

Abstract [INCOMPLETE]

(To be written after the report is completed.)

INTRODUCTION

Stream water-quality and the ecological health of urban stream corridors are complex issues that drive research, regulation, and use of stream corridors. Personnel from agencies and universities involved in such pursuits in the Southeastern Wisconsin area have joined together in an attempt to assess the recent history of urban streams and to use that knowledge to evaluate future stream-improvement projects to determine their likely success before implementation allowing for the projects with greater potential to receive priority. With the expertise of those from the planning, regulatory, and non-regulatory fields as well as academicians and engineers, the Milwaukee Metropolitan Sewerage District Corridor Study has been approached with a broad-based perspective and the intention of promoting sound resource-based management decisions.

Purpose and Scope

The Milwaukee Metropolitan Sewerage District (MMSD) Corridor Study is a cooperative project undertaken by MMSD, Wisconsin Department of Natural Resources (WDNR), Southeastern Wisconsin Regional Planning Commission (SEWRPC), United States Geological Survey (USGS), and local universities University of Wisconsin – Milwaukee, Marquette, and Wisconsin Lutheran College. The general purpose of the study is to ascertain the current state of water quality and ecological health in the stream corridors of the MMSD planning area (study area) and provide knowledge and tools by which to assess future project potential success.

The study itself is divided into three phases. Phase I involves the development of a data base to house data collected in the MMSD planning area (fig. 1) since 1970. The MMSD Corridor Study data base houses major data sets from MMSD, USGS, WDNR, and USEPA. It is likely that additional data sets including some provided by local universities and volunteer groups will continue to be incorporated into the data base following the publication of this report. The data base is available for query to those within the cooperating agencies to assist in informal decision-making processes. Data in the data base can be examined to provide insight into the success of past MMSD and other agency projects, and to assess future data needs. This report summarizes the historical data in the MMSD Corridor Study data

base as well as other information developed as part of the MMSD Corridor Study including published studies and available spatial data relating to the study area. This report highlights data gaps with regard to spatial extent of study, temporal extent of data availability, and analysis variability. The thrust of Phase I is to develop a knowledge base with which to plan the baseline monitoring called for in Phase II.

Phase II involves a rigorous field effort to fill in data gaps highlighted during the Phase I review. The baseline inventory will include surface-water chemistry, sediment chemistry, and ecological (fish, habitat, macroinvertebrates, algae, microbiology) assessments at a number of sites around the MMSD planning area. Staff from multiple agencies will likely cooperatively collect the data. Data collected during the baseline monitoring effort will reveal more information regarding the state of the stream corridors not available from the data base developed in Phase I and assist in making management decisions.

Phase III involves a long-term data collection effort at a subset of the baseline monitoring sites. Long-term monitoring will document and demonstrate changes in the health of aquatic ecosystems in the stream corridors of the MMSD planning area. The data base created in Phase I will be maintained throughout the three phases of the Corridor Study.

Description of MMSD planning area

Different factors influence concentrations of various constituents in surface-water, sediment and tissues, the diversity and populations of fish and macroinvertebrates, and the state of habitat and stream morphology within the MMSD planning area. Described below are physical features of the study area that may have influenced the chemistry and ecology data that has been collected for the data base and will continue to influence data collected in future monitoring efforts.

Location and Surface-Water Features

The MMSD planning area (fig. 1) is a 420 mi² area covering Milwaukee county and parts of Washington, Ozaukee, Waukesha and Racine counties. MMSD collects wastewater from all Milwaukee municipalities (except South Milwaukee) as well as 10 communities in the surrounding 4 counties.

There are seven major watersheds and parts or all of 36 subwatersheds (fig. 2) that make up the study area (Southeast-

ern Wisconsin Regional Planning Commission, 2002a; Southeastern Wisconsin Regional Planning Commission, 2002b). The Milwaukee River watershed accounts for a little less than a quarter of the total study area although over 85% of the headwaters of the Milwaukee River watershed fall outside of the study area. The Menomonee River watershed makes up a little over 30% of the study area and falls almost entirely within the study area. The Upper Root River watershed accounts for 17% of the study area and is a little over a third of the entire Root River watershed area. The Upper Fox River watershed makes up approximately 10% of the study area and is the only portion of the study area that does not drain to Lake Michigan (it drains eventually to the Mississippi River). The Kinnickinnic and Oak Creek watersheds fall completely within the study area and make up 6 and 7 percent of the total study area respectively. The remaining 5 percent of the study area drains directly to Lake Michigan.

Texture of Surficial Deposits

Surficial deposits in the MMSD planning area are comprised predominantly of clayey till ground and end moraine (fig. 3). There are also some areas of sandy loamy till in the northwest corner of the MMSD planning area and outwash sand and gravel and lake clay and silt in various areas of the study area. (Lineback and others, 1983)

Land-use/Land Cover and Population

The MMSD study area is heavily urbanized in the center of the study area with higher density areas of agricultural influence in the northern and southern portions of the study area (fig. 4). Two-thirds of the study area is covered by urban land-use, made up of commercial, industrial and other areas (17%), residential (26%), transportation (21%) and recreational areas (3%). Twenty percent of the study area is covered with agricultural land use. Another 3% of the study area is covered in forested land. Wetlands make up 7% of the study area and another 2% of the study area is open water. (generalized from Southeastern Regional Planning Commission, 1995).

The population (fig. 5) of the MMSD planning area is 1,092,624 as of data from the 2000 census, for which a population density of 2,618 people per square mile was calculated (U.S. Bureau of the Census, 2001). The population in 1990 of the MMSD planning area was slightly less than 2000, 1,090,046 people with a population density of 2,612 people per square mile (U.S. Bureau of the Census, 1991).

COMPILATION OF WATER-RESOURCES-RELATED INFORMATION

A literature review was completed for the study area in the summer of 2001. References to surface-water (quality and quantity) and aquatic biology studies were compiled and reviewed. Studies referred to in the review included those regarding any of the major watersheds covering the study area that referred to an aspect of water-resources.

Also, an inventory of spatial data for the study area was completed in the summer of 2002. Regional, state-wide, and national GIS (Geographic Information Systems) coverages that were relevant to the MMSD Corridor Study were included in the inventory.

Surface-water studies

One-hundred and sixty-nine reports were found describing the surface-water quality of the study area. One-hundred and seventeen studies regarding surface-water quantity were located. Results of the surface-water quality and quantity reviews are summarized in tables 1 and 2, respectively.

Each water-quality study was reviewed to determine if it contained information describing the following categories: lake or stream information; field measurements (pH, specific conductivity, water temperature, dissolved oxygen); major ions and/or dissolved solids; nutrients; pesticides; dissolved and/or total organic carbon; sediment; bacteria and/or viruses; trace elements and/or heavy metals; volatile organic compounds (VOCs), poly aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins, inorganic, organic contaminants; wastewater treatment plants; emerging contaminants such as human and/or animal hormones and caffeine; urban issues; modeling; or other significant water-quality issues.

Water-quantity studies were reviewed to determine if they contained information regarding the following categories: lake or stream information; discharge or stream stage; extreme flows (floods or drought); hydrologic budget; erosion and/or sedimentation; runoff calculations; modeling; precipitation and/or climate; geomorphology; urban issues; or other significant water-quantity issues.

Each study is described in tables 1 and 2 in several sentences regarding its spatial extent (local, regional, state-wide) and the major thrust of the study.

Ecological studies

One-hundred and nine studies were found that described ecology in the study area. Table 3 summarizes the results of the review of ecology studies.

Ecology studies were reviewed to determine whether the report discussed information for any of the following categories: lake or stream information; fish; macroinvertebrates; algae and/or macrophytes; amphibians and/or reptiles; birds; mussels; wildlife; toxic bioassays; endangered and/or threatened species; tolerant or intolerant species; non-native or invader species; habitat; wetlands; human effects and/or urban issues; community surveys; management issues; water quality interpretations based on ecology; biotic index values; other significant issues regarding ecology.

Each study is described in table 3 in several sentences regarding its spatial extent (local, regional, state-wide) and the major thrust of the study.

GIS data sets

In inventory of GIS spatial coverages was conducted to summarize digital thematic data available for the MMSD planning area. Coupling sampling site information as stored in the MMSD Corridor Study data base with spatial data such as land use, point source discharge locations, or census data can provide a more complete picture of the state of surface-water resources in the MMSD planning area.

Inquiries were made to local, state, and federal agencies in compiling the list of GIS coverages existing for the MMSD planning area. Table 4 describes selected GIS coverages available for the MMSD planning area that enhance the knowledge of the state of surface-water resources. There are additional GIS coverages available for parts of the MMSD planning area however this list includes primarily data that covers the entire MMSD planning area.

COMPILATION OF HISTORICAL DATA (1970-PRESENT)

Electronic water, sediment, and tissue chemistry and ecological assessment data were compiled as part of the MMSD Corridor Study. Evaluating historical data provides a basis for designing a baseline-monitoring network of sampling sites for Phase II of the Corridor Study. Understanding the changes that have taken place in the MMSD planning area and identifying areas where insufficient data exist to describe the water-resources are the focus of compiling data sets for the planning area.

Data scope

Data compiled for the Corridor Study were constrained spatially, chronologically, and with regard to subject matter. Data compilation included data collected beginning in 1970 through the present. Data included were limited to the MMSD planning area (fig. 1). Data were collected for the stream corridors, streams and areas immediately adjacent to the stream. Data were not collected for Lake Michigan. The types of data collected include surface-water, sediment, and tissue chemistry, fish, habitat, macroinvertebrate, algal, meteorological, and streamflow data.

Legacy data sources

Data sets of water-resources related information were compiled from many different sources. The majority of data compiled in the MMSD Corridor Study data base at the time of publication came from MMSD, USGS, USEPA, and WDNR. Major data sets included in the Corridor Study are described in table 5. Additional data sources such as University and volunteer data sets were not incorporated into the data base at the time of writing however plans are to include as much relevant and accessible data as possible. Data sets will continue to be compiled after this report has been published. Updates of ongoing data collection efforts such as described in table 5 will be incorporated in the Corridor Study data base.

Design of data base management system

The MMSD Corridor Study data base is housed at the USGS Madison Wisconsin office on an Oracle platform. Data are served to internal users via an Oracle Portal website. Users can query data with an Ad-hoc query tool called Oracle Discoverer. One class of Discoverer users, “superusers”, have received training to develop Ad-hoc queries for themselves and others in their agencies. The larger class of Discoverer users have the ability to execute queries developed by the superusers or data base administrator.

The structure of the data base is shown in fig. 6. Water quality, ecology, and hydrology data are all stored within one data base allowing for query of various kinds of data from multiple different agencies from one location. Where the information was easily accessible, sample collection methods, lab analysis methods, and information describing the laboratory that performed the analysis were included with the data.

Challenges to combining data sets included varying definitions of sampling sites, minimal documentation of constituents, insufficient lab analysis method description, and lack of sampling purpose information in an easily accessible format.

The amount of information describing the location of a sampling site varied among the data sets. Latitude and longitude information were required for all sampling site locations. A general site name was assigned to all sampling site locations; overlapping sites were given the same general name to allow for easier comparison of data at a location with multiple data points. Sites were determined to share a sample location through a visual examination of where a site plotted on a map (based on its latitude and longitude) as well as the name and location description given to the site.

Comparing data between data sets with minimal constituent definitions was especially challenging for chemistry-related constituents. For example, over 1000 parameters were pulled from the USGS QWDATA data base. Trying to

compare data between data sets based on a short parameter name or abbreviation required scrutiny by several professionals familiar with water, sediment, and tissue chemistry. Links of constituents between data sets were made to the best of their knowledge and available information for constituents and methods. Table 6 lists the constituents described to concentration level (those that have boxplots, maps with concentration data, and summary statistics tables) in this report and the original constituent name, units and other details as described from the data source.

Lab analysis methods were not available for all data. Comparison of data between data sets should be taken on a relative basis as the method of analysis can influence results. Analysis methods from 30 years ago will likely differ in some respects from those methods used currently. Reporting limits were available for some but not all data and they changed for constituents from the same data base source as well as between data base sources.

Sample purpose was available for some data but not for most. Some samples may have been collected as part of a routine sampling schedule which does not take into account flow levels when planning sampling events. Other samples may have been collected as part of an event-sampling, either for high or low flows. Some samples may have been collected as part of a monitoring program whereas others may have been targeted to sample in an area known to be contaminated areas.

EVALUATION OF HISTORICAL DATA

After the compilation of major data sets was completed, analysis of the data began. Constituents to be examined were selected based on their relevance to the study and whether there was a sufficient amount of data to provide insight as to changes in concentrations and sampling spatial and temporal distribution.

Appropriate use of MMSD Corridor Study Data base

Comparison of data within the MMSD data base must be done with caution and an understanding of the limitations of data compiled from different sources. Data compiled as part of the MMSD Corridor Study data base covers more than 30 years, sampling sites scattered over 400 square miles, and has been collected by many agencies for various purposes using different field collection and lab analysis methods. Field collection and lab analysis methods, sample purpose, and reporting limits were only easily available for part of the data. Many water chemistry constituents were reported with different detection limits for the same parameter. Some constituent concentrations were reported as zero when the concentration determined from analysis was below the detection limit. Lab analysis methods have improved for many constituents over the years resulting in being able to determine concentrations at lower levels than was possible with earlier data.

The following rules were used when creating the summary statistics tables and boxplots available in the appendices,

the maps of locations of constituent sampling and median concentrations, and when looking at trends and seasonality:

1. Where a remark flag indicated “<”, concentrations were set to half the original concentration or half the reporting limit concentration where the original concentration was zero. Concentrations of zero without a reporting limit were left as zero. These values were then used in the calculation of all summary statistics and in generation of boxplots.
2. In graphing boxplot data on a log scale, zero values were set to the next lowest value of 1×10^x . For example, if some concentrations of total phosphorus were reported as zero and the minimum concentration was 0.02, the values of zero would be set to 0.01 for the purposes of the boxplot since plotting zero values is not allowed on a log scale.
3. Concentrations have been rounded, the number of decimal places to which they have been rounded is indicated in the headnote to each appendix table.

Historical conditions

Descriptions of data in this report generally include for each constituent a text description, a map showing locations of sampling sites and some further information describing data (median concentrations, counts of samples collected at a site), and in a few cases graphs showing trends and or seasonality information. Included in the appendices are summary statistics tables and boxplots for most constituents.

Guidelines used by the USEPA, WDNR, and Canada for drinking water and/or for the protection of aquatic life are discussed for each constituent where available. Surface water is not used for drinking water in the Milwaukee area however drinking water guidelines are used for a relative comparison to concentrations because of a lack of other established criteria. Table 7 gives a summary of the types of guidelines referenced in this report. Where guideline concentrations fell near or within the range of concentrations for a constituent, the guideline concentration is indicated in the boxplot and was factored into setting breakpoints for mapping median concentrations.

All surface-water, sediment, and tissue chemistry constituents were analyzed for trends and seasonality by looking at the data for five sites. The five sites included Kinnickinnic River at 1st Street, Lincoln Creek at 47th Street, Menomonee River at 70th Street, Milwaukee River at Wells Street, and Oak Creek at Ryan Road. These sites were chosen because they had a relatively large amount of data for many constituents and well distributed over the MMSD planning area. There were a few cases where sufficient data was not available for the five sites in which case data for other sites was used to look for trends or seasonality. Graphs for seasonality and or trends are only shown where significant trends or seasonality were evident in the data.

Maps generally show sampling site locations and, where appropriate, median concentrations and the number of samples collected from 1970 through 2002. Median concentrations are depicted for sampling site locations by using color to indicate median concentrations falling within designated ranges. Subwatersheds with data for a constituent are also

shaded to indicate overall median concentration for the subwatershed based on the same ranges as the sampling site. The number of sites in a subwatershed and the total number of samples collected for those sites (often indicated by relative size of the dot) give readers a way to visually weigh the credibility of assigning a median concentration to a subwatershed. The ranges of median concentrations at sampling sites is generally larger than the median concentrations for subwatersheds meaning that the same range of colors shown for sampling sites may not be shown for subwatersheds. Subwatersheds that do not have any shading indicate no data has been collected in the subwatershed for that constituent. The ranges shown for a constituent are chosen based on a number of different factors including availability of USEPA, WDNR, or Canadian guideline concentrations, distribution of data over the range, categories for an index value, etc. Also, some maps indicate the number of samples collected by the size of the site location symbol, categories for which are listed in the legend, but generally run 1 to 10 samples, 11 to 100 samples, and more than 100 samples. Where many sampling locations on the main map appear very close together, an additional blown-up area near downtown Milwaukee is shown to allow readers to more easily determine the locations and median concentrations of sampling sites.

Because of constraints on the size of this report, maps of concentrations and sampling sites for constituents broken down by time periods were not included. Statistical scrutiny of data for a subset of sites for trends and seasonality for each constituent pointed to any significant changes that might have been seen in maps of concentration by decade or other such time periods. Figures 7 through 10 show locations of sampling sites that have been sampled since 1998 for four groups of constituents signifying those areas in the MMSD planning area that have been sampled in the recent past and may be part of a current monitoring program (especially for water chemistry, streamflow, stream stage, and precipitation).

Summary statistics including counts of samples collected, earliest and latest sample dates, detection limit values and minimum, maximum, mean, and percentiles are included in Appendix 1 for each constituent. The values used in calculating the summary statistics and depicting boxplot concentrations are as discussed in section “Appropriate use of MMSD Corridor Study Data base”. In cases where there were few concentrations above a detection limit and many different detection limits, boxplots were not drawn and some summary statistics were left out of the table due to skewedness of the data as a result of many non-detect concentrations. Subwatersheds with all or more than half of the samples having concentrations below a detection limit are noted in the text for each constituent.

Physical data

Rainfall and streamflow drive the dynamics of stream chemistry, geomorphology, and aquatic communities. Stream water quality commonly varies greatly in response to water discharge. Flooding, erosion, and sedimentation are major issues related not only to in-stream water quality but also may cause damage to structures as well as negative effects

on downstream areas. In addition, a great demand has been placed on water resources in Wisconsin by increased multiple uses such as maintenance of fish and wildlife habitat, irrigation of crops, dilution and assimilation of wastes, production of hydroelectric power, and maintenance of adequate flows for boating.

Stream discharge, stream stage, precipitation [INCOMPLETE]

USGS has collected discharge data at 42 sites (fig. 11; appendix 1.1) within the MMSD planning area for various periods of record beginning in 1970 and continuing until present. Mean daily discharge values are stored in the MMSD Corridor Study data base in cubic feet per second.

MMSD collects stream elevation data at four sites (fig. 11; appendix 1.1) in the MMSD planning area beginning in 1993 and continuing to the present. Hourly elevations (in feet above mean sea level) are stored in the MMSD Corridor Study data base.

MMSD maintains precipitation at 20 gauges around the MMSD planning area (fig. 11; appendix 1.1). Data is stored in the MMSD Corridor Study data base in cumulative inches per day at an hourly increment. Collection of precipitation data began in 1994 and continues to present.

Chemical indicators of water quality

Chemistry of the water, sediment, and tissues collected in surface-waters of the MMSD planning area reflect naturally occurring conditions as well as the influence of the urban environment surrounding them.

Field measurements and particulate data

Aquatic life are strongly influenced by the concentrations of various field constituents such as dissolved oxygen and biochemical oxygen demand as well as particulate matter in the water column.

pH

The pH of water effects the physiological functions of plants and animals and is an important indicator of the health of a water systems. The measurement of pH indicates if a water is either acidic or base, more precisely, it is the indica-

tion of hydrogen concentration in water, and is directly related to the ratio of hydrogen (H^+) and hydroxyl (OH^-) activities at any given temperature (U.S. Geological Survey, 1998). pH is reported on a scale of 0 to 14, with a value of 7 considered neutral. The pH of an aqueous solution is controlled by interrelated chemical reactions that produce or consume hydrogen (Hem, 1985). If hydrogen activity is greater than hydroxyl activity the solution is considered acidic (pH less than 7.0), if hydroxyl activity is greater than hydroxyl activity the solution is considered base, or alkaline (pH greater than 7.0).

Natural and anthropogenic sources can both effect pH. Carbon dioxide (CO_2) enters waterways through both natural and anthropogenic sources, including atmosphere, runoff, release from bacteria, and respiration from aquatic plants and forms a weak acid. Natural, unpolluted rainwater can have a pH as acidic as 5.6 because it absorbs CO_2 as it falls through the atmosphere. The pH of pure water at 25 degrees C is 7.0. River water in areas not influenced by pollution generally has a pH in the range of 6.5 to 8.5. Photosynthesis takes up dissolved carbon dioxide during daylight and releases CO_2 by respiration at night, pH fluctuations may occur and a pH near 9.0 may be reached. (Hem, 1985)

Other natural sources include the release of acidic and alkaline compounds from rocks and soils. When calcite is present, carbonates can be released increasing the pH; when sulfides are present, water and oxygen interact with minerals to form sulfuric acid lowering the pH. Water draining from marshes and forests is often slightly acidic due to the presence of acids produced by decaying vegetation (Murphy, 2002a). Anthropogenic sources can include mine drainage and air pollution. Exhaust from cars and power plant emissions increase the concentrations of nitrogen oxides and sulfur dioxide in the air. These pollutants react in the atmosphere to form nitric and sulfuric acid. Very high pH (greater than 9.5) and very low (less than 4.5) are unsuitable for most aquatic organisms. Young fish and immature aquatic insects are extremely sensitive to pH less than 5.0 and may die. Low pH can also affect aquatic life by altering stream chemistry. Low pH accelerates the release of metals from rock and sediments and these metals can affect fish metabolisms. pH above 9.0 can harm fish by denaturing cellular membranes (Murphy, 2002a). The USEPA Secondary Drinking Water Regulation (SDWR) and Canadian drinking water Aesthetic Objective (AO) both recommend pH values for drinking supply be between 6.5 and 8.5. Low pH can have a bitter metallic taste and be corrosive to plumbing; high pH has a slippery feel and soda taste and increases deposits in plumbing. The Canadian water quality guideline for protection of aquatic life has a standard for pH of 6.5-9.0.

Data for pH came from MMSD, USGS, and USEPA STORET data bases. Eighteen subwatersheds have 3 or more

readings of pH. There weren't any median concentrations at these subwatersheds that exceeded either above, or below any of the guidelines mentioned above (fig. 12; appendix 1.2; appendix 2.1). The Root River - Upper had the lowest median and maximum concentrations (7.38 and 8.06), while Honey Creek (8.15) and Butler Ditch (8.21) had the highest median concentrations. Ten subwatersheds had maximum readings above all three guidelines with the highest reading at the Menomonee River - Upper (11.0). Seven subwatersheds had readings below the guidelines with the lowest readings at Wilson Park Creek (5.06), and Menomonee River - Upper (5.10).

With regards to seasonal variability, four of the five sites have data throughout the year; Oak Creek at Ryan Road does not have data from early December to mid-March (appendix 3.1). The Milwaukee River and Menomonee River sites have similar variability; increasing pH values to early spring (early May), decreasing readings to around August, and slightly increasing until the end of the year. Oak Creek has a downward trend to near August and then increasing through the end of the data (early December). These seasonal variabilities follow the growing season for aquatic plants and could be due to the increased respiration of aquatic plants. There was much more seasonal variability at Lincoln Creek, increasing values from October to early March, but throughout the spring and summer it decreases and increases almost month to month. Trend analysis at the sites show similar trends at Kinnickinnic River, Menomonee River, Lincoln Creek and the Milwaukee River (appendix 3.2). There is a slight upward trend (in readings) in the early to mid 1980's followed by a slight downward trend until the latter 1990's (98-99) and a slight increase since. Lincoln Creek data sets starts in 1992 and shows a decrease to the late 1990's with a slight increase through 2002. Oak Creek at Ryan Road shows a different trend than the other 4 sights. Oak Creek has a slight downward trend from the start of the record through 2002. Possibly, there was a slight increase towards the end of the record but data is needed from subsequent years to see if this is occurring.

Alkalinity [INCOMPLETE]

MMSD, USGS, and USEPA STORET data bases provided alkalinity data for which median concentrations for sites in the MMSD planning area ranged from 0 to 340 milligrams per liter (mg/L) as CaCO₃ (fig. 13; appendix 1.3; appendix 2.2).

Only one sample was collected in the Honey Creek and Little Menomonee River subwatersheds and concentrations for both were below a detection limit. All other subwatersheds had samples with at least half of the concentrations

above a detection limit.

Hardness [INCOMPLETE]

Hardness data came from MMSD, USGS, and USEPA STORET data bases. Median concentrations for hardness ranged between 0.00 and 460.00 mg/L as CaCO₃ (fig. 14; appendix 1.4; appendix 2.3).

Specific conductivity

Specific conductance is the measure of a waters ability to conduct electricity. The higher the concentration of dissolved ions, the higher the specific conductance (SC). These ions can include the presence of dissolved solids such as; chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, and iron. Therefore, SC can be an indirect measurement of dissolved solids (Murphy, 2002b). Conductivity of the same water changes greatly with changes in temperature, complicating interpretation of data sets; normalizing the conductivity to a temperature eliminates this complication. Specific conductance measures how well water can conduct an electrical current for a unit length and unit cross-section at a certain temperature. Specifically, it is defined as the reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specific temperature (Hem, 1985).

Natural factors effecting SC include the release of ions from rocks and soils when water move over them. Rocks containing calcite, calcium, and carbonate will have ions dissolve in water and increase SC. Anthropogenic sources include acid mine drainage, agriculture run-off containing fertilizer (with phosphate and nitrate), and road run-off containing leaked automobile fluids and chemicals used for de-icing roads. In theory, pure water should have a SC of 0 μ S/cm at 25C. Distilled water has a SC of at least 1 μ S/cm at 25 degrees C. Rain water usually has a SC higher than distilled water because it dissolves gases and other airborne particulates. Sea water has a SC of 50,000 μ S/cm at 25 degrees C because of high amounts of dissolved salts.

There are not any specific regulatory levels, neither drinking water standards, or aquatic health guidelines for SC.

Specific conductivity data came from MMSD, USGS, USEPA STORET data bases. Nineteen of thirty-seven subwatersheds have measurements (3-10,522 μ S/cm readings) for SC (fig. 15; appendix 1.5; appendix 2.4). The median concentrations range from 522 μ S/cm at 25 degrees C at Butler Ditch to 1,361 μ S/cm at 25 degrees C at Root River -

Upper. In general, the higher median concentrations are in the southern half of the MMSD planning area. The highest maximum readings were in the following subwatersheds; Underwood Creek (8,000 $\mu\text{S}/\text{cm}$ at 25 degrees C), Kinnickinnic River (8,280 $\mu\text{S}/\text{cm}$ at 25 degrees C), Wilson Park Creek (12,100 $\mu\text{S}/\text{cm}$ at 25 degrees C), and Lincoln Creek (12,800 $\mu\text{S}/\text{cm}$ at 25 degrees C).

Four of the five sites where seasonality was examined (except for Oak Creek at Ryan Road) show similar seasonal variability (appendix 3.3). Increasing readings starting near October until April/May and followed by decreasing readings through the spring and summer. This would parallel the use of de-icing compounds on paved services. Oak Creek is more difficult to interpret as there were no readings from December through March. There does appear to be a slight decreasing trend in values from spring until fall. Temporal trend analysis for the Milwaukee River and Oak Creek sites show similar trends, decreasing values from the start of their record (1980 and 1985) respectively, with readings increasing (slightly) since 1999 (appendix 3.4). The Menomonee River at 70th Street shows a small increase from 1978 to 1984/85, decreasing (slightly) to 1987, and very little change through 2002; possibly there may be a very slight upward trend the last 2-3 years. Lincoln Creek at 47th Street. has a small upward trend in SC values from the start of the record (1994) through 2002. The Kinnickinnic River at 1st Street. values increase 1980-1986, a small decrease from 1987-89, an increasing trend from 1990-97/98, and a decreasing trend since then.

Dissolved oxygen

Dissolved oxygen ($\text{O}_2(\text{g})$) is perhaps the most biologically important dissolved gas in natural waters. With a few odd exceptions, all multicellular organisms, including plants and many bacterial species, rely on oxygen as an electron acceptor in respiration. The ultimate source of dissolved oxygen to surface waters is the atmosphere. Oxygen partitions to water according to well-known rate and solubility laws. The amount of oxygen that can be dissolved in fresh waters is controlled mainly by water temperature but the actual ambient concentration represents a highly dynamic (on a time scale of seconds to minutes) balance between the atmospheric source and various biotic and abiotic sinks. These include uptake by aquatic organisms and reaction with commonly-encountered reduced chemical species like sulfide, methane, and ammonium which are formed concurrent with organic matter decomposition.

Being critical to most aquatic organisms, various water quality standards for minimum dissolved oxygen concentrations have been propounded, sometimes tailored to the specific type of water (lake, stream, fresh, salt, etc.). Of these,

the Wisconsin Department of Natural Resources has selected a minimum of 5 mg/L as a protective level against fish kills and other deleterious effects on stream communities. Anthropogenic loading of decomposable organic matter or nutrients that cause algal blooms which later decompose are major sources of oxygen-consuming materials discharged to streams in the MMSD planning area.

MMSD, USGS, and USEPA STORET data bases contained dissolved oxygen data for many sites within the MMSD planning area. Although most sites had dissolved oxygen concentrations above the 5 mg/L standard, there were a few with median concentrations below this level including some on the Root River - Upper and near the confluence of the Kinnickinnic and Menomonee Rivers (fig. 16; appendix 1.6; appendix 2.5). Extrapolating individual site data to sub-watersheds, median concentrations were between 5.01 and 10.00 for all subwatersheds with data while somewhat less than half of the study area had no data (fig. 16). That said, all major watersheds had at least one site with very low dissolved oxygen levels that would almost certainly be cause for concern (appendix 1.6). Of these, the Menomonee River - Lower, Muskego Lake, and Root River - Upper tended to have the lowest dissolved oxygen concentrations (appendix 2.5).

There were no obvious trends in dissolved oxygen concentration versus sample year for the five highlighted sites (data not shown). In contrast, a pronounced seasonality was observed at all five sites with minimal values tending to occur in warm months (appendix 3.5). This pattern reflects the direct relation between oxygen utilization during organic matter decomposition and the inverse relation between solubility and water temperature.

Biochemical oxygen demand, 5 day

Five-day biochemical oxygen demand (BOD5) is an empirical measure of the oxygen-consuming material in a water sample. Because the experimental conditions are standardized at 20 °C over five days, it measures the potential oxygen demand rather than the true oxygen demand that exists in situ in a stream which may be limited by temperature or some other factor. Sources of oxygen consuming material include allochthonous and autochthonous organic matter and detritus, and reduced chemical species including sulfide, methane and ammonia which can be oxidized coupled to oxygen reduction.

There are no water quality standards for BOD5 for the MMSD-CS study area although effluents are sometimes mon-

itored and regulated for BOD5 load. In general, high values, indicating a high potential for oxygen uptake and hypoxia or anoxia, are of course less desirable.

BOD5 data are available in the MMSD Corridor Study data base from the MMSD, USGS, and USEPA STORET data bases. The vast majority of individual sites have BOD5 concentrations below 10.00 mg/L (fig. 17; appendix 1.7; appendix 2.6). The highest concentrations, between 1000.00 and 4890.00 mg/L occur at sites along the Mitchell Field Drainage Ditch and are associated with runoff of airplane deicing compounds applied at General Mitchell International Airport (Corsi and others, 2001). The maximum concentration (38,600.00 mg/L) for that subwatershed is an order of magnitude higher than that for next highest subwatershed (appendix 1.7). Somewhat lower concentrations (100.00 to 999.99 mg/L) occur at nearby sites in the Wilson Park Creek subwatershed. More than half of the subwatersheds have data and most of these have median BOD5 concentrations below 9.99 mg/L. Subwatersheds along the Lake Michigan shoreline, in addition to the West Milwaukee Drainage Ditch, have median concentrations between 100.00 and 999.99 mg/L. Sites in the Root River watershed tend to have the lowest BOD5 concentrations (appendix 2.6).

There were no significant temporal or seasonality trends for the BOD5 data.

Total suspended solids

Total suspended solids (TSS) is a measure of the all material, biotic and abiotic, that is retained on a filter. It is composed of suspended sediment mainly in the clay and silt size range, biomass (mainly live algae and zooplankton), and particulate detritus (dead organic matter). There are allochthonous and autochthonous sources for both the sediment fraction and the organic fraction. Suspended sediment ultimately comes from the watershed although a significant amount at any particular site may be resuspended from the stream bottom. Soil and surficial deposit characteristics in the watershed generally control the amount and size range of sediment coming into and transported in a stream. The main source of biomass is usually stream organisms but detritus may be dominated by allochthonous sources such as soil organic matter, leaf fragments, etc.. Primary production, input of soil organic matter, and resuspension of fine-grained organic-rich sediments largely determine the amount of organic matter in total suspended solids.

Total suspended solids has been selected (along with chlorophyll-a, total phosphorus and total nitrogen) by the

USEPA as a key nutrient criteria indicator in streams. Its importance is mainly as an indicator of erosion and transport of sediments from watersheds. Construction sites are often regulated to limit sediment washing off site into nearby surface waters. Also, buffer zones between agricultural sites and streams are increasingly utilized to decrease sediment inputs, and their associated nutrients, to surface waters. TSS often correlates with primary productivity in that eroded sediments are a large source of the limiting nutrient, phosphorus, to primary producer communities in streams. There is no TSS water quality standard for the streams in MMSD planning area although lower concentrations, indicative of clearer water, are usually more desirable.

Total suspended solids data came from MMSD and USEPA STORET data bases. The median concentration of TSS at individual sites ranges from 5 to 1000 mg/L (fig. 18; appendix 1.8; appendix 2.7). Highest medians (>750 mg/L) occur at sites in the Oak Creek watershed and in the Root River - Upper subwatershed of the MMSD planning area. The lowest median concentrations (< 249 mg/L) occur in the Wilson Park Creek and Mitchell Field Drainage Ditch subwatersheds (fig. 18) and in Willow Creek (appendix 2.7). About half of the subwatersheds have data (fig. 18). Of these, Root River - Upper and Oak Creek - Upper have the highest median concentrations, ranging between 750 and 1000 mg/L. Maximum individual TSS concentrations, however, were measured in the Milwaukee River - Lower (7,800 mg/L) and the Kinnickinnic River (7,210 mg/L) (appendix 1.8).

There was no obvious trend in TSS concentration with sample year at any of the five highlighted sites (data not shown). There was some indication of higher TSS concentrations during the late winter through spring months at the Menomonee and Milwaukee River sites (appendix 3.6). This might reflect sediment resuspension under the ice and new sediment inputs accompanying the spring thaw.

Residue on evaporation [INCOMPLETE]

Median concentrations of residue on evaporation (ROE) data ranged from 0 to 590 mg/L (fig. 19; appendix 1.9; appendix 2.8). ROE data comes from USGS and USEPA STORET data bases.

All the samples in the Dousman Ditch and Root River - Middle subwatersheds and more than half the samples in the North Branch Oak Creek and Root River - Lower subwatersheds had concentrations below a detection limit. Samples at all other subwatersheds had at least half of their concentrations above a detection limit.

Major ions

Elevated levels of major ions in surface water can indicate contamination from human sources such as road salt.

Sodium [INCOMPLETE]

Concentrations of dissolved sodium ranged from 1 to 71 mg/L as Na (fig. 20; appendix 1.10; appendix 2.9). Sodium data came from the USGS and USEPA STORET data bases.

Canada has set an aesthetic objective (AO) for sodium of 200 mg/L.

There is not a sufficient amount of data to identify trends or seasonality for sodium.

Chloride [INCOMPLETE]

Concentrations of total chloride ranged from 0 to 300 mg/L as Cl (fig. 21; appendix 1.11; appendix 2.10). Data from MMSD and USEPA STORET data bases provided chloride data to the MMSD Corridor Study data base.

The USEPA suggests a Secondary Drinking Water Regulation (SDWR) of 250 mg/L and Canada has suggested a concentration of 250 mg/L as an aesthetic objective for chloride.

All the samples in the Wilson Park Creek, Lake Michigan Direct, and Dousman Ditch subwatersheds had concentrations below a detection limit. All other subwatersheds had at least half of the samples with concentrations above a detection limit.

Potassium [INCOMPLETE]

Concentrations of dissolved potassium ranged from 1.6 to 3.4 mg/L as K (fig. 22; appendix 1.12; appendix 2.11). Potassium data came from the USGS and USEPA STORET data bases.

There is not a sufficient amount of data to identify trends or seasonality for sodium.

Nutrients

Concentrations of nutrients in surface water can determine whether there are enough nutrients for aquatic plant life to grow at a pace in equilibrium with other aquatic life or at an elevated level which adversely impacts other aquatic species.

Total nitrogen [INCOMPLETE]

MMSD, USGS, and USEPA STORET data bases contained total nitrogen data or components of total nitrogen. In most cases concentrations of total nitrogen were derived from adding either nitrate plus Kjeldahl nitrogen or nitrate plus total organic nitrogen plus ammonia nitrogen. Concentrations of total nitrogen ranged from 0.10 to 53.70 mg/L as N (fig. 23; appendix 1.13; appendix 2.12). Because total nitrogen concentrations were calculated from a number of different constituents, the number of samples with one or more components having concentrations below a detection limit is unknown.

The proposed USEPA nutrient criteria for Level III Ecoregion 53 is 1.59 mg/L as N for calculated concentrations of total nitrogen.

Total nitrate

Dissolved nitrate (NO_3^-) is a frequently occurring form of inorganic dissolved nitrogen in virtually all surface waters of the MMSD planning area. As a component of the nitrogen cycle, coupled with nitrogen being a major chemical component of all living organisms, it is rapidly taken up by algae, macrophytes, and other primary producer organisms. Natural sources to surface waters include oxidation of reduced nitrogen species (including ammonia) in either influent groundwater, surficial bed sediments, or in the water column of streams and lakes. Nitrate also has a considerable anthropogenic source as fertilizer applied in agricultural, urban, and suburban settings. In southeastern Wisconsin, nitrate is sometimes viewed as a hallmark of infiltration of excess fertilizer use in agricultural areas (Saad, 1997). This is due to its relatively conservative nature in ground waters where it tends to be physically transported rather than chemically altered or sorbed to aquifer matrices.

Nitrate is an important constituent in terms of human health in that concentrations in excess of 10 mg/L are correlated with "blue baby syndrome", a condition where the nitrate in ingested water competes with oxygen in infants. Nitrite (NO_2^-), another form of dissolved inorganic nitrogen in surface waters also can cause or contribute to blue baby syndrome but is usually present in much lower concentration compared to nitrate. Hence nitrate remains the focus of water quality standards to safeguard against blue baby syndrome and is therefore sampled very frequently in water

quality monitoring studies. The USEPA has set a maximum contaminant level (MCL) drinking water guideline concentration of 10.0 mg/L of NO₃ and has proposed a nutrient criteria concentration limit of 0.94 mg/L of total nitrate plus nitrite in rivers for Level III Ecoregion 53. Concentration limits of 10 mg/L have also been set by the WDNR for a water quality MCL and by Canada as a maximum allowable concentration (MAC) in drinking water.

Data for total nitrate came from the MMSD, USGS, and USEPA STORET data bases. All but one sampling site have median dissolved nitrate concentrations that are less than 1.99 mg/L, and one has a median concentration of between 2.00 and 2.49 mg/L (fig. 24; appendix 1.14; appendix 2.13). Extrapolating these site median concentrations to their associated subwatersheds, most subwatersheds can be characterized as having less than 1.99 mg/L median nitrate concentrations (fig. 24). Two subwatersheds, Wilson Park Creek and the Root River - Lower have median concentrations between 0.95 and 1.99 mg/L. One of these, Wilson Park Creek, had a maximum measured concentration of 10.70 mg/L which exceeded the water quality standard (appendix 1.14; appendix 2.13). Thirteen subwatersheds don't have any data (fig. 24). The Deer Creek, Lake Michigan Direct, Lake Michigan Tributary, Underwood Creek, Combined Sewer Service Area, and North Branch Oak Creek subwatersheds had samples where every concentration was below the detection limit. There were fewer than ten samples collected in each of the six subwatersheds. More than half the samples, of which there were seventeen, collected at the Little Menomonee River had concentrations below a detection limit. All other subwatersheds had at least half of their samples with concentrations above a detection limit.

There is some indication from the plots of nitrate concentration versus sample year that concentrations were minimal in the period from the late 1980s to the early 1990s at four of the five highlighted sites that had data through this period (appendix 3.7). This pattern can be explained by relatively low rainfall and runoff during this period that decreased direct and groundwater inputs of nitrate to surface waters relative to periods before and afterward. Nitrate also shows a distinct seasonality at the five highlighted sites, tending to be minimal during the warm months of the year (appendix 3.8). This pattern likely reflects both a strong input function to surface waters during spring and fall runoff in addition to biological uptake in the summer.

Total phosphorus

When a nutrient is found to be limiting in fresh water, it is usually phosphorus due to the relatively large biochemical requirement for this element compared to available supply. Therefore even small increases in phosphorus can lead to large increases in biomass (assuming no other limitation). Allochthonous sources of phosphorus in streams include wet and dry deposition and rock weathering. Within the stream, phosphorus exists in several organic and inorganic forms, both particulate and truly dissolved. Total phosphorus is usually dominated by particle-associated phosphorus

and is present assimilated in biomass and detritus, sorbed to various mineral phases (iron oxyhydroxides, clays, etc.), or precipitated as apatite $[\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})]$, vivianite $[\text{Fe}_3(\text{PO}_4)_2 \cdot (\text{H}_2\text{O})_8]$, or other authigenic minerals.

Autochthonous sources of dissolved phosphorus in streams are probably dominated by sorption/desorption equilibria associated with sediments which in turn are controlled by physiochemical characteristics of the sediments (particle size and composition, mainly). The kinetics of abiotic phosphorus sorption and desorption are sufficiently fast such that a dynamic equilibrium with the ambient dissolved pool exists. Therefore, the sediments act both as a source and a sink, controlled by the input history of phosphorus and the biological demand.

Total phosphorus has been selected (along with chlorophyll-a, total suspended sediments and total nitrogen) by the USEPA as a key nutrient criteria indicator in streams. Its importance is mainly as a proxy for phosphorus loading to surface waters since phosphorus is the most common limiting nutrient on primary production in fresh water. For the MMSD planning area, a level of 0.08 mg/L was selected as a maximum allowable limit.

Total phosphorus data came from MMSD, USGS, and USEPA STORET data bases. Many individual sampling sites in the MMSD planning area have median concentrations that exceed the limit of 0.08 mg/L (fig. 25; appendix 1.15; appendix 2.14). These sites are scattered over the entire study area though many occur in the Menomonee and Milwaukee River watersheds. Most subwatersheds have total phosphorus data although a few, especially those along the far western and far eastern edges, and some in the lower half of the study do not. Of the subwatersheds with data, somewhat more than half have median values that exceed 0.08 mg/L (fig. 25; appendix 2.14). All major watersheds have at least one site that exceeds the limit (appendix 1.15). Four subwatersheds, Dousman Ditch, South Branch Underwood Creek, Combined Sewer Service Area, and North Branch Oak Creek, had concentrations for all samples below a detection limit. In each of the four subwatersheds only one sample was collected. Fifteen samples were collected in the Little Menomonee River subwatershed and more than half had concentrations below a detection limit. Concentrations for samples in all other subwatersheds were above a detection limit in at least half of the samples.

There were no consistent trends in total phosphorus concentrations either with sample year or with julian day at the five highlighted sites (data not shown). The lack of higher concentrations during the classical algal bloom periods of spring and fall as can be seen for chlorophyll-a (fig. X.XX chlorophyll-a seasonality graph) suggests that inorganic phosphorus sorbed to suspended sediment is a major component of total phosphorus at these sites.

Dissolved phosphorus [INCOMPLETE]

Dissolved phosphorus data came from USGS and USEPA STORET data bases. Dissolved phosphorus concentrations

ranged from 0.006 to 0.530 mg/L as P (fig. 26; appendix 1.16; appendix 2.15).

Trace elements/metals

Detection of trace metals in surface water, sediment, and tissues can be a result of both the natural landscape based on geologic processes and surficial deposits and anthropogenic processes which contribute contaminants to streams.

Sediment provides habitat and a food source for a wide variety of benthic organisms. Exposure to certain substances in sediments such as trace elements could potentially be a significant hazard to the health of the benthic organisms and other species in the food chain above them. Because of this sediment quality guidelines (SQG's) were established as tools regarding the relationship between concentrations of chemicals and any adverse biological effects from exposure to these chemicals. The Canadian Council of Ministers of the Environment (2002a) have established SQG's for the protection of aquatic life. The formal protocol used to derive sediment quality guidelines relies both on a modification of the national status and trends program, and the spiked-sediment toxicity test. Canada's interim sediment quality guidelines (ISQG) are recommended if information is available to support only one approach. (Canadian Council of Ministers of the Environment, 1999). The Canadian probable effects level (PEL) is the concentration above which adverse biological effects are expected to frequently appear. Also referred to in this report is the MacDonald scale (MacDonald and others, 2000). MacDonald's thresholds are the threshold effect concentration (TEC), adverse effects are not expected below these concentrations, and probable effects concentration (PEC) where more adverse effects are expected at concentrations above the PEC.

Very few samples of trace metals in tissue are in the MMSD Corridor data base and will not be discussed in this report. Many concentrations for trace elements in water were below a detection limit. Many trace elements also had relatively high detection limits. Because of the large number of non-detects and high detection limits no maps of trace elements in water or boxplots were created, and summary statistic tables contain a subset of information because of data skewedness. Also, due to a small number of samples, no trends or seasonality analysis was done for trace metals in sediment or water.

Cadmium

Cadmium is found to some extent in all soils and rocks including coal and mineral fertilizers. Most cadmium used in the United States is extracted during the smelting of copper, zinc, and lead. Anthropogenic uses of cadmium include: electroplating and coating, pigments in paint, and plastics, batteries (nickel-cadmium and solar), machinery and baking enamels, and fluorescent tubes. Cadmium binds tightly to soil particles and doesn't break down in the environ-

ment, but may change form (Agency for Toxic Substances and Disease Registry, 1999b). Common sources of cadmium input to water are; dissolving of galvanized pipes, erosion of soils and rocks, point and non-point sources. Wisconsin was in the top 7 states, 1987-1993, in the release of cadmium to land (U.S. Environmental Protection Agency, 2002b).

Water

The Canadian drinking water MAC guideline, WDNR MCL, and USEPA MCL for drinking water all are 0.005 mg/L. The Canadian water quality guidelines for the protection of aquatic life is 0.017 mg/L. The USEPA MCL was established due to the possibility of kidney, liver, bone, and blood damage from long term exposure to cadmium concentrations above the MCL.

Cadmium data in water came from MMSD, USGS, and USEPA STORET data bases. Twenty-eight of the thirty-seven subwatersheds have no cadmium (in water) data (appendix 1.17). Five subwatersheds had samples collected that had all concentrations below a detection limit, three subwatersheds had more than half of their samples as non-detects. Nine subwatersheds had less than half their samples as non-detects, of these nine, none had median concentrations above the MCL. The following subwatersheds had maximum concentrations above all of the guidelines used for this report: Kinnickinnic River (60.0 µg/L), Menomonee River - Lower (41.0 µg/L), Menomonee River - Upper (9.0 µg/L) Underwood Creek (9.0 µg/L), Milwaukee River - Lower (942 µg/L), Mitchell Field Drainage Ditch (12 µg/L), Oak Creek - Lower (14 µg/L), Oak Creek - Middle (11 µg/L), and Oak Creek - Upper (8 µg/L).

Sediment

Cadmium data in sediment came from USGS and USEPA STORET data bases. Ten of the thirty-seven subwatersheds contain cadmium (in sediment) data, of those, five had two or fewer samples (fig. 27; appendix 1.18; appendix 2.16). Subwatersheds with median concentrations above both the Canadian ISQG (0.6 µg/g) and TEC (0.99 µg/g) were Lilly Creek (1.0 µg/g), Menomonee River - Upper (2.0 µg/g), and the Milwaukee River - Lower (3.0 µg/g). The Kinnickinnic River (4.4 µg/g) and Menomonee River - Lower (3.9 µg/g) had median concentrations above the PEL (3.5 µg/g). Maximum concentrations at Lincoln Creek (2.0 µg/g) was above the TEC; one sample at the Little Menomonee River (4.0 µg/g) was above the PEL. The highest maximum concentrations was found at the Kinnickinnic River (9.5 µg/g), Menomonee River - Lower (9.4 µg/g), and the Milwaukee River - Lower (6.1 µg/g) and were above all of the guidelines. The subwatersheds with the highest maximum concentrations found in water correspond with the highest maximum concentrations in sediment. One set of nested subwatersheds (Menomonee River - Upper and - Lower) have data for cadmium in sediment. The upper subwatershed had a median concentration of 2.0 µg/g and the

lower subwatershed a median concentration of 3.9 µg/g. One of two samples in the Muskego Lake subwatershed had a concentration below a detection limit. Samples in all other subwatersheds were above a detection limit in at least half the samples.

Mercury

Mercury enters the environment from both natural and anthropogenic sources. Natural sources include volcanoes, natural mercury deposits, and volatilization from the ocean. Anthropogenic sources include coal combustion, chlorine alkali processing, waste incineration, and metal processing. Best estimates to date suggest that human activities have doubled, or tripled the amount of mercury in the atmosphere, and the atmospheric burden is increasing by about 1.5 percent per year. (U.S. Geological Survey Mercury Studies Team, 2003a). Studies of sediment cores show that sediments deposited since the industrial revolution have mercury concentrations 3 to 5 times that of the pre-industrial sediments (U.S. Geological Survey Mercury Studies Team, 2003a). The highest deposition rates in the U.S. occur in the Southern Great Lakes, Ohio Valley, the Northeast, and parts of the Southeast. Globally, the United States contributes about 3 percent to the environment, but approximately two-thirds of this is transported outside our borders. Approximately 60 percent of the mercury deposition that occurs in the U.S. comes from domestic anthropogenic sources. The remaining 40 percent comes from anthropogenic sources outside of the U.S., re-emitted mercury from historic U.S. sources, and natural sources (U.S. Environmental Protection Agency, 2000f). There are 3 forms of mercury---methyl, elemental, and inorganic. Mercury released to the environment is usually in elemental, or inorganic forms. Biological processes change the chemical form of mercury to the organic form, methylmercury, which is the more toxic form found in aquatic species (U.S. Environmental Protection Agency, 2002e). Methylmercury bioaccumulates in all aquatic species, and is biomagnified as you proceed up the food chain. Mercury is the leading contaminant-related human-health advisory in the United States, accounting for almost 80 percent of all fish consumption advisories.

Water

Many changes have taken place with mercury analysis and collection techniques have changed greatly since the late 1980's. Analysis now can accurately quantify aqueous mercury samples at the sub-parts-per trillion range. Newer generation analytical instrumentation have allowed the development of analytical methods for environmentally relevant forms of mercury, including gaseous elemental mercury and methylmercury. New cleaning and field methodology have been developed to address sample contamination at these very low levels of detections. (U.S. Geological Survey Mercury Studies Team, 2003b).

The USEPA MCL to mercury is in response to potential kidney damage at concentrations above the MCL. WDNR and USEPA MCL are both 0.002 mg/L; and the Canadian guideline for the protection of aquatic species is 0.1 µg/L.

Mercury data came from the MMSD and USEPA STORET data bases. Nineteen of thirty-seven subwatersheds have had samples collected for mercury (appendix 1.19). Of these nineteen, eight of the subwatersheds had no-detects, and the remaining eleven had over half their samples as non-detects. Fourteen of the subwatersheds sampled had samples collected starting in the mid 1970's, and half of those had all of their samples collected in the 70's. Of the eleven subwatersheds with sample detects, all had maximum concentrations above the guidelines. The highest maximum concentrations were found in: Milwaukee River - Lower (1.50 µg/L), Root River - Upper (0.89 µg/L), Menomonee River - Lower (0.78 µg/L), and Root River - Middle (0.66 µg/L). Three watersheds had samples at subwatersheds in upper and lower segments; Menomonee River - Upper and - Lower, Oak Creek - Upper, - Middle and - Lower, and Root River - Upper, - Middle and - Lower. The Menomonee River and Oak Creek sites show similar findings, lower maximum concentrations at the upper end, and the higher maximum concentrations at the lower end. While the Root River was just the opposite, the highest maximum concentration was at the - Upper (0.89 µg/L), and decreased as you moved down the system, - Middle (0.66 µg/L), and the - Lower (0.34 µg/L).

Sediment

Data for mercury in sediment came from the USGS and USEPA STORET data bases. Nine subwatersheds have been sampled for mercury in sediment, only one subwatershed had more than half of its samples collected as non-detects (fig. 28, appendix 1.20; appendix 2.17). The three subwatersheds with non-detects had sampling begin in the early 1970's. Sediment quality guidelines for mercury are: Canadian ISQG (0.17 µg/g), MacDonald TEC (0.18 µg/g), Canadian PEL (0.486 µg/g), and MacDonald PEC (1.06 µg/g). Four subwatersheds had enough data for statistical analysis for median concentrations. The median concentration at the Menomonee River - Upper (0.12 µg/g) was less than all guidelines, The Kinnickinnic River (0.20 µg/g), Menomonee River - Lower (0.46 µg/g), and Milwaukee River - Lower (0.27 µg/g) exceeded both the Canadian ISQG and MacDonald TEC. None of the subwatersheds had median concentrations above either the Canadian PEL, or MacDonald PEC. Three subwatersheds had maximum concentrations above all guidelines; Kinnickinnic River (3.15 µg/g), Menomonee River - Lower (3.55 µg/g), and Milwaukee River - Lower (3.35 µg/g). The Menomonee River subwatershed was the only basin with mercury sediment data in upstream and downstream segments (Menomonee River - Upper and - Lower). The highest median and maximum concentrations of mercury of sediment were found in the lower subwatershed.

Copper

Copper is an essential element in plant and animal metabolism and occurs in the earth's crust as a metal. Copper does not break down in the environment. Metallic copper is used for money, electrical wiring, and plumbing. Copper is mixed with other metals to make brass and bronze. Copper salts are used in small amounts in water-supply reservoirs to discourage the excessive growth of algae. Other anthropological sources from copper are; extensive use in pesticide sprays, combustion of fossil fuels, and as preservatives for wood, leather and fabrics. Due to the widespread use, copper is therefore likely to be more readily available for solution in ground and surface water than its low average abundance in rocks might imply (Hem, 1985). Wisconsin is not in the top 10 states in release of copper to land or water (U.S. Environmental Protection Agency, 2002c). Concentrations of copper in bed sediment is well correlated with population density (Rice, 1999).

Water

The USEPA established an MCL for copper due to stomach distress (short term exposure) and possible damage to liver and kidneys for long term exposure. The USEPA MCL and WDNR MCL are both 1300 µg/L, the Canadian drinking water AO is 1000 µg/L. The Canadian standard for the protection of aquatic life is 2-4 µg/L.

Data for copper in water comes from MMSD, USGS, and USEPA STORET data bases. Twenty-two subwatersheds have been sampled for copper (appendix 1.21). Seven of those subwatersheds had no detects, and one subwatershed had over 50 percent of its samples as non-detects. None of the sites with data had maximum concentrations exceed any of the drinking water standards. All of the subwatersheds had maximum concentrations above the Canadian guideline for aquatic life. The highest maximum concentrations occurred in the following subwatersheds; Kinnickinnic River (275 µg/L), Menomonee River - Lower (600 µg/L), Menomonee River - Upper (321 µg/L), and the Milwaukee River - Lower (478 µg/L). Of the nested subwatersheds only the Menomonee River - Upper had higher median concentrations than the - Lower. Both the Root and Oak subwatersheds had just the opposite results, the highest median concentrations were in the upper subwatersheds.

Sediment

Sediment quality guidelines for copper are MacDonald TEC (31.6 mg/kg), Canadian ISQG (35.7 mg/kg), MacDonald PEC (149 mg/kg), and Canadian PEL (197 mg/kg).

Data for copper in sediment came from USGS and USEPA STORET data bases. Eight subwatersheds have data for copper, of those eight, three have just one sample in their subwatersheds, all of the samples were detects (fig. 29; appendix 1.22; appendix 2.18). The concentration for one sample in the Little Menomonee Creek subwatershed was

less than all standards. The median concentrations for the remaining seven subwatersheds exceed both the TEC and ISQG. None of the median or maximum concentrations at all subwatersheds exceeded either the PEC or PEL. The four highest maximum (and median) concentrations for copper in sediment were found at Kinnickinnic River, Little Menomonee River, Menomonee River - Lower, and Milwaukee River - Lower. This agrees with the findings from surface water, except, the Little Menomonee River was higher in sediment concentrations than the Menomonee River - Upper. The Menomonee River - Upper and - Lower subwatersheds had multiple samples for copper. The lower median concentrations was at the - Upper (37 µg/g) and the highest was in the - Lower (140 µg/g).

Lead

Lead is a naturally occurring metal, but most of the lead found in aquatic systems is from anthropogenic sources. Lead was historically used in household plumbing and service lines to the home and is still present in many older homes. Another source of lead from plumbing is the lead in some solder used for copper pipes. Today, most of the new anthropogenic lead additions to the environment are derived from material sources. Point sources of lead to aquatic systems include industrial effluents, municipal wastewater effluent, stack emissions, and fossil fuel combustion. Lead concentrations have declined due to the removal of leaded gasoline (Callendar and Rice, 2000). Concentrations of lead is well correlated with population density (Rice, 1999). From 1987 to 1993, Wisconsin was in the top 10 states in release of lead to land and water. (U.S. Environmental Protection Agency, 2002d).

Water

The WDNR MCL and USEPA MCL are both 0.015 mg/L TTAL. TTAL is “Treatment Techniques Action Level”, the concentration of a contaminant which, if exceeded, triggers treatment or other requirements which a water system must follow (Wisconsin Department of Natural Resources, 2003). The USEPA MCL was established due to potential health concerns related to the physical and mental development in infants, and potential kidney problems and high blood pressure in adults. The Canadian drinking water guideline is 0.010 mg/L, and the Canadian guideline for the protection of aquatic health is 1-7 µg/L.

MMSD, USGS, and USEPA STORET data bases provided data regarding lead in water. Twenty-one subwatersheds in the MMSD planning area have data for lead in water (appendix 1.23). Of those twenty-one subwatersheds, six had all samples as non-detects, and one other subwatershed had more than half of its samples as non-detects. Of the subwatersheds with sufficient data for statistical summary, seven subwatersheds had median concentrations at, or above all the guidelines. The remaining eight subwatersheds were at or above the guideline for the protection of aquatic health. The highest maximum concentrations were found at the Kinnickinnic River (1400 µg/l), and Menomonee

River - Lower (2200 µg/L).

Sediment

Sediment quality guidelines for lead are: Canadian ISQG (35.0 mg/kg), MacDonald TEC (35.8 mg/kg), Canadian PEL (91.3 mg/kg), and MacDonald PEC (128 mg/kg).

Lead in sediment data came from USGS and USEPA STORET data bases. Eleven of thirty-seven subwatersheds have data for lead in sediment, five of these basins have only one sample (fig. 30; appendix 1.24; appendix 2.19). A total of seventy-one samples were collected, of these, two were non-detects. Of the six subwatersheds with more than one sample, median concentrations were below all guidelines at Muskego Lake (6.5 µg/g), and Lilly Creek (30 µg/g); exceeded the ISQG and PEL at Menomonee River - Upper (45 µg/g) and exceeded all guidelines at Kinnickinnic River (271 µg/g), Menomonee River - Lower (225 µg/g), and Milwaukee River - Lower (150 µg/g). The lowest maximum concentrations were found in Muskego Lake (7.0 µg/g), Little Menomonee Creek (20.0 µg/g), and Root River - Middle (30.0 µg/g). The highest maximum concentration was found in the Honey Creek subwatershed (4100 µg/g) in 1980. Median concentration at Menomonee River - Lower was significantly higher than Menomonee River - Upper.

Arsenic

Sources of arsenic in surface water and sediments can be both natural and anthropogenic. Geologic sources of arsenic include sorbed arsenic in iron oxide coatings on minerals and impurities in pyrite and other metal sulfides (especially rock that contains iron and copper). Anthropogenic sources of arsenic include wood preservatives (presently about 90% of all arsenic produced is used for wood preservative as chromated copper arsenate) (Agency for Toxic Substances and Disease Registry, 1999a); glass production, poultry and swine feed production, semiconductor manufacturing and petroleum refining ([USEPA, rev July 1999]; Welch and others, 2000). Prior to the 1990's, pesticide applications of lead arsenate (primarily) on fruit orchards was the dominant use of inorganic arsenic, this use was banned in the 1990's.

Water

Arsenic is considered a highly undesirable impurity in water supplies because in small amounts it can be toxic to humans (Hem, 1985). The USEPA MCL for arsenic was established due to possible health effects related to exposure above the MCL. These health effects include; skin damage, circulatory system problems, and an increased risk of cancer. The USEPA revised its MCL for arsenic in drinking water from 50 µg/L to 10 µg/L on January 22, 2001. Pub-

lic water supplies must comply with the new standard beginning January 23, 2006. (U.S. Environmental Protection Agency, 2003). The WDNR maintains an MCL of 50 µg/L. Canada has an IMAC of 0.025 mg/L and an aquatic life criteria of 50 µg/L.

Arsenic in water data came from MMSD, USGS, and USEPA STORET data bases. Twenty-four of the subwatersheds in the MMSD planning area do not have any data for arsenic in water (appendix 1.25). The Combined Sewer Service Area, Honey Creek and Lake Michigan Tributary subwatersheds had samples collected for arsenic in the mid 70's to early 80's and none of the samples had a concentration above a detection limit. The Little Menomonee River, Oak Creek - Lower, Oak Creek - Middle, Oak Creek - Upper, and Root River - Middle subwatersheds had at least half of the samples collected as non-detects. Concentrations in other subwatersheds were above a detection limit in at least half the cases.

The following sites had at least one sample exceed the new USEPA MCL of 10 µg/L; Lincoln Creek (15.2 µg/L), the Milwaukee River - Lower (14.0 µg/L), and the Menomonee River - Upper (52.0 µg/L). Only the Menomonee River - Upper subwatershed had one sample with a concentration exceeding the WDNR MCL of 50 µg/L with a concentration of 52.0 µg/L.

Sediment

Canada has an ISQG of 5.9 mg/kg and a PEL of 17.0 mg/kg. A TEC of 9.79 mg/kg and a PEC of 33.0 mg/kg were recommended by MacDonald.

Data on arsenic in sediment came from the USGS data base. Thirty-three of the thirty-seven subwatersheds in the MMSD planning area have had no samples collected for arsenic in sediment (fig. 31, appendix 1.26; appendix 2.20). The Root River - Middle (2.0 mg/kg) and Lincoln Creek (4.0 mg/kg) had one sample collected with concentrations less than both the Canadian and MacDonald guidelines. Other rivers with only one sample were; Little Menomonee Creek (38.0 mg/kg) above both SQG's, the Little Menomonee River (6.0 mg/kg) above the ISQG. Two subwatersheds had median concentrations below the ISQG; Menomonee River - Upper (4.0 mg/kg), and Milwaukee River - Lower (5.1 mg/kg). The other subwatersheds had median concentrations above the ISQG; Kinnickinnic River (6.1 mg/kg), Lilly Creek (10 mg/kg), Menomonee River - Lower (7.0 mg/kg). The Menomonee River - Upper was the only subwatershed with more than one sample that never had concentrations exceed any SQG's.

Chromium

Chromium is a naturally occurring and vital element. Chromium is present in the environment in several different forms. The most common forms of chromium are chromium (0), chromium III (trivalent), and chromium VI (hexavalent) (Agency for Toxic Substances and Disease Registry, 1999c). Chromium occurs most as chrome iron ore and is widely distributed in soils and plants, but is rare in natural waters. Concentrations of chromium in natural waters, not effected by waste disposal, are commonly less than 10 µg/L. (Hem, 1985). Anthropogenic sources of chromium include: stainless steel, protective coatings on metals as a rust inhibitor, wearing down of asbestos brake lining on automobiles, pigments for paints, cement, paper, rubber, composition flooring, chemical synthesis, industrial water treatment (electroplating, leather tanning, and textile industries), astringents and antiseptics, and emissions from cooling towers (as rust inhibitors). Wisconsin is not listed by the USEPA as one of the top 10 states in the release of chromium. Most chromium in surface water is particulate and is very persistent and is ultimately deposited into sediments.

Water

Because of the potential for skin irritation, the USEPA has an MCL of 0.1 mg/L for drinking water, the WDNR has the same MCL. The Canadian drinking water guidelines has a lower MCL of 0.05 mg/L and the Canadian water quality guidelines for the protection of aquatic life has two standards; trivalent chromium (8.9 µg/L) and hexavalent chromium (1.0 µg/L).

MMSD, USGS, and USEPA STORET data bases provided data for chromium in water for the MMSD planning area. Twenty-one of thirty-seven subwatersheds have been sampled for chromium (appendix 1.27). Eight of the subwatersheds had all samples as non-detects, four more had at least half their samples as non-detects. The Kinnickinnic River (581 µg/L), Menomonee River - Lower (600 µg/L), and the Milwaukee River - Lower (8,864 µg/L) had the highest maximum concentrations, and the only maximum concentrations of the subwatersheds sampled above the WDNR Standard and USEPA MCL. There were 3 watersheds that had subwatersheds sampled with upper and lower segments. Only one of the set of subwatersheds show a slight increase, or no change in median concentrations from the upper to lower segments. The Menomonee River - Upper (5.0 µg/L), and Menomonee River - Lower (6.0 µg/L). The other two show either a slight decrease or no change from top to bottom: Oak Creek - Upper (6.0 µg/L), - Middle (5.0 µg/L), - Lower (5.0 µg/L), and Root River - Upper (4.7 µg/L), - Middle (4.7 µg/L), and - Lower (4.7 µg/L). Of the subwatersheds (12) with sufficient samples to calculate median concentration, none were above either the Canadian or EPA MCL for drinking water. Eleven of the twelve median concentrations exceeded the Canadian aquatic life guideline with the exception being the Little Menomonee River (1.5 µg/L).

Sediment

Sediment quality guidelines for chromium are: Canadian ISQG 37.3mg/kg, MacDonald TEC 43.4mg/kg, Canadian PEL 90mg/kg, and MacDonald PEC (111mg/kg).

Chromium data in sediment came from the USGS data base. Nine of thirty-seven subwatersheds had at least one sample collected for chromium and all of the samples collected had detectable concentrations of chromium (fig. 32; appendix 1.28; appendix 2.21). Five of the subwatersheds median concentrations did not exceed any sediment quality guidelines. Little Menomonee River subwatersheds median concentration of 70 µg/g exceeded the ISQG and TEC. The median concentrations at three subwatersheds; Kinnickinnic River (330 µg/g), Menomonee River - Lower (162 µg/g), and Milwaukee River - Lower (117 µg/g) exceeded all sediment quality guidelines used for this report. The highest sediment concentrations of chromium correspond with the highest concentrations found in water, the Kinnickinnic River (581 µg/g), Menomonee River - Lower (600 µg/g), and the Milwaukee River - Lower (8,864 µg/g). Only one set of nested subwatersheds (Menomonee River -Upper and - Lower) have data for chromium in sediment. The upper subwatershed had a median concentration of 30 µg/g and the lower subwatershed a median of 162 µg/g.

Nickel

Nickel is a very abundant element and much of it that occurs in the environment is found in soils and sediments. Nickel attaches to particles that contain iron or manganese which are often present in soil (Agency for Toxic Substances and Disease Registry, 1999d). The anthropogenic sources of nickel include: nickel is a very important industrial metal, it is used in the production of stainless steel, and other corrosive-resistant metal, battery manufacturing, color ceramics, and as a catalyst in organic chemical manufacturing, and petroleum refining. Because of its significant cultural use, nickel can be contributed to the environment in significant amounts by waste disposal (Hem, 1985). Nickel is one of the most mobile of heavy metals in the aquatic system. This mobility is controlled by the ability of various sorbents to scavenge it from solution. Nickel does not appear to collect in fish, plants or animals used as food. (Agency for Toxic Substances and Disease Registry, 1999d)

Water

The USEPA remanded its MCL and MCLG for nickel on February 9, 1995. There currently is no federal legal limit on the amount of nickel in drinking water. The USEPA is reconsidering the limit on nickel at this time (U.S. Environmental Protection Agency, 2002g). The USEPA recommends that children drink water containing no more than 40 µg/L of nickel per liter of water for 1-10 days of exposure (Agency for Toxic Substances and Disease Registry, 1999d). There are currently no Canadian drinking water guidelines; the WDNR MCL standard for nickel is 100 µg/l.

The Canadian guideline for the protection of aquatic health lists a standard of 15-150 µg/l.

MMSD, USGS, and USEPA STORET data bases provided nickel in water data for the MMSD Corridor Study data base. Twenty-three of thirty-seven subwatersheds in the MMSD planning area have had samples collected for nickel (appendix 1.29). Ten of these subwatersheds had all of their samples as non-detects, and another four had over half of their results as non-detects. All of the non-detects samples were collected in the mid 1970's (except CSO area from 1982) and had higher detection limits than those of samples collected in later years. The highest maximum concentrations were found at Oak Creek - Upper (270 µg/L), Root River - Upper (270 µg/L), Root River -Middle and - Lower (240 µg/L each), Menomonee River - Upper (116 µg/L) and - Lower (150 µg/L) and exceed the two standards for nickel. The maximum concentration at the Milwaukee River - Lower (3810 µg/L) subwatershed was significantly higher than any other result in the MMSD planning area.

Sediment

Currently, there are no Canadian sediment quality guidelines for nickel. The MacDonald sediment quality guidelines for freshwater ecosystems has a TEC of 22.7 mg/kg, and a PEC of 48.6 mg/kg for nickel.

Nickel in sediment data came from the USGS data base. Eight of thirty-seven subwatersheds had samples collected for nickel with a total of 64 samples, only 1 of 64 results were a non-detect (fig. 33; appendix 1.30; appendix 2.22). Five subwatersheds had more than one sample collected. Of these five, the median concentration at Kinnickinnic River (30 µg/g), Menomonee River - Lower (29 µg/g), and Milwaukee River - Lower (23 µg/g) exceeded the TEC guideline, no median concentrations exceeded the PEC. One subwatershed had a maximum concentration slightly exceed the PEC, the Menomonee River - Lower (49 µg/g). Every subwatershed, except for Little Menomonee Creek had a maximum concentration above the TEC. Maximum and median concentrations of nickel in sediment were higher at the Menomonee River - Lower than Menomonee River - Upper subwatersheds.

Zinc

Zinc is a very common element in rock, about the same abundance as copper or nickel, but is substantially more soluble in water than the other two metals. Zinc occurs in the air, soils and water naturally. Zinc is an essential mineral to plant and animal metabolism and is found in all foods (Hem, 1985). Most of the zinc in soils stays bound to the soil particles. Zinc accumulates in fish and other aquatic organisms, but not plants (Agency for Toxic Substances and Disease Registry, 1999e). Today, most of the new anthropogenic sources of zinc are derived from material resources (Callendar, and Rice, 2000). Zinc is a component of brass, bronze, and galvanized metals. Zinc compounds are used

to make paint, rubber, dye, and wood preservatives. Fossil fuel combustion is the main contributor worldwide anthropogenic emissions of zinc (Callendar, and Rice, 2000). Concentrations of zinc in bed sediment is well correlated with population density in the United States (Rice, 1999).

Water

The USEPA has established secondary maximum contaminant levels (SMCL) for fifteen contaminants that are goals, but does not enforce. These SMCL's are established for aesthetic considerations (taste and odor, and color) and are not considered to present a risk to human health. The USEPA does not have an MCL for zinc, but a SCML of 5.0 mg/L related to odor and taste. The Canadian drinking water guideline is also 5.0 mg/L and is an AO. The WDNR does not have a drinking water standard for zinc. The Canadian water quality guideline for the protection of aquatic life has a guideline of 30 µg/l.

Data for zinc in water came from the MMSD, USGS, and USEPA STORET data bases. Twenty subwatersheds had samples collected for zinc, of those twenty, five subwatersheds samples were all “non-detects” (appendix 1.31). Median concentrations at Underwood Creek (90 µg/L), Mitchell Field Drainage Ditch (80 µg/L), and Little Menomonee River (30 µg/L) were the only watersheds with median concentrations above the Canadian guideline for aquatic health. Every subwatershed had their maximum concentrations exceed the aquatic health guideline. The USEPA SMCL and Canadian drinking water aesthetic objectives were not exceeded by either median, or maximum concentrations in any of the samples collected. The highest median concentrations were at: Menomonee River - Lower (1500 µg/L), Kinnickinnic River (710 µg/L), Underwood Creek (670 µg/L), and Little Menomonee River (450 µg/L). Median concentrations were higher in the Menomonee River - Lower than - Upper (31 vs. 20 µg/L). But in the case of Oak and Root, Oak Creek - Lower was slightly lower than - Upper (13 vs. 14 µg/L), and Root River - Lower was also slightly lower than the median concentration at the - Upper (17 vs. 18 µg/L).

Sediment

The Canadian sediment quality guidelines for the protection of aquatic life for zinc are the ISQG(123mg/kg), and PEL (315 mg/kg), and, MacDonald's consensus based sediment quality guidelines are TEC (121 mg/kg) and PEC (459 mg/kg).

Data for concentrations in zinc in sediment came from the USGS data base. Nine of thirty-seven subwatersheds had a total of 76 samples collected for zinc in sediment (fig. 34; appendix 1.32; appendix 2.23). The samples collected were all above their respective detection limits. Four of the subwatersheds had more than one sample and their median con-

centrations are; Kinnickinnic River (540 µg/g), Lilly Creek (130 µg/g), Menomonee River - Upper (140 µg/g), Menomonee River - Lower (503 µg/g), and Milwaukee River - Lower (318 µg/g). The median concentrations at Lilly, and Menomonee River - Upper exceed the TEC and ISQG, the Milwaukee River also exceeded the PEL, and medians at the Kinnickinnic and Menomonee River - Lower exceeded all guidelines. The sample collected at the Little Menomonee Creek (93 µg/g), and Root River - Middle (52 µg/g) did not exceed any guidelines. Three subwatersheds had maximum concentrations above both the TEC and ISQG, the remaining four watersheds had maximum concentrations above all of the guidelines with the highest maximum at Menomonee River - Lower (850 µg/g), and Kinnickinnic River (677 µg/g). The median and maximum concentrations at the Menomonee River - Lower (503 and 850 µg/g) were higher than Menomonee River - Upper (140 and 260 µg/g).

Pesticides

For the purposes of this report, discussion of pesticides has been broken into two sections: (1) historically-used and now banned pesticides and (2) pesticides still in use.

Historically-used pesticides are low-solubility, hydrophobic compounds that when transported to aquatic systems partition into sediment and bioaccumulate in aquatic organisms. Because they can cause unintended effects on non-target organisms, they are a long-lived threat to the health of streams and the organisms (including humans) that utilize the streams. Chlordane, dieldrin, DDT, and DDD are insecticides formerly used on crops; all crop use of these compounds were banned between 1972 (DDT) and 1983 (chlordane). Limited use of dieldrin and chlordane was allowed after that time for termite control but all uses were banned in 1987 and 1988, respectively. However, these compounds and others listed in Appendix 1.33 (the others are breakdown products and/or related chemicals whose source is from pesticide mixtures containing the main compound) are frequently detected in sediment and the tissues of animals exposed to contaminated sediments. Although the concentrations are usually low, these compounds bioaccumulate in -- build up in the tissues of -- fish, birds, and mammals (Agency for Toxic Substances and Disease Registry website, ToxFAQs page <http://www.atsdr.cdc.gov/toxfaq.html>).

Consensus-based Threshold Effect Concentrations (TECs) have been developed for each of the historical pesticides selected for this report (MacDonald and others, 2000).

Pesticides currently in use are generally highly soluble, hydrophilic compounds and thus are primarily found dissolved in the water compartment of aquatic systems. These modern pesticides have short half-lives and a seasonal periodicity related to application. Application generally occurs for agricultural herbicides in conjunction with plant-

ing; urban use of pesticides is generally on an as-needed basis and thus may occur anytime during the growing season. Concentrations in surface waters are highest during and following rainfall events that occur after planting and before significant crop growth slows runoff; in southern Wisconsin this period generally occurs sometime during mid-May through mid-June.

Atrazine, a possible human carcinogen, has also recently been linked to hormonal changes in amphibians resulting in deformities and loss of reproductive capabilities (NEED REF).

Historical-use pesticides [INCOMPLETE]

The following pesticides were selected from the MMSD Corridor Study database for description in this report: chlordane; dieldrin; DDT; DDE; DDD; p,p'DDT; p,p'DDE; and p,p'DDD in sediment, and dieldrin, chlordane cis and trans isomers, nonachlor cis and trans isomers, p,p'DDT, p,p'DDE, and p,p'DDD in tissue. These pesticides were chosen for description because they had a relatively large amount of data to examine (generally more than 10 samples) and are commonly analyzed for in urban areas and areas adjacent to agricultural lands. Pesticide data in sediment came from both the USGS and USEPA STORET databases. Tissue data examined in this report was only from the USEPA STORET database although there is additional data in the MMSD Corridor study database from USGS but with a limited number of samples. Figure 35 shows the locations of pesticide sampling in tissue and sediment.

Of the selected pesticides in sediment, only dieldrin was not found to be at a concentration above the detection limit. The following of the selected pesticides in tissue were found only at concentrations below the detection limit: chlordane cis and trans isomers, nonachlor cis isomer, p,p'DDT, and p,p'DDD

Modern-use pesticides [INCOMPLETE]

Pesticides in current use appear are most effectively analyzed for in surface-water analysis. Atrazine, deethyl atrazine, diazinon, metolachlor, prometon, simazine, and 2,4 D constituents had a significant amount of data to examine for this report and can be found in urban areas or streams draining agricultural lands. Pesticide data in water examined for this report came from the USGS database although data is also available in the MMSD Corridor Study database from USEPA STORET but with a limited number of samples. Figure 35 shows locations where surface water was analyzed for pesticides.

Data selected for analysis were collected at two sites: the Milwaukee River at Estabrook Park in Milwaukee (91 samples) and Lincoln Creek at 47th St. in Milwaukee (10 samples) during the period from 1993 through 2002 and 2001

through 2002, respectively.

All of the selected pesticides were observed at concentrations above the detection limit in at least one sample. However, the maximum concentration of any of the selected pesticides was not above MCL's or other health advisory levels.

Organics

Polychlorinated biphenyls (PCBs) are one type of organic compound that have been sampled for in the MMSD planning area.

PCBs [INCOMPLETE]

Despite being banned since the 1970's, polychlorinated biphenyls (PCBs) are ubiquitous contaminants, present not only in industrial areas where they were manufactured and used in cutting oils, sealants, hydraulic fluids and pesticides, but also in remote locales such as the polar regions due to atmospheric transport and deposition. PCBs are a set of 209 related chlorinated organic compounds, some of which have demonstrated toxicity (McFarland and Clarke, 1989). Major present day sources include stream bed sediments and, in some cases, the atmosphere. Being relatively hydrophobic and lipophilic, these compounds tend to adsorb onto clay surfaces or be associated with lipids and other subcellular components present in aquatic organisms. Therefore major loss mechanisms for truly dissolved PCBs in water include partitioning to suspended and bottom sediments, and passive uptake by algae. In addition, because PCBs tend to be refractory in most aquatic environments, it is often possible to determine the particular commercial mixtures of PCBs, termed Aroclors®, that were released to the stream. Under certain conditions, Aroclor® mixtures undergo weathering wherein selective solubilization, volatilization, and/or microbially-mediated decomposition of some congeners can significantly change the Aroclor® mixture, sometimes beyond recognition.

Total PCBs are most often determined by summing all measurable congeners from a congener-specific analysis of a sample. Aroclors® are determined either from older methods that do not include analysis of individual congeners or by matching the suite of measured in individual congeners with that of known Aroclor® mixtures using computer programs.

So-called "toxic" PCB congeners can be defined as a subset of total PCB congeners that are ranked on scale that considers both intrinsic toxicity and prevalence in environmental samples (McFarland and Clarke, 1989). In terms of toxicity, they include PCB congeners that are directly toxic including some of the co-planar congeners, and congeners

that are indirectly toxic including those that induced bioactivating enzyme systems. For the purposes of this report, we include PCB congener Groups 1A, 1B, or 2 as defined in MacFarland and Clarke (1989) as "toxic" congeners. Among the most toxic, Group 1A congeners, so-called pure 3-methylcholanthrene-type inducers, were congeners 77, 126, and 169, non-ortho-substituted coplanar congeners. These congeners are similar in structure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD or simply 'Dioxin'), the 'gold standard' of toxicity against which all organic compounds are measured. Group 1B congeners are mixed-type inducers that have been observed frequently in environmental samples. These include 105, 118, 128, 138, 156, and 170. Group 2 congeners are phenobarbital-type inducers prevalent in the environment and include 87, 99, 101, 153, 180, 183, and 194.

Although USEPA has set an MCL of 0.0005 mg/L for total PCBs in drinking water (U.S. Environmental Protection Agency, 2002a), the combined focus on both demonstrated toxicity and prevalence in the environment of individual PCB congeners is probably a more predictive approach to setting protective standards.

PCB data is available in the MMSD Corridor Study data base from the USGS, USEPA STORET, and WDNR data sets. Sampling sites for total PCBs in water, sediment, and tissue are scattered throughout the MMSD planning area although most occur in the Menomonee River - Lower, Milwaukee River - Lower, Lincoln Creek, and Kinnickinnic River subwatersheds (fig. 36; appendix 1.34; appendix 1.35). More than half of the subwatersheds have PCB data associated with at least one medium.

Sampling sites for toxic PCBs in water and sediment are a subset of the sites for total PCBs and are those for which at least one toxic PCB congener was quantified (fig. 37; appendix 1.36). The Milwaukee River - Lower had the highest number of detects which is in rough proportion to the larger number of analyses done in that subwatershed (appendix 1.36).

Ecological indicators of water quality

Aquatic life of a stream corridor are dependant on the water and sediment chemistry as well as the flow regime of the river. The makeup of the aquatic community can provide indicators as to the quality of the water chemistry of the stream.

Macroinvertebrates

Data for macroinvertebrates in the MMSD Corridor study data base came from a data base maintained for the WDNR by Professor Stan Szczytko at the University of Wisconsin - Stevens Point. The majority of the data was collected by

the WDNR but other agencies, universities, and groups also contributed samples. Community level data and counts of species are available for most samples.

Invertebrate data in the MMSD Corridor Study database were collected from 1979 through 1999 for 27 of the 37 subwatersheds in the MMSD planning area. Two basic metrics were calculated with the data: the percentage of Invertebrates in the insect orders Ephemeroptera-Plecoptera-Trichoptera (EPT) and the Hilsenhoff Biotic Index (HBI). EPT taxa are generally considered to be relatively intolerant of water quality degradation (Lenat, 1988; Hilsenhoff, 1988 and 1998). The proportion of EPT individuals and taxa tends to decrease with decreasing water quality. Median EPT percentages for sites and subwatersheds are shown in figure 38 (appendix 1.37; appendix 2.24). The HBI is a rapid screening method designed to assess oxygen depletion in streams resulting from organic matter pollution; however, the index may also be sensitive to other types of pollution such as from some chemicals. The HBI represents the number of arthropod invertebrates in certain species multiplied by their pollution tolerance value, divided by the number of arthropods in the sample. HBI scores are 0.00 (Excellent) to 10.00 (Very Poor), and the values for each water quality rating according to Hilsenhoff (1988) are shown in figure 39 (appendix 1.38; appendix 2.25).

Most of the invertebrate samples from the MMSD planning area contained less than 25% EPT taxa, and median values for more than half the subwatersheds were less than or equal to 10%. These low percentages may be due to inadequate habitat for these taxa in low-gradient streams with predominantly clayey surficial deposits; however, it also may indicate degraded water quality. Adjacent samples from several sites ranged from at least 50% EPT to less than 25% EPT, so this suggests that perhaps gradient and substrate are not as much a factor as water quality in these areas (for example, see the Milwaukee River-Lower (near Estabrook Park), Oak Creek -Middle and Lower). The ranges of EPT values were quite wide for many subwatersheds. The subwatersheds with the highest median EPT values were Cedar Creek, Oak Creek - Middle, and Root River - Middle and Lower. Median EPT values ranged from 40-51% and suggest relatively good water quality at many sites in these three subwatersheds.

Median HBI values were greater than 5.01 for all but two subwatersheds, indicating "fair" water quality at best for these subwatersheds overall. One exception was Little Menomonee Creek where only one sample was collected (1997) and this sample indicated "good" water quality. The other exception was Willow Creek and, although a single HBI value indicated "good" water quality, other HBI values from this subwatershed indicated "fair" to "fairly poor" water quality. Only one sample fell into the HBI rating of "very good", and this sample was from the Whitnall Park Creeks subwatershed but as with Willow Creek, other HBI values for this subwatershed indicated "fair" to "fairly poor" water quality. Median HBI values for 21 of 27 subwatersheds were at least 5.76 and this corresponded to rat-

ings of "fairly poor" water quality. In four subwatersheds, the median HBI values showed "very poor" water quality: Little Menomonee River, North Branch Oak Creek, Upper Oak Creek, and East Branch Root River, and the highest median value occurred in the Little Menomonee River.

Fish

Fish data in the MMSD Corridor Study data base came from the WDNR Biology Data base and a series of fish surveys completed by the WDNR in and around the Milwaukee River. Count of species, and in some cases length, weight, and sex are available for fish samples. Figure 40 shows the locations of WDNR Biology data base and WDNR Milwaukee fish survey sampling sites.

Fish data are often used to assess and monitor environmental quality in an approach generally termed "bioassessment" or "biomonitoring" (Plafkin and others, 1989). These bioassessment and biomonitoring techniques have been shown to be a useful way to detect and quantify environmental degradation in aquatic systems (Lyons, 1992b). Of all types of biota, fish, along with macroinvertebrates, have been shown to be particularly effective for use in bioassessments. Wisconsin began development of an Index of Biotic Integrity (IBI) for fish in warmwater streams of the state in the mid-1980s and published the resulting "how to" guide in 1992 (Lyons, 1992b).

The IBI was originally developed during the late 1970's and early 1980's to assess biotic integrity and environmental quality in small streams in Indiana and Illinois (Karr, 1981; Karr and others, 1986). This original IBI has been modified to fit the physical and biological characteristics of streams throughout North America (Lyons, 1992b). Biotic integrity has been defined as "a balanced, integrated, adaptive community of organisms having a species composition, diversity, and natural habitat of the region" (Karr and Dudley, 1981).

Based on data in the MMSD Corridor Study data base, a total of 79 species of fish have been found in waterbodies in the MMSD planning area. In addition, various hybrid sunfishes, minnows, and bullheads have been documented. Of the three decades for which data exist, the 1970's were the busiest from a fish sampling standpoint, with fewer sites sampled in each succeeding decade (2000-2002 samples have been grouped with samples collected through the 1990's). The distribution of sampling sites (fig. 40) provides good coverage from a spatial standpoint; however, when only recent (1990-present) data are considered the sites are concentrated in the Milwaukee and Lower Menomonee River watersheds (fig. 41; appendix 1.39).

IBI scores in the Milwaukee River watershed from samples collected in the 1990s-2000s ranged from "very poor" at

all sites on Lincoln Creek to "excellent" at one site on the mainstem Milwaukee River. Several other samples collected on the Milwaukee River indicated "good" biotic integrity/environmental quality, an indication that many parts of this major river system supports a relatively healthy fishery. Samples collected in the mainstem of the lower Menomonee River Basin, conversely, scored "very poor" in 3 of 4 samples (the other was "fair").

Chlorophyll-a

Chlorophyll-a is perhaps the most common algal pigment found in most natural fresh waters. Algae synthesize chlorophyll-a as a means to harvest energy for sunlight during photosynthesis. It is generally assumed to be a good proxy for algal biomass although cellular quotas can be plastic, varying with the amount of photosynthetically available radiation at a given time. Chlorophyll-a is degraded abiotically or microbially either in dead algal cells or in zooplankton guts, producing pigment degradates including pheophytin and pheophorbide. These compounds are sometimes summed with chlorophyll-a to get total pigments which better reflects the total amount of algal biomass as opposed to live algae which only is indicated by chlorophyll-a.

Chlorophyll-a has been selected (along with total phosphorus, total suspended sediments and total nitrogen) by the USEPA as a key nutrient criteria indicator in streams. Its importance is mainly as a proxy for the loading of limiting nutrients (mainly phosphorus) to surface waters and as an indicator of potential oxygen-consuming material. For the MMSD planning area, a level of 0.55 mg/m³ was selected as a maximum allowable limit (U.S. Environmental Protection Agency, 2000).

Median values of chlorophyll-a for individual sites range from 0.92 to 18.97 for the MMSD planning area (fig. 42). Lower concentrations occur in the southern part of the planning area and higher concentrations occur in the northeastern portion of the planning area. The highest concentrations occurred at sites in the Milwaukee River - Lower (628.52 mg/m³), the Kinnickinnic River (358.52 mg/m³), and the Menomonee River - Upper (318.23 mg/m³) (appendix 1.40). About half of the subwatersheds have sufficient data to assign a median value. Of these, median concentrations range between 1.46 and 14.99 mg/m³ (fig. 42). The Milwaukee River - Lower has the highest median chlorophyll-a concentration of all subwatersheds with data (appendix 2.26).

Trends in chlorophyll-a versus sample year indicate a lack of relatively high concentrations at three of the five highlighted sites (Kinnickinnic, Menomonee, and Milwaukee Rivers) during the period between the late 1980s and early 1990s (appendix 3.9). This might be related to low rainfall and concomitantly low nutrient inputs during this time period. There is some indication of higher chlorophyll-a concentrations during the spring and fall, corresponding to

classical algal bloom periods, at the Kinnickinnic River, Menomonee River, and Milwaukee River sites although the pattern isn't particularly pronounced (appendix 3.10).

Habitat and geomorphic data

Habitat and geomorphic data in the MMSD Corridor Study data base were collected by WDNR and MMSD (through a contract with Inter-Fluve, Inc.) (fig. 43; appendix 1.41).

Habitat data in the MMSD Corridor Study data base were collected by the WDNR starting in 1991 and derived from the WDNR Biology data base. The types of information collected in WDNR habitat surveys include the percent of canopy/shading of the stream channel, type of fish cover, stream bottom cover, percent macrophyte cover, and many other channel characteristics. These data can be used to analyze the change in habitat over time, determine aspects of the habitat characteristics that could be limiting aquatic life, and suggest management options designed to rehabilitate habitat (Wisconsin Department of Natural Resources, 2002). Habitat assessments were done in 20 of the subwatersheds with one to nine sites located in each subwatershed. Seventeen of the 44 sites were surveyed more than once, some up to eight times. The Lincoln Creek subwatershed has a relatively large number of sites (nine) where habitat assessments were performed with an average of four samples taken at each site. However, only one or two assessments were done in most other subwatersheds. No habitat index values were available for the data in the MMSD planning area and summarizing the extensive amount of habitat data was not within the scope of this report.

Additional stream channel morphology and streambed measurements were recorded during the MMSD Menomonee River Sediment Transport study. The purpose of the MMSD Menomonee River Sediment Transport study was to provide a planning tool for the Menomonee River watershed that would allow MMSD to plan flood management, and channel stabilization and rehabilitation projects that would improve flood conveyance and aquatic habitat (Inter-Fluve, Inc, 2001). A subset of the data collected for the study that has been compiled in the MMSD Corridor Study data base include channel cross section information, pebble counts, and streambed sediment and grain size analysis. All data were collected between March 2000 and May 2001. Sites are located in 9 of the 13 subwatersheds of the Menomonee River Watershed, with 1 to 59 sites in each subwatershed. There are no data for subwatersheds outside of the Menomonee River watershed.

Microbiology

The majority of human pathogens transmitted by water originate from contamination of those waters by fecal material. It is generally assumed that human-pathogen-laden waters stem from human wastewater effluent. However, the

relative contributions that animal and livestock wastes have on human pathogen loads is unknown and is a topic of current investigation (Madigan and others, 1997).

Although the dangers associated with waters contaminated with fecal material are greatly magnified when such water is used for drinking, the recreational use of sufficiently contaminated waters also constitutes a human health risk. In response to this danger, the USEPA recommends the testing of recreational waters for the presence of fecal contamination using fecal indicator organisms. These organisms provide an indirect indication of the presence of potential pathogens in the water. The two fecal indicators commonly used in the Milwaukee area are fecal coliforms and *Escherichia coli* (Madigan and others, 1997).

Elevated concentrations of microbiological organisms in surface water can indicate contamination by agricultural or human sources.

Fecal coliform

Fecal coliforms were recommended for the testing of recreational waters by the USEPA in 1976. Accompanying this recommendation was an acceptable limit guideline of 200 colonies per 100 mL (U.S. Environmental Protection Agency, 1976). Fecal coliform data for the planning area has been collected primarily by MMSD; smaller data sets have been supplied by the USGS and the USEPA.

Samples have been collected for 19 subwatersheds in the planning area. There are 12 subwatersheds with recent (i.e. 2001) data. Of these 12 subwatersheds, 9 have more than 100 sample results associated with them (appendix 1.42). In addition to routine monitoring data, the fecal coliform data also includes targeted sampling efforts. For example, one of the 12 recently sampled subwatersheds was sampled as part of a targeted study looking at the effect of the Wisconsin State Fair on fecal coliform levels in nearby Honey Creek during August 2001 (written communication, Eric Waldmer, MMSD, 2002). An additional targeted sampling effort took place in the Underwood Creek subwatershed in June 1975; the purpose of this sampling effort was to determine the location of a known sewerage system leak (REFERENCE). Both of these studies targeted times when fecal coliforms in the subwatershed were anticipated to be higher than usual. Given that these are the only samples recorded for their respective subwatersheds, their depiction in figure 44 is likely not representative of typical fecal coliform levels in these subwatersheds.

Overall, the median concentrations at sampling sites range from 1 to 400,000 colonies per 100 mL. The medians of all thirteen of the afore-mentioned subwatersheds exceed the USEPA recommended 200 colonies per 100 mL (appen-

dix 2.27). The other six subwatersheds sampled fall well below the guideline, having no recorded samples above a detection limit. However, none of these subwatersheds have been sampled since 1981, and all have 3 or fewer recorded samples (appendix 1.42).

The fecal coliform data do not show significant trends or seasonality (data not shown). The Kinnickinnic River at 1st Street site shows a moderate decrease in levels after 1988 and slightly higher levels from 1999 through 2001. These trends are present, but less pronounced in the data for the Milwaukee River at Wells Street site. Seasonally, fecal coliform levels tend to have higher values in the middle of the year, with peaks occurring near Julian days 181 and 271 however elevated concentrations of fecal coliforms may occur with significant storm events that happen more frequently in the summer but can also occur at other times of the year.

Escherichia coli

Epidemiological studies indicate that, when compared to fecal coliforms, levels of *Escherichia coli* (*E. coli*) correlate more strongly with illnesses attributable to swimming in fecal-contaminated water (Dufour and Cabelli, 1984). In response, the USEPA has modified their guidance to recommend the use of *E. coli* as a fecal indicator in freshwater, setting the single sample maximum allowable density for a designated beach area to 235 colonies per 100 mL (Dufour and Ballentine, 1986).

MMSD is the only agency that has collected *E. coli* data in the planning area. Samples have been recorded for six subwatersheds in the planning area. This is a relatively recent data set, with the range in collection dates spanning only from October 2000 to November 2001 (appendix 1.43). The only known targeted study took place at Honey Creek in conjunction with fecal coliform sampling. This sampling effort sought to determine the effect of the Wisconsin State Fair on *E. coli* levels in the subwatershed. Given that is the only sampling effort recorded for the Honey Creek subwatershed, its depiction in figure 45 is likely not representative of typical *E. coli* levels in the subwatershed.

Overall, the median concentrations at sampling sites range from 140 to 4,850 colonies per 100 mL. The medians of five of the six subwatersheds exceed the USEPA recommended 235 colonies per 100 mL (appendix 2.28). The Milwaukee River - Lower subwatershed is the only subwatershed with a median concentration below the recommended guideline (220 colonies per 100 mL). With 138 results, this subwatershed also has nearly twice the number of recorded results of the next-most-sampled subwatershed (appendix 1.43).

Given the relatively limited number of samples and the short time span of the data set not enough data is present to

indicate any trends or seasonality (data not shown). Like fecal coliforms, *E. coli* may also correlate with storm events and therefore may appear to have higher concentrations in summer months when higher volume precipitation events are more likely to occur.

GAPS IN THE DATA [INCOMPLETE]

The goal of this report is to describe the historical stream corridor data for the MMSD planning area. Knowledge of historical conditions can then be used in planning for Phase II of the MMSD Corridor Study, baseline monitoring. Illumination of spatial, temporal, or analytical gaps in data may drive decisions in where to locate sampling sites and which types of analyses to run.

Maps of sampling locations (fig. 7 through 50) illustrate gaps in spatial coverage of sampling sites in particular where subwatersheds are left unshaded because no sampling sites exist in the basin. Distribution of sampling sites may indicate subwatersheds that are adequately covered with recent sampling sites (fig. X through X) and other subwatersheds that are under-sampled.

Tables of summary statistics (tables 1.1 through 1.44) indicate the number of samples collected for each subwatershed and the latest date a site in the subwatershed was sampled. Figures X through X show sites sampled at least once since January 1, 1998 for various types of analyses. Knowing the locations of sites currently being monitored by MMSD, USGS, WDNR or another agency may allow for cooperation between the MMSD Corridor Study and the monitoring agency for collection into Phase II or suggest locations not to sample to avoid duplication of sampling efforts.

Absence of data for emerging contaminants such as human hormones and drugs, caffeine, and other constituents that indicate an urban signal were not available in the MMSD Corridor Study data bases or any of its sources. Minimal *E. Coli* data was available for the MMSD Planning area.

SUMMARY [INCOMPLETE]

(To be written after the report is completed)

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