-34-3	24	Ethylbenzene	100-41-4
6	1,1-Dichloroethene (Vinylidene chloride)	75-35-4	25	Ethylene chloride (1,2-Dichloroethane)	107-06-2
7	1,2,4-Trimethylbenzene	95-63-6	26	Ethylene dibromide	106-93-4
8	1,2-Dichlorobenzene	95-50-1	27	Methyl bromide	74-83-9
9	1,2-Dichloropropane	78-87-5	28	Methyl chloroform (1,1,1-Trichloroethane)	71-55-6
10	1,3,5-Trimethylbenzene	108-67-8	29	Ortho-Xylene	95-47-6
11	1,3-Butadiene	106-99-0	30	Styrene	100-42-5
12	1,3-Dichlorobenzene	541-73-1	31	Tetrachloroethylene (perchloroethylene)	127-18-4
13	1,4-Dichlorobenzene	106-46-7	32	Toluene	108-88-3
14	4-Ethyltoluene	622-96-8	33	trans-1,3-Dichloropropylene	10061-02-6
15	Benzene	71-43-2	34	Trichloroethylene	79-01-6
16	Carbon tetrachloride	56-23-5	35	Trichlorofluoromethane (Freon 11)	75-69-4
17	Chlorobenzene	108-90-7	36	Trichlorotrifluoroethane (Freon 113)	76-13-1
18	Chloroform (Trichloromethane)	67-66-3	37	Vinyl chloride	75-01-4
19	cis-1,2-Dichloroethylene	156-59-2			

VOC samples are collected following the U.S. federal reference method TO-15^{vi} in evacuated, summa-polished, stainless steel canisters, two-valve model. The canisters are deployed using a Xon Tech model 910A canister sampler. The samples are analyzed using a Varian Saturn model

2000 gas chromatograph/mass spectrometer. VOC samples are collected from midnight to midnight once every six days, which ensures some measurements on each day of the week and in all seasons.

Carbonyls

Carbonyls are a subset of VOCs. They are organic compounds that contain a carbon-oxygen double bond (C=O), such as an aldehyde or ketone. Because of their chemical properties, carbonyl samples must be collected and analyzed separately from the VOCs. Carbonyl samples are collected and analyzed following following U.S. EPA compendium method TO-11A^{vii}. Table 1.3 lists the carbonyls that MPCA monitors. Carbonyls are also collected from midnight to midnight once every six days.

Table 1.3. Carbonyls Currently Monitored in Ambient Air by the MPCA

#	COMPOUND NAME	CAS #	#	COMPOUND NAME	CAS #
1	Acetaldehyde	75-07-0	5	Crotonaldehyde	123-73-9
2	Acetone	67-64-1	6	Formaldehyde	50-00-0
3	Benzaldehyde	100-52-7	7	Propionaldehyde	123-38-6
4	Butyraldehyde	123-72-8			

Total Suspended Particulate (TSP)/Metals

TSP includes all of the particles suspended in the air, regardless of their size. Since TSP is measured by mass, the concentrations are dominated by large particles. Current TSP concentrations, containing the large particle fraction, are generally not considered to be of concern in the metropolitan area. However, the filters that collect TSP can later be analyzed for metals. Some metals such as chromium are of human health concern. The MPCA is collecting TSP in order to analyze metals in the future. TSP samples are collected and analyzed following manual reference method 40 CFR Part 50, Appendix B. Metals will be analyzed using inductively coupled plasma spectroscopy (ICP) following U.S. EPA compendium method IO 3.4^{viii}. TSP is also collected from midnight to midnight once every six days.

The MPCA has not yet begun analyzing the TSP filters from this study for metals, therefore, metals information is not available for this report. MPCA hopes to analyze the collected filters for metals in 2003.

Fine Particulate Matter (PM_{2.5})

PM_{2.5} is a complex mixture of very small droplets and solid particles in the air. They are smaller than 2.5 microns in diameter. PM_{2.5} is associated with increased symptoms, hospitalizations and deaths due to respiratory disease, lung cancer and heart disease and can worsen the symptoms of

asthma. MPCA has a growing concern about concentrations of PM_{2.5} in metropolitan air. The PM_{2.5} for this study was collected on filters according to the U.S. federal reference method RFPS-0598-119. The filters are collected from midnight to midnight, either every day, every third day, or once every six days depending on the monitoring site.

2. Results and Discussion

This report is based on air toxics data MPCA has collected and analyzed through September 2002. Depending on when the monitoring sites for this study were opened or monitors added, three to nine months of data are available. Therefore, this preliminary analysis focuses on general descriptive results. Seasonal and source analysis will be completed after a year of data is available at all sites.

The MPCA air toxics monitoring provides a general understanding of Minnesotans' average long-term exposure to outdoor concentrations of pollutants. Since the concentrations provided by MPCA monitors are averaged over 24 hours and gathered in fixed locations once every six days, the results do not answer questions regarding any short-term higher exposures. In addition, breathing outside ambient air is only one way in which people are exposed to air toxics. Recent studies indicate that the public is exposed to significantly higher concentrations of many air toxics in their homes, workplaces, and vehicles^x.

The preliminary analysis for this study tried to answer two questions: 1) Do individual pollutants monitored in the Twin Cities exceed health benchmarks?; 2) Are pollutant levels higher at certain sites in the metro area? The first question was addressed by comparing the average concentrations found at the sites included in this study with health benchmarks for long term exposures. The second question was addressed by comparing the pollutant concentration averages between the sites^x.

Standards and Health Benchmarks

One way to gain an understanding on whether or not to be concerned about the levels of pollutants in the air is to compare the ambient concentrations to a *standard* or *health benchmark*. *Standards* such as the National Ambient Air Quality Standards (NAAQS)^{xi} are chemical concentrations associated with monitoring requirements, specific averaging times and enforcement consequences. The U.S. EPA tries to set the NAAQS at a concentration below clearly defined human health effects.

An *inhalation health benchmark* is a health-based estimate of specific chemical exposures that are likely to be without appreciable risk of harmful effects on humans. The point at which health effects will occur at exposures to concentrations higher than the inhalation health benchmarks is not precisely known. The MPCA uses inhalation health benchmarks from the Minnesota Department of Health's Health Risk Values (MDH HRVs)^{xii}, the U.S. EPA's Integrated Risk Information System (IRIS)^{xiii}, and the California Office of Environmental Health Hazard Assessment (OEHHA)^{xiv}. For a complete list of health benchmarks used for comparison with MPCA monitoring data see Appendix B.

Because there are economic consequences for exceeding an enforceable *standard*, there is clear pressure not to set them farther below human effect levels than necessary. In contrast, *health benchmarks* such as the MDH HRVs are derived as protective levels, using greater margins of safety when greater uncertainties exist.

Due to the nature of MPCA’s air toxics monitoring, average concentrations are compared to chronic (long-term) standards or health benchmarks. It is not appropriate to compare high concentrations on a single day to chronic benchmarks or standards because these health numbers are set to be protective over a lifetime of exposure. It would be more appropriate to compare single high concentration values to acute or short-term benchmarks which are normally much higher than chronic benchmarks. The non-cancer benchmarks are defined as concentrations below which there is likely to be no public health concern over a lifetime of exposure. The cancer benchmarks are defined as pollutant concentrations posing not more than a potential one in a 100,000 increased lifetime cancer risk from inhalation.

Health benchmarks frequently change as more information regarding pollutant health effects becomes available. Therefore, it is important to think of them as guidelines and not fixed values delineating safety.

Pollutants Over Health Benchmarks

The U.S. EPA’s 2002 NATA modeling analysis identified ten pollutants above a health benchmark in Minnesota. These ten pollutants are listed Table 2.1 below.

Table 2.1. Pollutants Exceeding a Health Benchmark in the U.S. EPA’s NATA Analysis

1,3-Butadiene	Chromium
Acrolein	Ethylene Dibromide
Benzene	Ethylene Dichloride
Carbon Tetrachloride	Formaldehyde
Chloroform	Polycyclic Organic Matter (POM)

*The NATA analysis lacked a health benchmark for particulate matter from diesel emissions, so no comparison to health benchmarks could be made. Preliminary cancer benchmarks indicate the diesel particulate matter may be a concern.

Of those ten, MPCA ambient air monitoring has confirmed that two of these pollutants (benzene and formaldehyde) are found at concentrations above health benchmarks at some locations in the Twin Cities metropolitan area. Carbon tetrachloride has been monitored above health benchmarks in the past, but is currently at concentrations below the health benchmark at all monitoring locations.

Ethylene dibromide and ethylene dichloride have not been detected at MPCA air monitoring locations, although the health benchmark for ethylene dibromide is lower than the detection limit. Chloroform has not been found above detection limits at Twin Cities metro area ambient monitors in 2002. The MPCA began monitoring 1,3-butadiene and acrolein after they were indicated to be of concern in EPA modeling. Thus far, neither of these compounds have been found above detection limits at Minnesota monitoring locations. However, 1,3-butadiene has a cancer health benchmark of 0.04 ug/m3, which is below MPCA’s detection limit. In addition, the monitoring methodology for acrolein monitoring is still under development and results are uncertain.

The MPCA plans to begin analysis of the TSP filters for metals in 2003. Therefore, chromium concentrations are unavailable at this time. In addition, the MPCA does not monitor for semi-volatile compounds such as polyaromatic hydrocarbons (PAHs), which are a major component of polycyclic organic matter (POM) and diesel emissions.

Air Toxics

Of the 44 compounds monitored by the MPCA, 21 were below the MPCA detection limit, 15 were detected, but were below chronic health benchmarks, 6 did not have a health benchmark available, and 2 (benzene and formaldehyde) were found above chronic health benchmarks at one or more Twin Cities monitoring locations. Acrolein monitoring is still under development and concentrations are not reported at this time.

Table 2.2 lists the pollutants analyzed and found to be below MPCA detection limits at all sites in the Twin Cities area.

Table 2.2. Pollutants Analyzed and Found to be Below MPCA Detection Limits

1,1,2,2-Tetrachloroethane	1,3-butadiene	Ethylene chloride
1,1,2,3,4,4-Hexachloro-1,3-butadiene	1,3-Dichlorobenzene	Ethylene bromide
1,1,2-Trichloroethane	Chlorobenzene	Methyl bromide
1,1-Dichloroethane	Chloroform	trans-1,3-Dichloropropylene
1,1-Dichloroethene	cis-1,2-Dichloroethylene	Vinyl chloride
1,2-Dichlorobenzene	cis-1,3-dichloropropylene	Benzaldehyde
1,2-Dichloropropane	Freon 114	Crotonaldehyde

Table 2.3 lists the pollutants monitored above MPCA detection limits at one or more locations in the metropolitan area. These pollutants all have available health benchmarks and their average concentrations were below health benchmarks. Appendix C provides boxplots illustrating the concentrations for these pollutants along with comparisons between sites and health benchmarks.

Table 2.3. Pollutants Detected, but Below Health Benchmarks

m,p-Xylene	Ethylbenzene	Toluene
1,4-Dichlorobenzene	Methyl chloroform	Trichloroethylene
Carbon Tetrachloride	o-Xylene	Freon 11
Freon 12	Styrene	Freon 113
Dichloromethane	Tetrachloroethylene	Acetaldehyde

Six pollutants were measured above MPCA detection limits at locations in the Twin Cities, but lacked health benchmarks for public health analysis. These pollutants are listed in Table 2.4.

See Appendix D for boxplots providing concentrations and comparisons between sites for these pollutants.

Table 2.4. Pollutants Detected, but Lacking Health Benchmarks

1,2,4-Trimethylbenzene	4-Ethyltoluene	Butyraldehyde
1,3,5-Trimethylbenzene	Acetone	Propionaldehyde

Benzene

Benzene is one of two pollutants consistently measured near or above health benchmarks at some Twin Cities monitoring locations. The health benchmark for benzene is for protection from cancer. This cancer HRV is actually a range of concentrations from 1.3-4.5 $\mu\text{g}/\text{m}^3$. The range reflects the uncertainty surrounding setting health benchmarks. Basically, individuals that breathe benzene for a lifetime at concentrations between 1.3-4.5 $\mu\text{g}/\text{m}^3$ will have no more than a one in 100,000 additional risk of cancer from that exposure. Benzene is a probable human carcinogen, although it is unknown at what level above the health benchmark cancer might be expected in humans.

The concentration results for benzene at the monitoring sites in this study are given in Table 2.5. None of the benzene concentrations at these sites were above the health benchmark.

Table 2.5. 2002 Average Results for Benzene

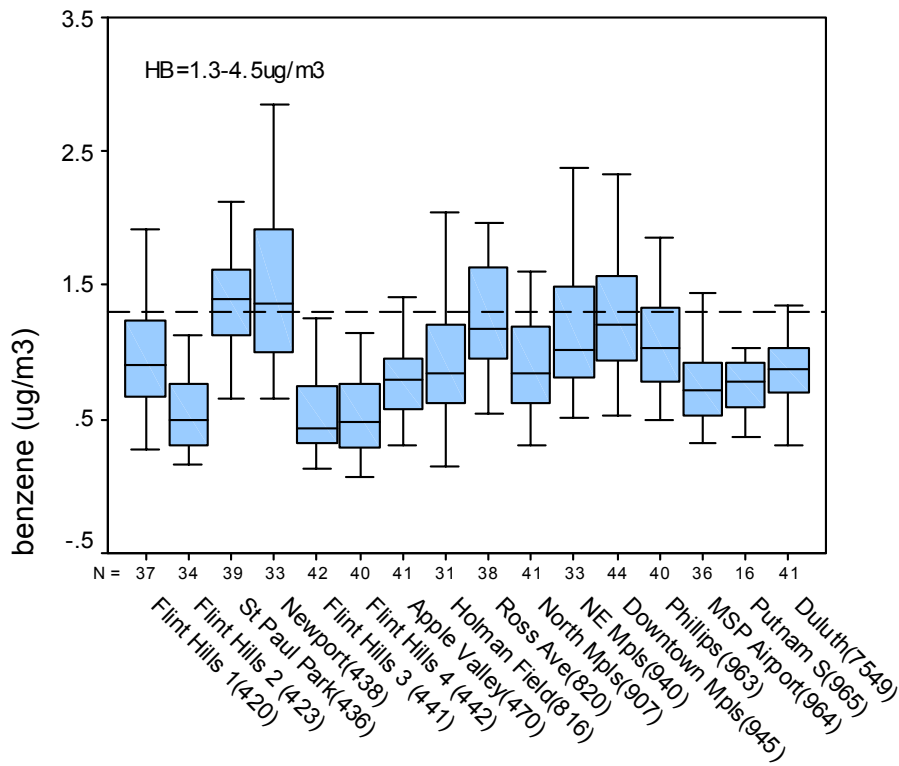
Site	Average Concentration (ug/m3)	95% Confidence Interval*	Health Benchmark	% of Health Benchmark
North Mpls	1.1	± 0.29	1.3-4.5	85-24%
NE Mpls	1.2	± 0.23	1.3-4.5	92-27%
Phillips	1.1	± 0.16	1.3-4.5	85-24%
MSP Airport	0.81	± 0.13	1.3-4.5	62-18%
Putnam School	0.98	± 0.39	1.3-4.5	75-22%

*The 95% confidence interval gives a range that is 95% sure to contain the true average.

**Includes data from January 2002 or site start date through September 2002.

The concentration results for benzene were also compared to other monitoring sites throughout the Twin Cities and in Duluth. The boxplot in Figure 2.1 compares the concentration results between sites.

Figure 2.1. 2002 Benzene Concentration Comparison Between Sites



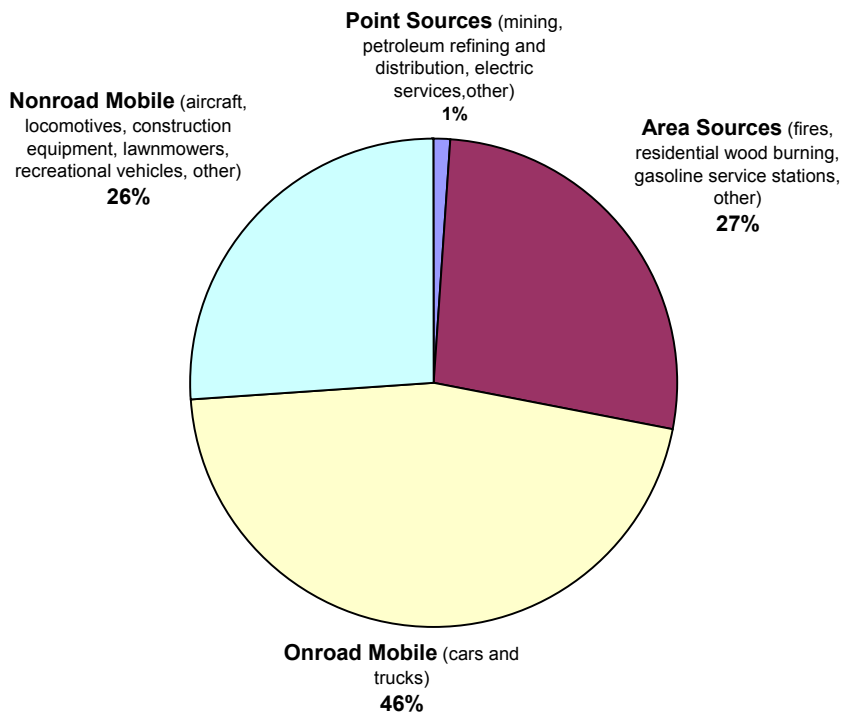
MPCA, October 2002

Boxplots: The center line within each box represents the median for the site. The box itself encompasses the 25th percentile to the 75th percentile of data. The bars at each end of the box represent the highest and lowest values that are not considered outliers. A horizontal dotted line is located at the benzene health benchmark. N=the number of samples analyzed for a given site. HB=the health benchmark for benzene. Boxplots include data from January 2002 or site start date through September 2002.

Average annual benzene concentrations thus far in the study only exceeded the low range of the benzene health benchmark at St. Paul Park and Newport. The St. Paul Park, Newport, and Ross Avenue sites were significantly higher than most of the other monitoring locations. The Flint Hills 2,3, and 4 sites had the lowest concentrations of benzene.

Benzene is primarily emitted from on-road and non-road mobile sources as it is an additive to fuels. Figure 2.2 shows the percent of air emissions that come from principle source categories in Minnesota.

Figure 2.2. Contribution of Principal Source Categories to Benzene Emissions



MPCA 1999 Minnesota Air Toxic Emission Inventory

For further information on benzene and efforts by the MPCA to lower benzene concentrations in the Twin Cities, see MPCA’s January 2001 report to the legislature on *Air Quality in Minnesota* and the January 2003 update *Air Quality in Minnesota: Into the Future*.

Formaldehyde

Formaldehyde is the other pollutant consistently measured above its health benchmark in the Twin Cities. The health benchmark for formaldehyde is for cancer. This cancer HRV is 0.8 $\mu\text{g}/\text{m}^3$. Formaldehyde is a probable human carcinogen according to EPA’s IRIS database, although it is unknown at what level above the health benchmark cancer might be expected in humans.

The average concentration results for formaldehyde at the monitoring sites in this study are given in Table 2.6. All of the sites were nearly three times the health benchmark.

Table 2.6. 2002 Average Results for Formaldehyde

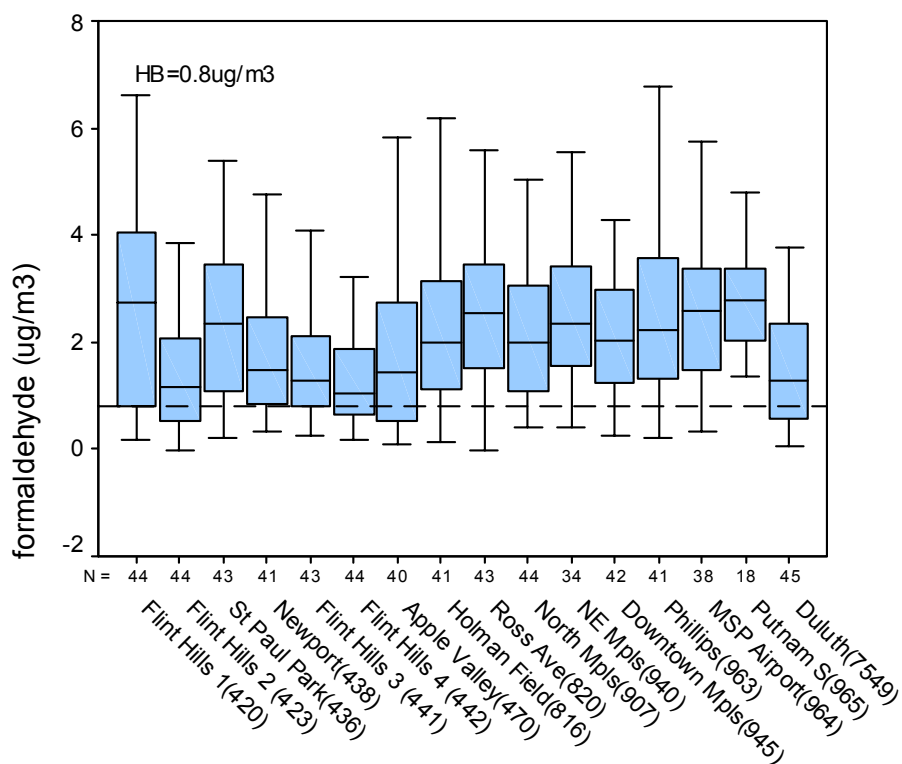
Site	Average Concentration (ug/m3)	95% Confidence Interval*	Health Benchmark	% of Health Benchmark
North Mpls	2.3	±0.45	0.8	290%
NE Mpls	2.5	±0.53	0.8	310%
Phillips	2.5	±0.52	0.8	310%
MSP Airport	2.5	±0.48	0.8	310%
Putnam School	2.8	±0.55	0.8	350%

*The 95% confidence interval gives a range that is 95% sure to contain the true average.

**Includes data from January 2002 or site start date through September 2002.

The concentration results for formaldehyde were also compared to other monitoring sites throughout the Twin Cities and in Duluth. The boxplot in Figure 2.3 compares the concentration results between sites.

Figure 2.3. 2002 Formaldehyde Concentration Comparison Between Sites



MPCA, October 2002

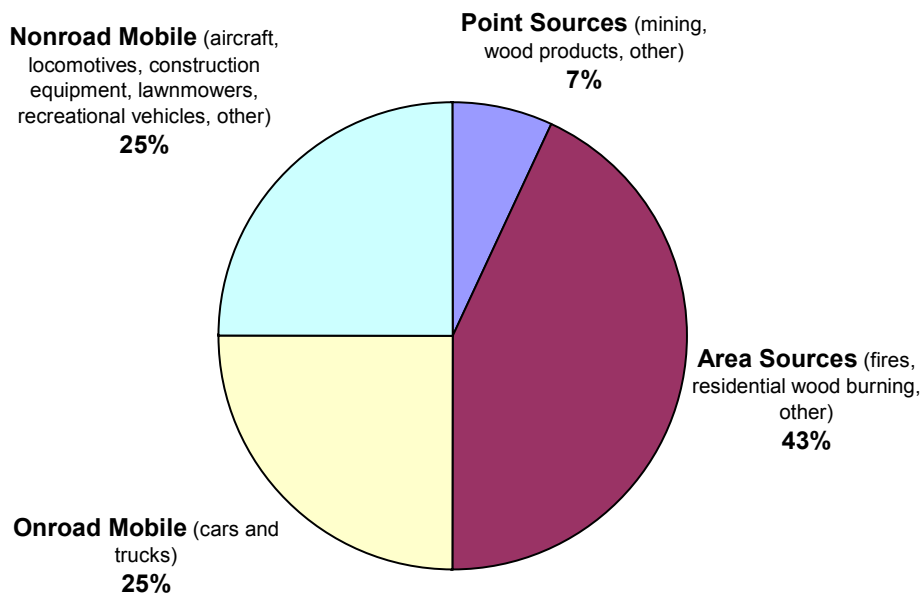
Boxplots: The center line within each box represents the median for the site. The box itself encompasses the 25th percentile to the 75th percentile of data. The bars at each end of the box represent the highest and lowest values that are not considered outliers. A horizontal dotted line is located at the health benchmark for formaldehyde. N=the

number of samples analyzed for a given site. HB=the health benchmark for formaldehyde. Boxplots include data from January 2002 or site start date through September 2002.

Average annual formaldehyde concentrations thus far in the study exceeded the formaldehyde health benchmark at all monitoring sites. In general, formaldehyde concentrations are similar throughout the metro area, although concentrations of formaldehyde at Flint Hills 1 and Ross Avenue were significantly higher than a few of the other sites including Duluth.

Formaldehyde is primarily emitted from onroad and nonroad mobile sources. Figure 2.4 shows the percent of formaldehyde air emissions that come from principle source categories in Minnesota.

Figure 2.4. Contribution of Principal Source Categories to Formaldehyde Emissions



MPCA 1999 Minnesota Air Toxic Emission Inventory

For further information on formaldehyde, see MPCA's January 2001 report to the legislature on *Air Quality in Minnesota* and the January 2003 update *Air Quality in Minnesota: Into the Future*.

Carbon Tetrachloride

Carbon tetrachloride was one of the pollutants identified above health benchmarks by the U.S. EPA NATA modeling study and in previous years was monitored above the health benchmark in the Twin Cities. Carbon tetrachloride is a substance that destroys the ozone layer in the upper atmosphere. Its purposeful production was effectively banned in the United States in 1996 through the Montreal Protocol treaty. Despite a long atmospheric life, carbon tetrachloride concentrations have been gradually decreasing nationwide.

The concentration results for carbon tetrachloride at the monitoring sites in this study are given in Table 2.7.

Table 2.7. 2002 Average Results for Carbon Tetrachloride

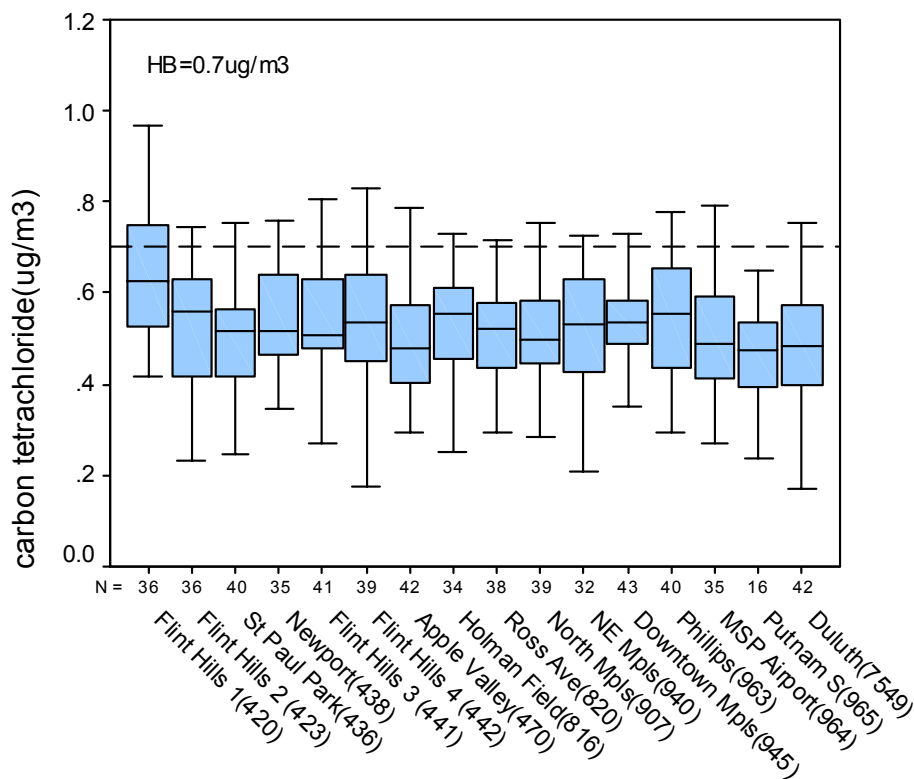
Site	Average Concentration (ug/m3)	95% Confidence Interval*	Health Benchmark	% of Health Benchmark
North Mpls	0.50	±0.046	0.7	71%
NE Mpls	0.53	±0.051	0.7	76%
Phillips	0.54	±0.047	0.7	77%
MSP Airport	0.49	±0.049	0.7	70%
Putnam School	0.49	±0.092	0.7	70%

*The 95% confidence interval gives a range that is 95% sure to contain the true average.

**Includes data from January 2002 or site start date through September 2002.

The concentration results for carbon tetrachloride were compared across monitoring sites. Figure 2.5 shows a boxplot comparing the concentration results between sites.

Figure 2.5. 2002 Carbon Tetrachloride Concentration Comparison Between Sites



MPCA, October 2002

Boxplots: The center line within each box represents the median for the site. The box itself encompasses the 25th percentile to the 75th percentile of data. The bars at each end of the box represent the highest and lowest values that

are not considered outliers. A horizontal dotted line is located at the health benchmark for carbon tetrachloride. N=the number of samples analyzed for a given site. HB=the health benchmark for carbon tetrachloride. Boxplots include data from January 2002 or site start date through September 2002.

Currently, average carbon tetrachloride concentrations are found below the HRV of 0.7 $\mu\text{g}/\text{m}^3$ at all locations in the Twin Cities. This concentration is similar to levels of carbon tetrachloride found across the nation. The Flint Hills 1 site was the only site that was significantly different from some of the other metro sites and Duluth for carbon tetrachloride. Further study is necessary to determine if a local source exists near that location.

Total Suspended Particulate (TSP)

TSP was measured at all of the monitoring sites added for this metropolitan study. TSP has a Minnesota annual standard of 150 $\mu\text{g}/\text{m}^3$. The results for the monitoring sites in this study are given in Table 2.8.

Table 2.8. 2002 Average results for TSP

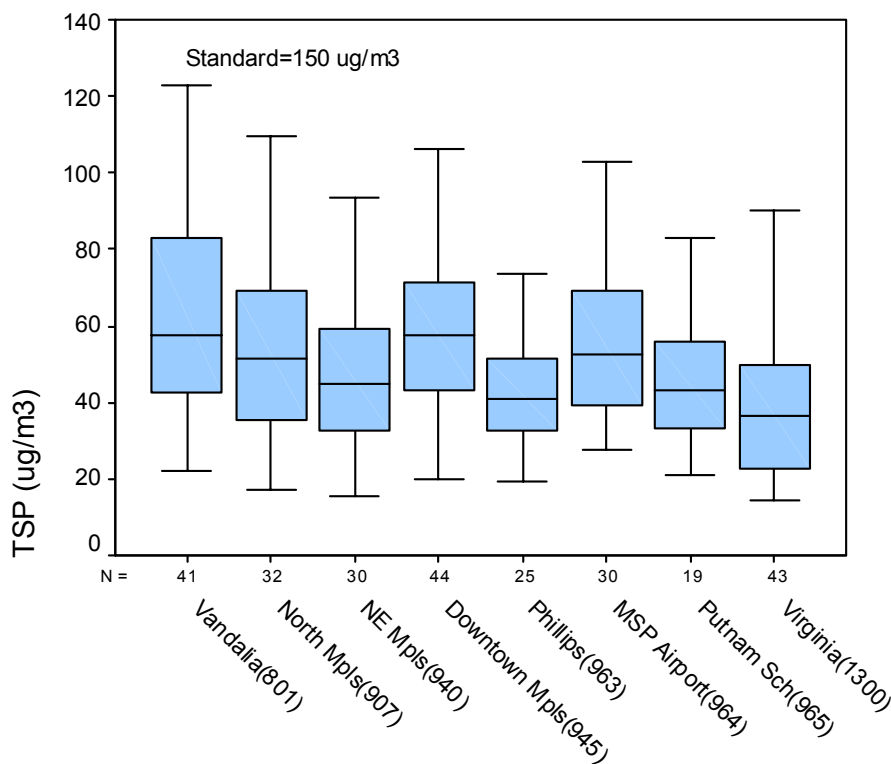
Site	Average Concentration ($\mu\text{g}/\text{m}^3$)	95% Confidence Interval*	Standard	% of Standard
North Mpls	54	± 8.7	150	36 %
NE Mpls	46	± 7.4	150	31%
Phillips	42	± 6.2	150	28%
MSP Airport	55	± 7.4	150	36%
Putnam School	46	± 8.5	150	31%

*The 95% confidence interval gives a range that is 95% sure to contain the true average.

**Includes data from January 2002 or site start date through September 2002.

The concentration results for TSP were also compared to other monitoring sites throughout the Twin Cities and in Virginia. The boxplot in Figure 2.6 compares the concentration results between sites.

Figure 2.6. 2002 TSP Concentration Comparison Between Sites



MPCA, October 2002

Boxplots: The center line within each box represents the median for the site. The box itself encompasses the 25th percentile to the 75th percentile of the data. The bars at each end of the box represent the highest and lowest values that are not considered outliers. N=the number of samples analyzed for a given site. Boxplots include data from January 2002 or site start date through September 2002.

The averages for all of the sites are less than half the annual standard of 150 $\mu\text{g}/\text{m}^3$. Vandalia and Downtown Minneapolis have statistically the highest concentrations of TSP. The rest of the sites, including Virginia, are not statistically different.

Fine Particulate Matter (PM_{2.5})

PM_{2.5} has an annual standard of 15 $\mu\text{g}/\text{m}^3$. However, some studies indicate that the standard may not be low enough to protect public health. With improving research methods, health scientists have studied areas with lower levels of air pollution and have been unable to identify a threshold for some of the more serious health effects of particulate matter. It is not clear if there is a threshold below which no effect occurs, but none has been found at relevant ambient levels. The components of PM_{2.5} that pose the greatest risk to health are also a subject of active research. The results for the monitoring sites in this study are given in Table 2.9.

Table 2.9. 2002 Average results for PM_{2.5}

Site	Average Concentration (ug/m3)	95% Confidence Interval*	Standard	% of Standard
North Mpls	10.7	±1.4	15	71%
NE Mpls	11.0	±2.7	15	73%
Phillips	10.0	±0.72	15	67%
MSP Airport	10.4	±2.0	15	69%
Putnam School	12.3	±1.3	15	82%

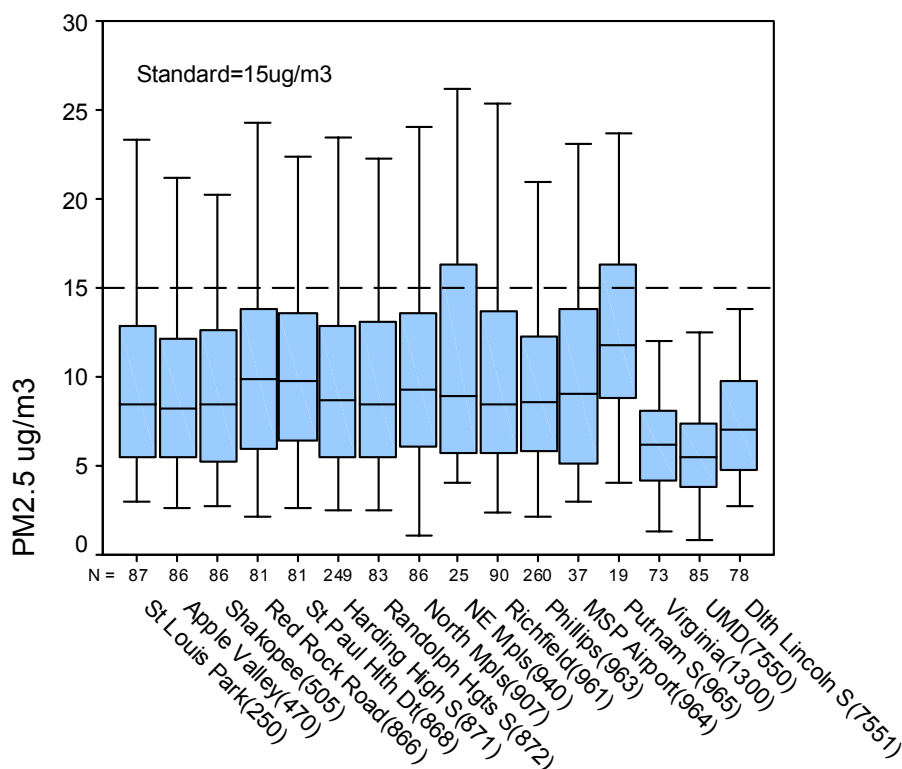
*The 95% confidence interval gives a range that is 95% sure to contain the true average.

**Includes data from January 2002 or site start date through September 2002.

Previous monitoring data indicates that concentrations of PM_{2.5} are higher in the winter than in the summer in Minnesota. Higher average concentrations of PM_{2.5} are expected after a full year of data has been collected.

The concentration results for PM_{2.5} were also compared to other monitoring sites throughout the Twin Cities and in Virginia and Duluth. The boxplot in Figure 2.7 compares the concentration results between sites.

Figure 2.7. 2002 PM_{2.5} Concentration Comparison Between Sites



MPCA, October 2002

Boxplots: The center line within each box represents the median for the site. The box itself encompasses the 25th percentile to the 75th percentile. The bars at each end of the box represent the highest and lowest values that are not considered outliers. A horizontal dotted line is located at the PM_{2.5} standard. N=the number of samples analyzed for a given site. The number of samples varies significantly between PM_{2.5} sites depending on when the site started collecting data and whether data is collected every day, every third day, or every sixth day. Boxplots include data from January 2002 or site start date through September 2002.

The averages for all of the sites are below the standard of 15 µg/m³. PM_{2.5} concentrations are very consistent across the Twin Cities metropolitan area. None of the metro sites were significantly different from one another. The Virginia and the Duluth UMD monitoring sites had statistically lower PM_{2.5} concentrations than many of the Twin Cities locations.

PM_{2.5} is primarily emitted from the combustion of fossil fuels. Sources of PM_{2.5} emissions will be further explained in MPCA's April 2003 *Annual Pollution Report: 2001 Air Emissions and Water Discharges*.

3. Limitations of MPCA Air Monitoring

This is a preliminary report on the results of the Twin Cities Metropolitan Area air toxics monitoring special study since only three to nine months of data has been collected at each site. The MPCA prefers to have a full year of data at each site in order to allow for seasonal analysis since comparison of sites with data collected during different seasons can have significantly different concentrations. For example, formaldehyde concentrations are higher in the summer than the winter. Therefore, apparent differences between sites may actually be differences between seasons.

Due to the monitoring frequency of one average 24-hour sample every six days, the MPCA's data is best suited to comparison with chronic or long-term benchmarks. High, short-term exposures can easily be missed due both to the monitors fixed locations and weekly frequency. Depending on location and wind direction, the highest concentrations in the area may not occur at the monitoring site.

In many ways, *air modeling* (a computer-assisted forecasting technique) is better suited to identifying high short-term exposures. Modeling takes into account high emissions from individual sources as well as worst-case meteorological conditions in order to predict short-term high concentrations near emission sources. For this reason, the MPCA traditionally uses air modeling for risk assessment to identify high exposures near individual emission sources. Air monitoring is used to better understand long-term neighborhood and regional exposures to pollutants.

The MPCA's monitoring is limited to volatile organic compounds, carbonyls, particulates, and metals. The MPCA air laboratory is not equipped to monitor semi-volatile compounds such as polyaromatic hydrocarbons and dioxins. These compounds may also pose risks both through inhalation of air and through deposition and accumulation in water, soil, and the food-chain.

Finally, this analysis focused on chemical-by-chemical exposure. In reality, people are exposed to hundreds of chemicals throughout the day. The health effects of pollutants may be harmful in an additive manner and should not necessarily be treated as if exposure is occurring in isolation. Therefore, even if a pollutant is below its health benchmark, it may still pose a concern to human health when multiple pollutant exposures occur both outdoors and in other locations. In addition, many pollutants do not have health benchmarks. The data is simply not available to estimate the risk to human health of certain exposures.

4. Conclusions and Next Steps

The MPCA's preliminary analysis of the data for the Twin Cities Metropolitan Area air toxics monitoring special study came to the following conclusions:

- Of the ten pollutants identified to be of potential concern in the Twin Cities, only two of them, benzene and formaldehyde, were confirmed by MPCA air monitoring to be above or in the range of health benchmarks.
- Of the remaining 44 compounds monitored by the MPCA, 21 were below the detection limit, 15 were detected but were below health benchmarks, and 6 did not have an available health benchmark.
- The majority of monitoring sites throughout the Twin Cities did not have significant differences in concentrations of the 44 pollutants monitored.
- Although PM_{2.5} concentrations are currently below the NAAQS, the MPCA should continue to track trends and follow ongoing scientific literature regarding health effects since effects may occur below the current standard.

This report includes a very preliminary analysis of metropolitan air toxics monitoring. In the next year, the MPCA plans to continue with the following steps:

- Complete at least a full year of data collection and analysis at all monitoring sites.
- Begin metal analysis of the particles captured on TSP filters for a better understanding of metal concentrations in the Twin Cities area.
- Complete seasonality and source apportionment for pollutants and monitoring sites of particular concern.
- Include a cumulative exposure analysis of pollutants, taking into account that exposures do not occur in isolation.
- Continue communication with legislatures, local officials, neighborhood groups and other interested parties. Groups contacted in 2002 include the Mississippi Corridor Neighborhood Coalition, the Southeast Como Improvement Agency and the South Metro Airport Action Council.

Although funds are not currently available, the MPCA believes it would also be valuable to improve emissions inventories and regional air quality modeling of the Twin Cities to better identify hot spots or local areas of air pollution concern that air monitoring is not suited to capture. In addition, the MPCA believes monitoring for semi-volatile chemicals such as PAHs and dioxin would help define the risks of air pollution in the Twin Cities metropolitan area.

References

ⁱ <http://www.pca.state.mn.us/air/staffpaper-airtoxics.html>

ⁱⁱ <http://www.pca.state.mn.us/hot/legislature/reports/2001/airquality.html>

ⁱⁱⁱ For more information on EPA's National-Scale Air Toxics Assessment see <http://www.epa.gov/ttn/atw/nata/>

^{iv} The MPCA relies upon state and federal health benchmarks to assess the effects of air toxics. Health benchmarks represent air concentrations (or measures) below which there is little appreciable risk of harmful effects on humans. They are not enforceable regulatory standards. Many chemicals do not have health benchmarks.

^v CAS #=The Chemical Abstract Service Registry Number. The CAS Registry Number is accepted nationally and internationally as an identifier for specific, definable chemical substances.

^{vi} U.S. EPA. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed. Compendium Method TO-15. EPA/625/R-96/010b. Cincinnati, OH: U.S. Environmental Protection Agency Office of Research and Development, 1999.

^{vii} U.S. EPA. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed. Compendium method TO-11A. EPA/625/R-96/010b. Cincinnati, OH: U.S. Environmental Protection Agency Office of Research and Development, 1999.

^{viii} U.S. EPA. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. Compendium method IO-3.4. EPA/625/R-96/010a. Cincinnati, OH: U.S. Environmental Protection Agency Office of Research and Development, June 1999.

^{ix} Personal communication from Dr. Gregory Pratt, Minnesota Pollution Control Agency Research Scientist.

^x Statistical analyses were done using SPSS (SPSS, Inc., Chicago, IL, USA).

^{xi} For further information on the NAAQS see the following EPA website: <http://www.epa.gov/airs/criteria.html>

^{xii} Minnesota Department of Health, Health Risk Value Rule promulgated March 25, 2002, Minnesota Rules Parts 4717.8000 to 4717.8600.

^{xiii} <http://www.epa.gov/iris/>

^{xiv} http://www.oehha.ca.gov/air/hot_spots/index.html

Appendix A-MPCA Active Sites, November 2002

MPCA SITE ID	CITY NAME	ADDRESS	SITE NAME	DATE SITE STARTED	pm25	tsp	voc	carb
52	Chaska	Chaska water tower	Chaska	11/10/02			✓	✓
250	St Louis Park	5005 Minnetonka Blvd	St. Louis Park	1/1/72	✓			
420	Rosemount	12821 Pine Bend Trails	Flint Hills 1	1/1/72			✓	✓
423	Rosemount	2142 120th St. E	Flint Hills 2	9/1/90			✓	✓
436	St Paul Park	649 5th St	St. Paul Park	2/27/89			✓	✓
438	Newport	NE Corner OF 4TH Ave & 2nd St	Newport	6/14/95			✓	✓
441	Rosemount	12555 Clayton Ave.	Flint Hills 3	5/25/99			✓	✓
442	Rosemount	County Rd 42 SE of Koch	Flint Hills 4	5/30/00			✓	✓
460	Eagan	3450 Dodd Rd	Gopher	1/1/83		✓		
470	Apple Valley	Garden View Elementary School	Apple Valley	10/3/00	✓		✓	✓
505	Shakopee	917 Dakota St. Shakopee, MN	Shakopee	1/1/00	✓			
801	St Paul	2179 University Ave	Vandalia	1/1/65		✓		
816	St Paul	Holman Field	Holman Field	1/1/66			✓	✓
820	St Paul	1038 Ross Ave	Ross Avenue	1/1/66			✓	✓
866	St Paul	1450 Red Rock Rd	Red Rock Road	4/1/97	✓			
868	St Paul	555 Cedar St	St. Paul Health Dept	2/17/98	✓			
871	St Paul	1540 East 6th Street	Harding High Sch	10/2/98	✓			
872	St Paul	348 Hamline Ave	Randolph Hghts Sch	4/19/99	✓			
907	Minneapolis	4646 N Humboldt	North Mpls	1/1/66	✓	✓	✓	✓
940	Minneapolis	143 13th Ave NE	NE Mpls	1/1/78	✓	✓	✓	✓
961	Richfield	Richfield Intermediate School	Richfield	4/12/99	✓			
963	Minneapolis	2727 - 10th Ave. So.	Phillips	1/1/01	✓	✓	✓	✓
964	MSP Airport	MSP Airport	MSP Airport	2/1/02	✓	✓	✓	✓
965	Minneapolis	1616 Buchanan St.	Putnam Sch	6/6/02	✓	✓	✓	✓
966	Minneapolis	309 2nd Ave. S	Downtown Mpls	10/2/02		✓	✓	✓
1300	Virginia	City Hall Roof	Virginia	1/1/68	✓	✓		
3051	Mille Lacs	HCR 67 Box 194	Mille Lacs	6/17/97	✓			
3052	St. Cloud	1321 Michigan Ave N.	St. Cloud	10/2/98	✓			
4415	Priam	7231 Hwy 23 SW	Priam	11/10/00		✓		
5008	Rochester	1801 9th Ave S.E.	Rochester	9/25/97	✓			
6018	Hastings	1600 Hwy 55	Hastings	5/23/90	✓			
7416	Cloquet	175 University Rd.	Cloquet	5/24/01	✓			
7549	Duluth	1532 W Michigan St	Garfield/Michigan	1/2/94			✓	✓
7550	Duluth	1202 East University Circle	UMD	10/2/98	✓			
7551	Duluth	2427 W. 4th Street	Dlth Lincoln Sch	1/1/00	✓			
7555	Duluth	Waseca Industrial Rd.	Duluth-Waseca Rd	7/30/01		✓		

Appendix B-Health Benchmarks, November 2002

CAS #	Chemical Name	Acute			Annual Cancer Assessment			Annual Chronic Noncancer		
		Tox Value Source	Acute Tox Value (ug/m3)	Toxic Endpoint	Tox Value Source	Unit Risk (ug/m3)-1	10-5 Cancer Tox Value (ug/m3)	Tox Value Source	Chronic Tox Value (ug/m3)	Toxic Endpoint
75-07-0	Acetaldehyde				HRV	2.20E-06	5	IRIS	9	olfactory epithelium degeneration
67-64-1	Acetone									
107-02-8	Acrolein	CAL EPA	0.19	respiratory system; eye				IRIS	0.02	nasal squamous metaplasia
107-05-1	Allyl chloride				CAL EPA	6.00E-06	1.7	IRIS	1	neurotoxicity
100-52-7	Benzaldehyde									
71-43-2	Benzene	HRV	1000	developmental	HRV	2.2E-6-- 7.8E-6	1.3-4.5	CAL EPA	60	Hematopoietic system; development; nervous system
106-99-0	Butadiene, 1,3-				HRV	2.80E-04	0.04	IRIS	2	Ovarian atrophy
123-72-8	Butyraldehyde									
56-23-5	Carbon tetrachloride	CAL EPA	1900	developmental	IRIS	1.50E-05	0.67	CAL EPA	40	Alimentary system; development; nervous system
108-90-7	Chlorobenzene							CAL EPA	1000	Alimentary system; kidney; reproductive system
67-66-3	Chloroform	HRV	150	developmental	IRIS	2.30E-05	0.43	CAL EPA	300	Alimentary system; kidney; development
4170-30-3	Crotonaldehyde									
541-73-1	Dichlorobenzene(m), 1,3-									
95-50-1	Dichlorobenzene(o), 1,2-							HEAST	200	decreased body weight gain

CAS #	Chemical Name	Acute			Annual Cancer Assessment			Annual Chronic Noncancer		
		Tox Value Source	Acute Tox Value (ug/m3)	Toxic Endpoint	Tox Value Source	Unit Risk (ug/m3)-1	10-5 Cancer Tox Value (ug/m3)	Tox Value Source	Chronic Tox Value (ug/m3)	Toxic Endpoint
106-46-7	Dichlorobenzene(p), 1,4-				CAL EPA	1.10E-05	0.91	IRIS	800	increased liver weight
75-71-8	Dichlorodifluoromethane (CFC-12)							CAL EPA	1000	Alimentary system
540-59-0	dichloroethylene,1,2-									
542-75-6	Dichloropropene, 1,3-				IRIS	4.00E-06	2.5	HRV	20	upper respiratory system
76-14-2	Dichlorotetrafluoroethane (Freon-114)									
77-73-6	Dicyclopentadiene							HEAST	0.2	kidney dysfunction
100-41-4	Ethyl benzene	HRV	10000	developmental				IRIS	1000	developmental toxicity
75-00-3	Ethyl chloride (Chloroethane)	HRV	100000	developmental				IRIS	10000	delayed fetal ossification
106-93-4	Ethylene dibromide (Dibromoethane)				HRV	2.20E-04	0.05	CAL EPA	0.8	Reproductive system
107-06-2	Ethylene dichloride (1,2-Dichloroethane)				IRIS	2.60E-05	0.38	CAL EPA	400	Alimentary system (liver)
75-34-3	Ethylidene dichloride (1,1-Dichloroethane)				CAL EPA	1.60E-06	6.3	HEAST	500	kidney damage
622-96-8	Ethyltoluene									
50-00-0	Formaldehyde	HRV	94	irritant - eye and respiratory system	HRV	1.30E-05	0.8	CAL EPA	3	Respiratory system; eyes
87-68-3	Hexachlorobutadiene				IRIS	2.20E-05	0.45	CAL EPA	90	Alimentary system; kidney
74-83-9	Methyl bromide (Bromomethane)	HRV	2000	CNS				HRV	5	upper respiratory system

CAS #	Chemical Name	Acute			Annual Cancer Assessment			Annual Chronic Noncancer		
		Tox Value Source	Acute Tox Value (ug/m3)	Toxic Endpoint	Tox Value Source	Unit Risk (ug/m3)-1	10-5 Cancer Tox Value (ug/m3)	Tox Value Source	Chronic Tox Value (ug/m3)	Toxic Endpoint
71-55-6	Methyl chloroform (1,1,1-Trichloroethane)	HRV	140000	CNS				CAL EPA	1000	Nervous system
75-09-2	Methylene chloride (Dichloromethane)	HRV	10000	CNS	HRV	4.70E-07	20	CAL EPA	400	Cardiovascular system; nervous system
123-38-6	Propionaldehyde									
78-87-5	Propylene dichloride (1,2-Dichloropropane)							IRIS	4	nasal mucosa hyperplasia
100-42-5	Styrene	HRV	21000	irritant - eye and respiratory system				HRV	1000	nervous system
79-34-5	Tetrachloroethane, 1,1,2,2-				IRIS	5.80E-05	0.17			
127-18-4	Tetrachloroethylene (Perchloroethylene)	HRV	20000	irritant - eye, and respiratory system; CNS	CAL EPA	5.90E-06	1.7	CAL EPA	35	Kidney; alimentary system (liver)
108-88-3	Toluene (methyl benzene)	HRV	37000	irritant- eye and respiratory system; CNS				HRV	400	nervous/upper respiratory sys.
120-82-1	Trichlorobenzene, 1,2,4-							HEAST	200	non-adverse liver weight changes
76-13-1	Trichloro-1,2,2-trifluoroethane, 1,1,2- (Freon 113)							CAL EPA	90000	alimentary system
79-00-5	Trichloroethane, 1,1,2- (vinyl trichloride)				IRIS	1.60E-05	0.63	CAL EPA	100	Alimentary system; kidney; nervous system; cardiov
79-01-6	Trichloroethylene (trichloroethene)	HRV	2000	developmental	CAL EPA	2.00E-06	5	CAL EPA	600	Nervous system; eyes

CAS #	Chemical Name	Acute			Annual Cancer Assessment			Annual Chronic Noncancer		
		Tox Value Source	Acute Tox Value (ug/m3)	Toxic Endpoint	Tox Value Source	Unit Risk (ug/m3)-1	10-5 Cancer Tox Value (ug/m3)	Tox Value Source	Chronic Tox Value (ug/m3)	Toxic Endpoint
75-69-4	Trichlorofluoromethane (CFC-11)							CAL EPA	20000	Nervous, alimentary, respiratory, and cardiovascular systems
95-63-6	Trimethylbenzene, 1,2,4-									
108-67-8	Trimethylbenzene, 1,3,5-									
75-01-4	Vinyl chloride (chloroethene)	CAL EPA	180000	irritant - eye and respiratory system; CNS	HRV	8.80E-06	1	IRIS	100	Liver cell polymorphism
75-35-4	Vinylidene chloride (1,1-Dichloroethylene)				IRIS	5.00E-05	0.2	IRIS	200	Liver (fatty change)
1330-20-7	Xylenes (isomers and mixture)	HRV	43000	irritant - eye and respiratory system; CNS				CAL EPA	700	Nervous system; respiratory system

HRV=Minnesota Department of Health, Health Risk Values, 2002, Minnesota Rules Parts 4717.8000 to 4717.8600

IRIS=U.S. EPA's Integrated Risk Information System, <http://www.epa.gov/iris/>

CAL EPA=California Office of Environmental Health Hazard Assessment(OEHHA), http://www.oehha.ca.gov/air/hot_spots/index.html

HEAST=U.S. EPA Health Effects Assessment Summary Tables, 1997, EPA/540/R-97/036.

Appendix C-Pollutants Below Health Benchmarks

Boxplots: The center line within each box represents the median for the site. The box itself encompasses data from the 25th percentile to the 75th percentile. The bars at each end of the box represent the highest and lowest values that are not considered outliers. When possible, a horizontal dotted line is located at the health benchmark. N=the number of samples analyzed for a given site.

HB=Health Benchmarks: Health Benchmarks are provided in order from the following sources, the Minnesota Department of Health (MDH) Health Risk Values (HRVs), the Environmental Protection Agency (EPA) Integrated Risk Information System (IRIS), and the California Office of Environmental Health Hazard Assessment (OEHHA). These benchmarks are current as of fall 2002. The benchmarks included are for chronic (long-term exposure). The benchmarks are either for cancer or other long-term effects. The cancer health benchmarks are based on a one in 100,000 risk level.

