Institute for Urban Environmental Risk Management
Marquette University, Milwaukee WI 53201-1881

TECHNICAL REPORT NO. 7

EVALUATION OF WATER QUALITY AND ECOLOGICAL RISKS

Alena Bartošová, MSc.
Research Associate

Vladimir Novotny, Ph.D., P.E.
Primary Investigator

Pavel Hajda, Ph.D.
Research Associate

Project sponsored by the Grant No. R82-5759 to Marquette University from the
US EPA/NSF/USDA STAR Watershed Program

Barbara M. Levinson
EPA Project Officer

Milwaukee, Wisconsin
October 2000

Acknowledgments

The research contained in this report was sponsored by the U.S. Environmental Protection Agency/National Science Foundation/U.S. Department of Agriculture STAR Watershed Program by a Grant No. R82-5759 to Marquette University. The authors greatly appreciate this support. The findings and conclusions contained in this report are those of the authors and not of the funding agencies nor the STAR program.

Additionally, the authors would like to acknowledge the generous assistance by the personnel of the Milwaukee Metropolitan Sewerage District and Southeastern Wisconsin Regional Planning Commission in terms of data required for research.

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CHAPTER 1

INTRODUCTION

The EPA's Advisory Committee (US EPA, 1990) identified four broad categories of risks: (1) human cancer risk, (2) human non-cancer risk, (3) ecological risk, and (4) welfare risk. This report focuses on aquatic ecological risk. Risk is expressed as a probability of damage or adverse ecological effect to an aquatic system. Ecological risk analysis is an evolving discipline that is based from ecology, toxicology, environmental chemistry, and the more traditional engineering risk analysis. The number of chemicals potentially posing environmental risk is overwhelming. The environmental chemistry of these compounds is not completely understood. Also, our understanding of ecological systems is limited.

The effects of contaminants on living organisms are generally evaluated using the basic concepts that were originally formulated by Sprague (1969):

Acute toxicity. The exposure of organisms to a compound or a mixture of compounds will result in a crisis, usually short in time during or following the exposure.

Chronic toxicity. The exposure will have a sublethal damaging impact on the organisms occurring over a longer period of time up to the entire life cycle.

Lethal toxicity. Exposure will result in death of organism.

Sublethal toxicity. Exposure is damaging to the organism, but it will not result in death.

Cumulative toxicity. The effects on the organisms are brought about, or increase in strength, by successive exposure

This report focuses on detail evaluation of water quality for two watersheds located in southeastern Wisconsin: Oak Creek and Menomonee River. The Oak Creek watershed is still rural but rapidly developing while the Menomonee River watershed has been already developed with the exception of its upstream areas. Although the main focus is to evaluate toxicity of water column, conventional pollutants such as dissolved oxygen or nutrients have been included in evaluation. Toxicity has been evaluated using traditional approach of water quality criteria and more detail approach of risk evaluation.

CHAPTER 2

WATERSHED DESCRIPTION

This chapter provides basic description of watersheds selected for evaluation in an extent necessary to understand the background and the differences between these watersheds. The mostly rural Oak Creek watershed represents rapidly urbanizing watersheds. The Menomonee River watershed has been already developed, especially downstream of Menomonee Falls. The reader is referred to comprehensive plans for more thorough information (SEWRPC, 1976, 1986).

Oak Creek

The Oak Creek discharges into Lake Michigan in the City of South Milwaukee, WI. About 21.1 km of the stream is perennial. From its source near the intersection of Sherwood Drive and Southland Drive, the creek flows southerly to south of Ryan Road and then easterly for approximately 7.1 km to Shepard Avenue. The creek then flows north for 8.4 km and finally turns to south-east to its confluence with Lake Michigan. The North Branch of Oak Creek (9.3 km long perennial stream) joins Oak Creek north of Ryan Road between 13th Street and Howell. The third perennial stream is the Mitchell Field drainage ditch (4.5 km long perennial stream). It drains about 38% of the General Mitchell Field Airport (330 ha) that lies within the watershed; its confluence with Oak Creek is north of Drexel Avenue.

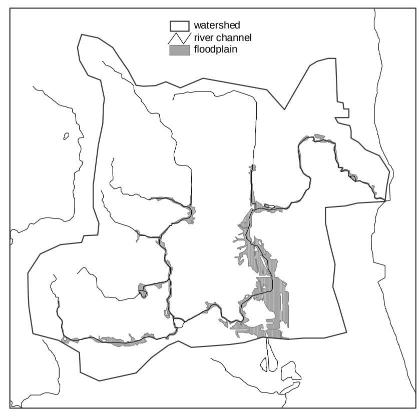

Figure 2.1. The Oak Creek watershed with 100-yr floodplain.

Table 2.1. Basic watershed characteristics. Oak Creek watershed.

Area	69.8 km^2 (27.24 mi^2)
Percent urbanized	44.6%
Population (1980)	39,700

Table 2.2. Land use distribution (1980). Oak Creek watershed (from EPA, 1998).

Land Use	Percent Total
Cropland and Pasture	55.4
Residential	22.8
Other Urban or Built-Up	6.5
Trans, Comm, Util	6.0
Commercial and Services	5.8
Industrial	3.6

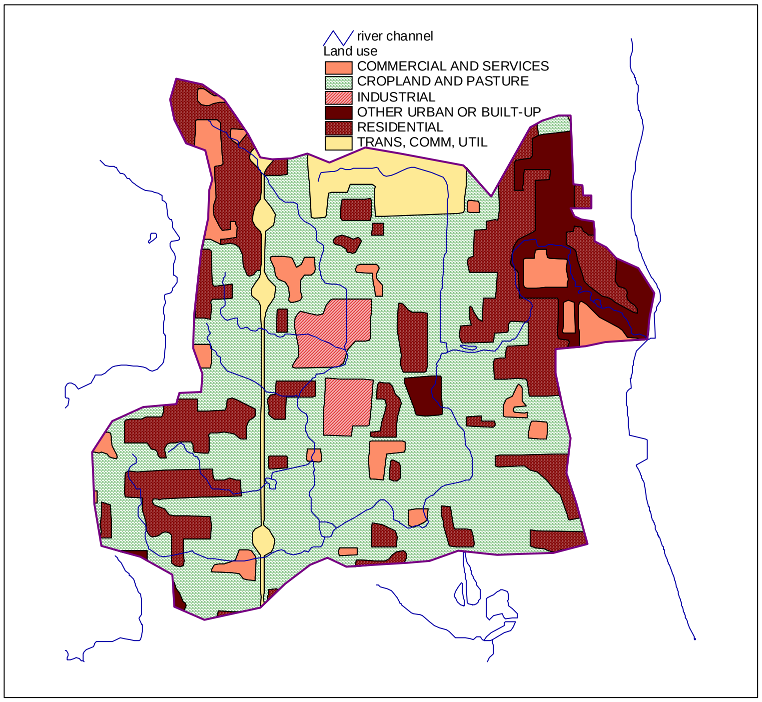

Figure 2.2. Land use (1980). Oak Creek watershed (from EPA, 1998).

The Oak Creek watershed can be characterized as mostly rural with a great potential for future development. Agricultural land (cropland and pasture) represents the prevailing type of the land use in the watershed (see Table 2.2 and Figure 2.2). Most of the agricultural land is located in the western and southern portions of the watershed. The soils within the Oak Creek watershed are silty clay loams, loams, and sandy loams, and are developed on gently sloping or rolling morainal topography. Most of the soils are relatively fertile. Pollution sources can be categorized as municipal, industrial, agricultural, landfill, and stormwater. A contribution of pollution from the point sources is negligible compared to that from the nonpoint sources. Rural sources dominate among the nonpoint sources (20-50%).

Flow has been measured at the USGS station number 04087204, "Oak Creek at South Milwaukee, WI," from October 1963 to current year. The station is located on the left bank of Oak Creek, 8 m (25 ft) downstream from the 15th Avenue bridge in South Milwaukee and 2.8 mi upstream from mouth. The data file containing average daily discharges was downloaded from the WI USGS web page (USGS, 1998). The flow regime for 1964-1997 can be summarized as follows: annual mean 0.65 m^3/s (23.1 cfs); seven-day minimum 0 m^3/s; 10% exceedance 1.39 m^3/s; 50% exceedance 0.22 m^3/s; and 90% exceedance 0.05 m^3/s.

Menomonee River

The Menomonee River has its source in the northeastern corner of Germantown in Washington County. From its junction with the Little Menomonee River (Hwy 100 and W. Hampton), it flows southeasterly through the cities of Milwaukee and Wauwatosa. Near North Avenue it is joined by the Underwood Creek. The Honey Creek joins the Menomonee River from the south near the 72nd Street. The Menomonee River discharges into the Milwaukee River about 1.4 km upstream from the confluence of the Milwaukee River with Lake Michigan. There are 14 minor lakes within the watershed, each having a surface area of less than 20 ha.

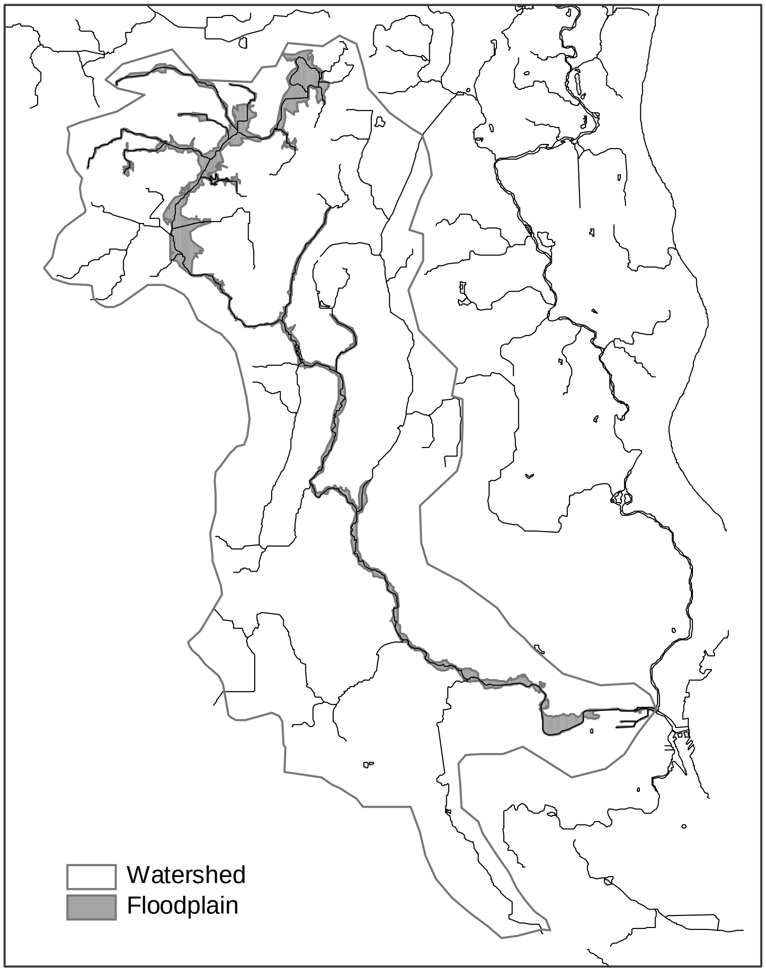

Figure 2.3. The Menomonee River watershed with 100-yr floodplain.

Table 2.3. Basic watershed characteristics. Menomonee River watershed.

Area	350.7 km^2 (137 mi^2)
Percent urbanized	52.8%
Population	348,165 (1970)
	964,640 (1990)
	962,570 (1996)

Population density ranges from less than 350 to more than 25,000 persons per square kilometer with an average of 2,750 inh./km^2. About 85% of population is served by public water supply. Lake Michigan water is the major source of municipal water supply, serving about 80% of the population. The rest relies on groundwater resources. There are six dams and several channel drops in the watershed. Channel modifications are concentrated in the urban areas. The 115-km river system contains 42% of minor channelization, 22% of major channelization, and 3% of conduit, accounting for a total of 67% of river length.

The soils within the Menomonee River watershed are silt loams or gravelly loams. Most of the natural soils are relatively fertile. Artificial fill materials and paved surfaces have modified the natural character of the soils with regard to drainage and fertility in urbanized areas.

Table 2.4 and Figure 2.4 show the land use distribution for the Menomonee River watershed. About 46% of the total area is still in rural use, representing a great potential for nonpoint source pollution. Rural areas prevail in the northern portion of the watershed, while the southern portion of the watershed is mainly urban.

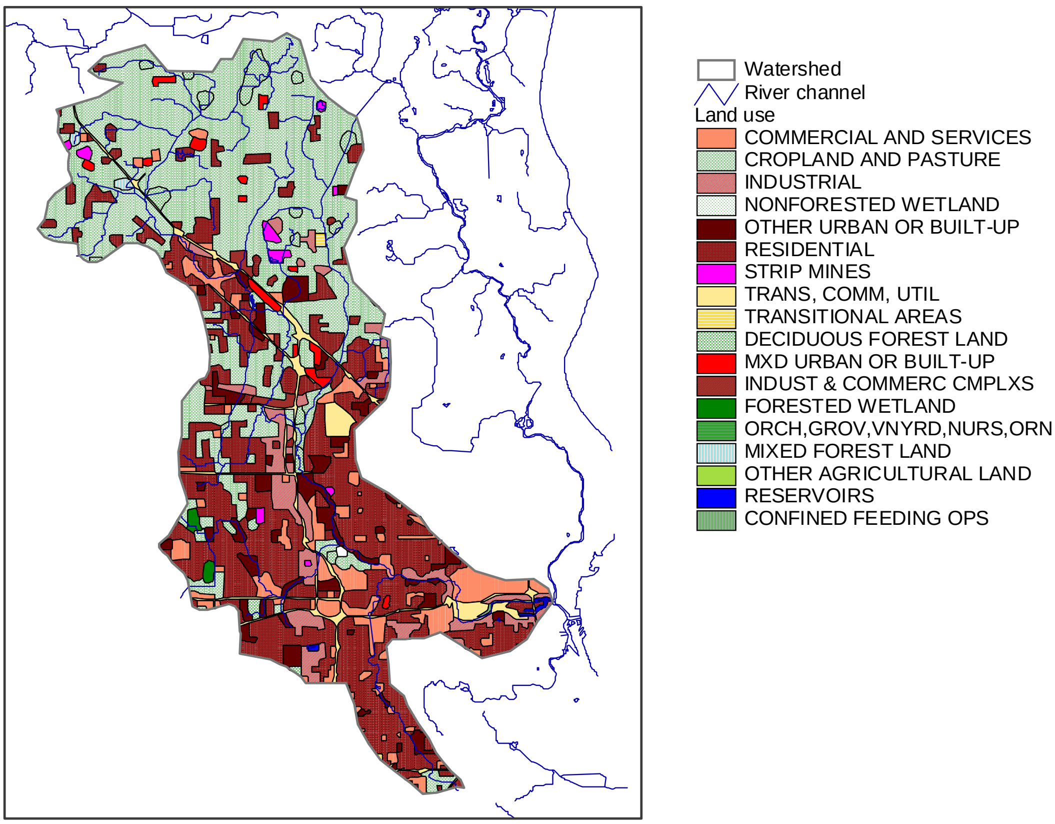

Figure 2.4. Land use (1980). Menomonee River watershed (from EPA, 1998).

Table 2.4. Land use distribution (1980). Menomonee River watershed (from EPA, 1998).

Land Use	Percent Total
Commercial and Services	7.6
Confined Feeding Ops	0.1
Cropland and Pasture	42.7
Forest Land	2.6
Forested Wetland	0.3
Industrial & Commercial	6.0
Mixed Urban or Built-Up	1.1
Other Urban or Built-Up	5.2
Reservoirs	0.2
Residential	29.7
Strip Mines	0.7
Trans, Comm, Util	2.4
Transitional Areas	0.1

The complete list of gauge stations in the Menomonee River watershed is included in the Appendix. Table 2.5 shows only those stations that continue to operate. The data are available for downloading at the USGS web page (USGS, 1998). Table 2.6 summarizes the available flow information.

Table 2.5. List of active gauge stations. Menomonee River watershed.
Type Q: average daily flows. Type Q_P: peak flows.

Station Number	Station Name	Type	Period of Record
04087030	Menomonee River at Menomonee Falls	Q Q_P	11/1974-9/1977 1979-1997
04087088	Underwood Creek at Wauwatosa	Q Q_P	11/1974-12/1979 07/1980-09/1997
04087100	Honey Creek at Milwaukee	Q_P	1959-1996
04087120	Menomonee River at Wauwatosa	Q Q_P	10/1961-09/1997 1961-1997

Table 2.6. Summary of the discharge data. Menomonee River watershed (Water Yearbook 1996).

Flow Quantity [m^3/s] (cfs)	Wauwatosa (1962-1995)	Menomonee Falls (1975-1995)
annual mean	2.9 (101)	0.82 (29)
seven-day minimum	0.088 (3.1)	0.023 (0.82)
10% exceedance	6.5 (230)	1.8 (62)
50% exceedance	1.2 (42)	0.40 (14)
90% exceedance	0.37 (13)	0.12 (4.2)

CHAPTER 3

IN-STREAM WATER QUALITY

Water Quality Criteria

Acute toxicity criteria are determined for the one-hour average concentration, not to be exceeded more than once in three years on an average. *Chronic toxicity criteria* are specified for the four-day average concentration, not to be exceeded more than once in three years on an average. Since most of the water quality constituent concentrations follow a log-normal distribution, the acute toxicity criterion corresponds to the 99.9 percentile log-cumulative probability characteristics of maximum daily concentration. Similarly, the chronic toxicity criterion would be violated if 99.5 percentile of average daily concentrations exceeded the criterion.

The toxicity levels of compounds for aquatic organisms have been established in toxicity bioassay tests. The most important parameter in the toxicity bioassay test is the dose or concentration at which 50% of the test organisms survive or their life functions are not affected by the dose. The *lethal dose* or *concentration* (LD or LC) implies that an exposure of the test organism has resulted in death. The 50% survival dose or concentration value then represents LC_{50} or LD_{50} and it is a representative of the acute toxicity. The *effective dose* or *concentration* (ED or EC) is a term used when other effects are considered such as impact on reproduction or respiratory stresses.

The chronic criteria are not based on a dose-response relationship but rather on an observed long-term impact of the contaminants on the life function of organisms. The endpoints of the chronic test are the *no observed effect concentration* (NOEC) and *low observed effect concentration* (LOEC). The NOEC is the highest concentration of toxicant that causes no observable effects. The LOEC is the lowest concentration of toxicant that causes an observed effect. The LC_{50} (or EC_{50}) acute toxicity values and chronic toxicity observations have been used as a basis for the development of the single-chemical numerical water quality criteria.

Acute toxicity criterion or criterion of maximum concentration (CMC) is determined using LC_{50} (or EC_{50}) data for at least three different families of species. Geometric mean of all LC_{50} (or EC_{50}) values for each species represent species mean value (SMAV). Geometric mean of SMAV within a genus is then the *genus mean acute value* (GMAV). Assuming that GMAVs are log-normally distributed, the final acute value (FAV) is determined as the concentration exceeded by 95%. The acute toxicity criterion (CMC) is then CMC = α FAV, where α corrects the FAVs derived from the 50% lethality to those that would correspond to a threshold-lethal effective concentration (US EPA, 1991). The recommended value is $\alpha = 0.5$.

Chronic toxicity criterion or criterion of continuous concentration (CCC) also evolves from toxicity tests. A chronic value is calculated as the geometric mean from NOEC and LOEC. If sufficient chronic values are available (at least 3 different species), then they are analyzed similarly to the procedure for CMC. Otherwise, ratios of LC_{50} to the available chronic values (ACR) are used to determine the chronic toxicity criteria. The ACRs are needed from at least three families, including one fish, one invertebrate, and one acutely sensitive species. A final acute-chronic ratio (FACR) is calculated from species geometric mean ACR values. The minimum allowable ACR is 2.

The EPA water quality criteria for heavy metals are expressed in relation to hardness [mg $CaCO_3$/l] as

$$CC = \exp\{\alpha \ln hardness + \beta\} \quad \textbf{(3.1)}$$

where CC is the acute (CMC) or chronic (CCC) toxicity criterion [μg/l], and α and β are the metal specific coefficients. Table 3.1 lists the coefficients for both acute and chronic toxicity for selected heavy metals.

Table 3.1. Coefficients for water quality criteria calculation for heavy metals.

Metal	**Acute toxicity**		**Chronic toxicity**	
	α	**β**	**α**	**β**
Cadmium	1.128	-3.828	0.7852	-3.490
Copper	0.9422	-1.464	0.8545	-1.465
Lead	1.273	-1.460	1.273	-4.705
Zinc	0.8473	0.8604	0.8473	0.7614

Reference Streams

Natural background water quality is expressed as the physical, chemical and biological characteristics that result from interactions between structural and functional characteristics within an ecosystem. Reference site data provide an estimate of the temporal and spatial variation in fish and habitat parameters that is caused by factors other than changes in land use, such as climatic variations (floods, droughts), geological development, soil composition, vegetative cover, etc. Two different types of reference sites have been established (Wang et al., 1997). *Paired reference sites* (PRR) are matched with a specific site or group of sites, and are chosen to have the same combination of stream size, summer water temperature, and stream gradient as their corresponding site. They are located as close as practical to the appropriate watershed so that they will experience similar weather patterns. *Regional least-impacted reference sites* (REG) are not closely matched with a specific site as paired reference sites, although they do come from the same ecoregion. REG sites are chosen to represent the best attainable environmental quality for “typical” stream within the ecoregion. Their watersheds are relatively unimpacted by environmental degradation.

Streams in the studied area are warmwater and generally low gradient, although moderate-gradient stretches also occur. The following sites has been identified as reference sites for Menomonee River and Oak Creek watersheds: Underwood Creek (PRR), Little Menomonee River (PRR), East Branch Milwaukee River (REG), and Oconomowoc River (REG). The PRR sites have degraded fish communities dominated by tolerant species. The portion of Little Menomonee River channel by the PRR site was straightened. The REG sites have high-quality warmwater fish communities with a high diversity of species (Wang et al., 1997). Table 3.2 lists the monitoring stations used as reference sites.

Table 3.2. List of water quality stations. Reference streams [STORET].

Station number	Name	Period of record	Agency
04086198	East Branch Milwaukee River near New Fane, WI	1993-1995	USGS
04086200	East Branch Milwaukee River at New Fane, WI	1982	USGS
203094	Milwaukee R East Br New Fane	1993	DNR
683136	Oconomowoc River	1973-1975	DNR
683141	Oconomowoc River	1973-1975	DNR
463001	Little Menom Riv @ Donges Bay Rd	1975-1977	DNR
683090	Ditch @ Underwood PKY - Sampler	1977	DNR
413007	Underwood Creek @ USH 45	1975-1977	DNR
04087088	Underwood Creek @ Wauwatosa	1973-1994	USGS

Table 3.3. Summary of water quality data–conventional pollutants (mg/l). Reference streams. average [range]

Station number	DO	N-NH_{3+4}	N-NO_{3+2}	TP	SS	Cl
REG						
04086198	8.5 [2.7-14.3]	0.02*	0.09*	0.03*	NA	13*
04086200	9.5 [8.7-10.2]	0.04*	0.11 [0.05⌫-0.16]	0.04 [0.03-0.05]	10.8 [0-89]	14*
683136	11.7 [6.9-14.0]	0.04 [0.0-0.14]	1.36 [0.82-1.84]	0.05 [0.02-0.09]	NA	13 [9-15]
683141	11.0 [6.6-13.5]	0.06 [0.0-0.10]	0.86 [0.45-1.27]	0.06 [0.03-0.09]	NA	14 [11-16]
PRR						
463001	10.1 [7.0-14.3]	0.34 [0.02-2.8]	4.37 [0.3-13.2]	0.25 [0.02-5.80]	116 [0-6536]	40.9 [4-160]
683090	NA	0.11 [0.02-0.26]	0.91 [0.3-6.2]	0.36 [0.15-0.69]	31 [12-103]	61 [8-190]
413007	13.2 [8.0-20.0]	0.15 [0.02-0.93]	0.70 [0.01-6.4]	0.26 [0.01-4.6]	154 [0-5202]	270 [19-4500]
04087088	NA	NA	NA	NA	280 [31-1120]	NA

⌫ ... value is a detection limit * … one measurement onlyNA … not analyzed

Table 3.4. Summary of water quality data–heavy metals (μg/l). Reference streams. average [range]

Station number	**Cd**	**Cr**	**Cu**	**Pb**	**Ni**	**Zn**	**Hg**
REG							
04086198	0.2 ⌫	3 ⌫	3 ⌫	3 ⌫	20 ⌫	50 ⌫	0.2 ⌫
PRR							
463001	1.31 [0.2 ⌫-17]	6.1 [3-⌫ 58]	25.3 [3-98]	3.6 [3 ⌫-10]	20.2 [20 ⌫-26]	43 [20 ⌫-230]	0.2 [0.2 ⌫-0.2]
413007	2.11 [0.2 ⌫-17]	48.3 [3 ⌫-629]	100 [9-1132]	322 [3-4000]	30.5 [20 ⌫-64]	230 [30-1980]	0.29 [0.2 ⌫-0.6]
04087088	1.85 [1 ⌫-9]	9.5 [4-19]	30.6 [12-140]	24.5 [12-46]	9.5 [3-36]	155 [60-670]	0.2 [0.1 ⌫-1.4]

⌫ ... value is a detection limit

Table 3.5. Summary of water quality data–sediment contamination (mg/kg dry wt). Reference streams.

Station number	TOC	TP	Cd	Cr	Cu	Pb	Zn	Hg
203094 – REG	48,900	730	0.35	16.4	24	11.6	37.5	0.08

Table 3.3 shows the difference between the REG and PRR sites. The REG sites reflect the background quality of upstream reaches. Although the oxygen regime of the PRR sites is unimpacted, the nutrient content (nitrogen forms, phosphorus), suspended solids and chlorides concentration is elevated. Note that the water quality in Oconomowoc River is likely influenced by existence of the lakes formed by the river.

Heavy metal concentrations were reported only on the PRR sites (Table 3.4). The site at Underwood Creek (413007) has the highest concentration of heavy metals. This can be explained by its location near busy US Highway 45. It shows the impact of transportation on water quality. Note that this site was analyzed during years 1975-1977, i.e. before the ban of leaded gasoline. The heavy metal concentrations measured at East Branch Milwaukee River were reported as “actual value known to be less than detection limit”. Table 3.5 show the results of sediment analysis for East Branch of Milwaukee River at New Fane. This is the only reference site where the sediment was analyzed.

Oak Creek

Summary of Monitoring Programs

Water quality has been monitored by several agencies. The EPA water quality retrieval system (STORET) contains water quality data from 6 stations in the watershed as monitored by Wisconsin DNR (WI DNR) and USGS. However, most of these data were measured in 1970s with variable frequency. Milwaukee Metropolitan Sewerage District (MMSD) carries out a separate monitoring program in the Oak Creek watershed. The regular MMSD monitoring program of the Oak Creek watershed started in 1985 and continues until today. Seven stations are sampled regularly during non-winter months (with the exception of 1992 year).

A supplemental monitoring program has been conducted by Water Quality Center of Marquette University as a part of this project. Water column samples and a sediment sample were taken from four sampling sites at Oak Creek during wet weather and dry weather flows. The samples were analyzed for conventional parameters (COD, pH, SS, VSS, TS, total hardness, $N\text{-}NO_{2+3}$, TKN, and TP), total and dissolved heavy metals (Cd, Cu, Pb, and Zn) and PAHs. Cyanides were only analyzed in winter samples.

Figure 3.1 shows the location of stations monitored by WI DNR, USGS (data available through STORET), and Marquette University Water Quality Center. Table 3.6 lists the monitoring sites and summarizes the period of record for these stations. The parameters and monitoring frequency vary from station to station. Generally, basic water quality parameters, such as DO, BOD, pH, temperature, and nutrients, were measured at all the stations. Heavy metals were analyzed at most stations.

The key locations for water quality analyses were identified as follows:15th Avenue Bridge at South Milwaukee (04087204, RI-27), Nicholson (413068, RI-26, MU-3), and Howell (RI-24, MU-2). These are the sites with the most data available. The USGS site 04087204 has only limited water quality data available. This is mainly a stream gage station, measuring regularly only flow and temperature. The data on lead concentration gathered by MMSD were divided into two subsets: before 1987 and after 1987; to separate the periods before and after the ban of leaded gasoline. The detail analyses further in this report were conducted on MMSD data only with respect to the record length.

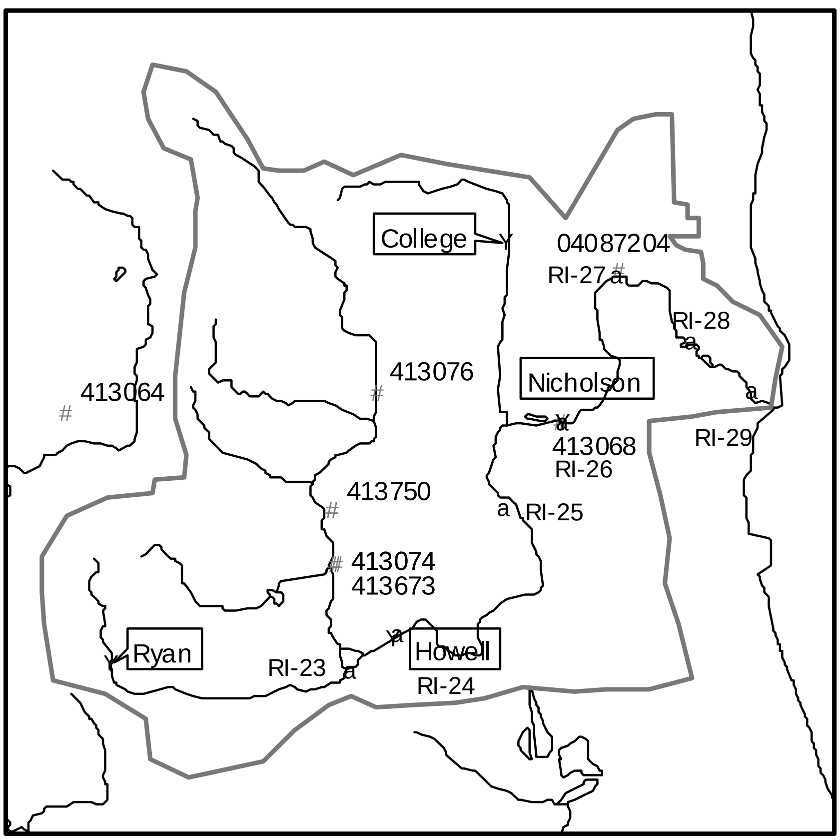

Figure 3.1. Location of water quality monitoring stations in the Oak Creek watershed.

Table 3.6. List of selected water quality stations. Oak Creek watershed.

Station number	Name	Period of record	Agency
413074	Oak Creek @ Puetz Rd. & RR Track [N.Br.]	1975-1976	DNR
413673	N. Br. of Oak Creek @ Puetz Rd.	1990-1996	DNR
RI-23	Ryan Road @ railroad crossing	1985-1997	MMSD
RI-24	Highway 38 - Howell	1985-1997	MMSD
MU-2	Howell	1998-1999	MU
RI-25	Forest Hill Road	1985-1997	MMSD
413068	Oak Creek @ Pensylvania Ave	1975-1976	DNR
RI-26	Nicholson - Pensylvania Ave	1985-1997	MMSD
MU-3	Nicholson	1998-1999	MU
04087204*	Oak Creek @ South Milwaukee	1972-1995	USGS
RI-27	15th Avenue	1985-1997	MMSD

* .. water quality data limited to temperature and SS

Table 3.7. Summary of water quality data–conventional pollutants (mg/l). Oak Creek watershed. average [range] KEY LOCATIONS ONLY

Station number	BOD$_5$	DO	N-NH$_{3+4}$	N-NO$_{3+2}$	TP	SS	Cl
413074	4.4 [3.7-6.1]	10.2 [5.7-16.6]	0.25 [0.03-0.93]	0.36 [0.01-1.5]	0.114 [0.040-0.170]	21 [3-88]	238 [75-513]
413673	2.9 [0.8-5.8]	10.5 [5.8-16.8]	0.04 [0.02-0.09]	0.49 [0.02-1.6]	0.087 [0.039-0.152]	23 [5-79]	180 [52-345]
RI-23	2.5 [0.3-8.1]	7.7 [0.5-15]]	0.74^{TKN} [0.05-2.47]	0.65 [0.04-3.51]	0.070 [0.003-0.442]	25 [3-508]	174 [4-455]
RI-24	2.4 [0.4-8.4]	8.5 [0.9-15.9]	0.72^{TKN} [0.04-4.01]	0.44 [0.03-2.11]	0.084 [0.08-0.894]	32 [3-618]	197 [6-932]
MU-2	NA	NA	0.96^{TKN} [0.46-1.4]	0.62 [0.30-0.75]	0.25 [0.04-0.67]	51 [7-164]	NA
RI-25	2.3 [0.6-5.9]	7.3 [0.9-17.3]	0.87^{TKN} [0.10-3.6]	0.44 [0.03-2.00]	0.103 [0.009-1.08]	34 [3-970]	165 [6-922]
413068	5.2 [3.3-6.5]	10.4 [7.2-17.1]	0.24 [0.02-1.00]	0.70 [0.01-2.3]	0.105 [0.060-0.190]	25 [4-80]	178 [54-325]
RI-26	2.4 [0.7-7.6]	6.8 [0.4-13]	1.32^{TKN} [0.05-97]	0.62 [0.04-2.31]	0.106 [0.11-1.36]	27 [3-602]	152 [6-940]
MU-3	NA	NA	1.28^{TKN} [0.61-2.68]	0.77 [0.35-1.1]	0.3 [0.03-1.04]	67 [3-346]	NA
RI-27	2.4 [0.5-7.5]	9.9 [5.1-18]	0.78^{TKN} [0.05-3.01]	0.59 [0.04-2.14]	0.077 [0.008-0.902]	28 [3-588]	146 [5-943]

* … measured only once NA … not analyzed ^{TKN} ... Total Kjeldahl Nitrogen

Table 3.7 summarizes the results of water quality analyses for conventional pollutants. The minima of oxygen level often fall beyond the 1 Day Minimum Criterion of 3 mg DO/l for warmwater. Table 3.8 shows the percentage of samples at selected sites that fail the oxygen critera. The worst situation is at stations RI-23 and RI-25 where about 5-6% of samples have DO less than 3 mg/l. Further analyses reveal that low oxygen level is almost exclusively associated with low flow conditions (flow < 5 cfs), although not all low flow samples show depleted oxygen. The flow of 5 cfs would correspond to roughly 65% exceedance at South Milwaukee station 04087204 (Water Resources Yearbook, 1997).

Table 3.8. Percentage of samples below oxygen level criteria. Oak Creek watershed.

Station number	RI-23	RI-24	RI-25	RI-26	RI-27
P(DO < 6 mg/l)	29.8 %	11.5 %	35.8 %	40.0 %	1.5 %
P(DO < 3 mg/l)	6.5 %	1.5 %	5.0 %	2.0 %	0.0 %

Both nitrogen and phosphorus concentrations exhibit positive correlation with flow, thus indicating the prevalence of diffuse pollution. Figures 3.2 and 3.3 show the trends for phosphorus and nitrate concentration at monitoring station RI-23. Figure 3.2 also indicates the presence of point sources of phosphorus. Similar relationships were found for other monitoring stations.

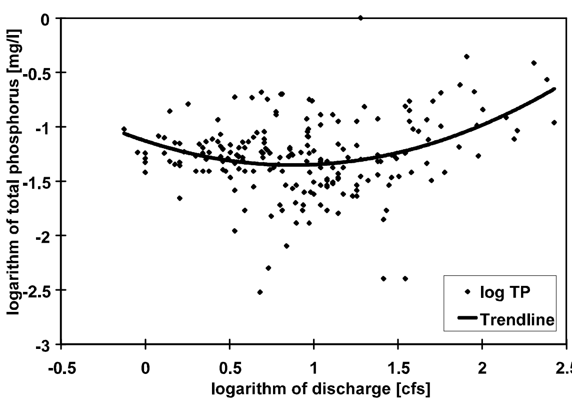

Figure 3.2. Phosphorus concentration versus flow at monitoring site RI-23. Log-log scale.

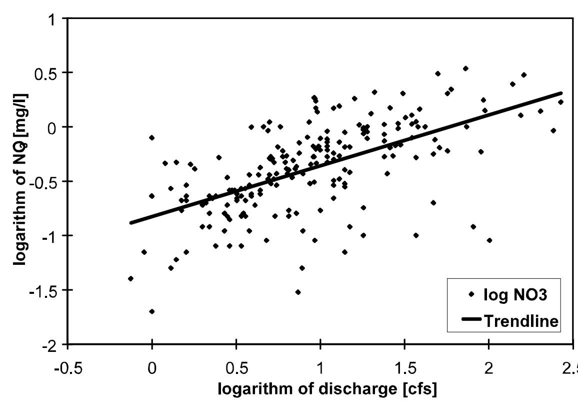

Figure 3.3. Nitrate concentration versus flow at monitoring site RI-23. Log-log scale.

Marquette University Water Quality Monitoring

The monitoring program of Water Qaulity Center by Marquette University focused on key locations in the Oak Creek watershed (see Figure 3.1). The site at Ryan Road (MU-1) provides information on background quality as affected by present residential landuse. The impact of Mitchell Field Airport was monitored at College Avenue (MU-4). The sites at Howell Road (Highway 38) and Nicholson Avenue (Pennsylvania Ave.) complement the monitoring and tie it with the existing data.

The following parameters were monitored: pH, suspended solids, volatile suspended solids, total solids, hardness, COD, total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen, total phosphorus, total and dissolved heavy metals (Cd, Cu, Pb, Zn), cyanides (winter sampling), and PAH (sampled twice). Total of 24 water column samples were analyzed. The sampling covered both low and high flow periods with wide range of flows. Sediments were analyzed in October 1999 for pH, %total solids, % volatile solids, COD, nitrate and nitrite nitrogen, TKN, total phosphorus, total and dissolved heavy metals (Cd, Cu, Pb, Zn), and PAH.

The winter samples at College Avenue showed significantly higher concentration of total nitrogen than other sites, about ten times higher than reference at Ryan Road. This maybe the effect of airport deicing operations. Separate analysis of new and used deicing fluids from Mitchell Field Airport confirm high nitrogen content (Gamble, 1999). New deicing fluids show ammonia nitrogen content of 0.67 mg N/l and organic nitrogen content of 1,440 mg N/l. Used deicing fluids contain 2.1 mg N/l as ammonia nitrogen and 237 mg N/l as organic nitrogen. Also, only at this site, the concentration of nitrogen decreases with increasing flow. Sediment analysis confirm high nitrogen concentration in accumulated solids (1,260 mg N/kg as TKN), about 3-4 times higher than in sites upstream of the confluence with the Mitchell Field Drainage Ditch (see Table 3.9).

Table 3.9. Sediment analysis [mg/kg dry weight]

	COD	NO_{2+3}-N	TKN	TP	Cd	Cu	Pb	Zn
College	42,600	2.4	1,260	1,710	1.7	117	0.03	100
Howell	130,000	< 2.7	3,170	8,630	2.4	105	0.02	97
Nicholson	35,800	2.2	358	420	1.4	12.2	0.01	14
Ryan	12,500	2.7	495	746	1.1	899	0.02	251

Monitoring of heavy metals contamination included determination of total and dissolved concentration in water column. The ratios of dissolved concentration to total concentration follow approximately normal distribution for all analyzed metals (Table 3.10). The ratio varies with concentration of suspended solids and hardness.

Table 3.10. Ratio of dissolved to total concentrations for heavy metals. Oak Creek watershed.

	Cd	Cu	Pb	Zn
average	0.268	0.377	0.208	0.458
standard deviation	0.298	0.325	0.382	0.254

The elevated concentration of cadmium was detected on May 7, 1999. The concentration reached 37 mg Cd/l (dissolved: 35 mg Cd/l) and 28 mg Cd/l (dissolved: 7 mg Cd/l) at Howell and Nicholson sites, respectively. Since no other monitoring stations reported similar concentration (see Table 3.11), we can assume that this was an accidental spill. It is interesting to observe how the ratio between total and dissolved concentration changed dramatically. The hardness reported for those sites is 134 and 346 mg/l as $CaCO_3$, respectively. Cyanides were found only at College site at level of 4.3 μg/l in February 1999.

Evaluation of Heavy Metals

The heavy metal concentrations are generally higher than those reported for reference streams. Table 3.11 shows average and range of values for selected monitoring sites. As mentioned previously, the number of measurements available from STORET is limited. Also, most of these data were collected in 1970's. The detail discussion on toxicity and water quality criteria focuses on data collected by MMSD.

Table 3.11. Summary of water quality data – heavy metals (μg/l). Oak Creek watershed. average [range]

Station number	Cd	Cr	Cu	Pb	Ni	Zn	Hg
413074	0.2 [0.2⌫]	3.92 [3⌫-8]	3.92 [3⌫-7]	5.75 [3⌫-14]	18.5 [0.3⌫-20]	40 [20⌫-80]	0.208 [0.2⌫-0.3]
413673	0.2⌫ [0.2⌫]	3⌫ [3⌫]	4.5 [3⌫-6]	4.5 [3⌫-6]	NA	21.5 [10⌫-33]	0.03⌫ *
RI-23	2.5 [1⌫-8]	NA	8.9 [2-111]	54.8 [1⌫-415]	NA	17.6 [5-110]	NA
RI-24	2.6 [1⌫-11]	NA	7.8 [2-33]	54.3 [1⌫-389]	NA	19.4 [5-119]	NA
MU-2	9.7 [0.2⌫-37]	NA	16.8 [5-34]	7.2 [2-12]	NA	44 [24-69]	NA
RI-25	2.5 [1⌫-7]	NA	7.4 [2-37]	49.9 [1-394]	NA	17.3 [5-80]	NA
413068	0.24 [0.2⌫-0.7]	73.3 [3⌫-420]	4.17 [3⌫-6]	4.42 [2⌫-12]	20⌫ [20⌫]	23.3 [20⌫-30]	0.2⌫ [0.2⌫]
RI-26	2.7 [1-14]	NA	8.1 [2-97]	48.2 [1-360]	NA	19 [5-190]	NA
MU-3	7.9 [0.2-27.7]	NA	20.4 [4-46]	7.1 [4-10]	NA	43.6 [20-101]	NA
RI-27	2.6 [1-8]	NA	7.5 [2-27]	53.6 [1-408]	NA	16.9 [4.4-84]	NA

⌫ ... value is a detection limit * ... measured only once NA .. not analyzed

The further analysis are thus limited to the monitoring stations R-23, RI-24, RI-25, RI-26, and RI-27. Figure 3.4 compares the distribution of measurements in these stations. On 5% confidence level, the measurements come from the same distribution with exception of measurements from station RI-23. The mean is significantly higher than the mean from other stations. The average hardness is 444 and 360 mg $CaCO_3$/l for monitoring station RI-23 and for the group of remaining stations, respectively.

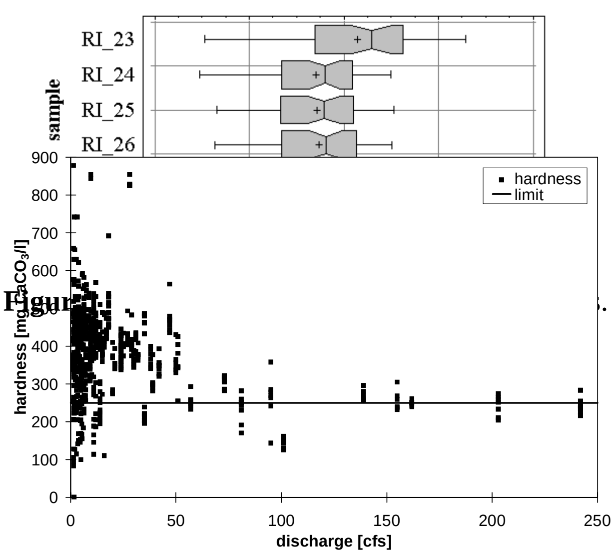

Figure 3.5. Hardness versus discharge. Oak Creek watershed.

Hardness is strongly influenced by hydrologic regime. Generally, baseflow exhibits high hardness due to geology of the watershed. Rainfall and surface runoff dilute water and decrease the hardness. There is a greater range of values during low flows than during high flows (Figure 3.5). However, there seems to be a limit of 250 mg $CaCO_3$/l associated with high flows.

Water quality criteria for Oak Creek have been calculated using Eq. 3.1 with the selected hardness of 250 mg $CaCO_3$/l. The criteria are summarized in Table 3.12. The acute and chronic toxicity criteria correspond to 99.5% and 99.9% values, respectively.

Table 3.12. Water quality criteria for heavy metals [μg/l] in Oak Creek.

Toxicity	**mg $CaCO_3$/l**	**Cd**	**Cu**	**Pb**	**Zn**
Acute	360	16.6	59.3	417	346
	444	21.1	72.2	545	414
Chronic	360	3.1	35.3	15.2	314
	444	3.7	42.3	21.2	375

Statistical analyses indicate that metal concentrations follow a log-normal distribution. Log-probability charts were used to estimate values that are reached with probability of 99.5% and 99.9% (i.e., probability of exceedance is 0.5% and 0.1%, respectively). These values are summarized in Table 3.13. The concentration of lead significantly decreased over the monitoring period. This can be associated with the effort to ban leaded gasoline that accelerated in mid 1980's.

In some cases, large number of samples exhibited concentration ‘less than detection limit’. Than, the distribution would be fitted through the remaining data points. Only cadmium measurements were consistently below the detection limit. This likely resulted in higher error in estimating the values with desired exceedance than in other cases with sufficient data points.

Table 3.13. Characteristic values for water quality evaluation -- total conc. [μg/l]. Oak Creek watershed.

Station	**Cd**		**Cu**		**Zn**	
	99.5%	**99.9%**	**99.5%**	**99.9%**	**99.5%**	**99.9%**
RI-23	11	17	46	70	100	152
RI-24	16	26	40	50	106	158
RI-25	9	12	46	53	85	124
RI-26	16	40	41	61	178	282
RI-27	18	11	37	53	95	144

Table 3.13 contd.

Station	**Pb (pre-1987)**		**Pb (post-1987)**	
	99.5%	**99.9%**	**99.5%**	**99.9%**
RI-23	723	1211	202	409
RI-24	663	1085	183	377

RI-25	610	993	139	270
RI-26	602	974	158	332
RI-27	722	1208	178	376

The concentrations as given in Table 3.13 are total concentrations. The criteria given in Table 3.12 were derived from toxicity bioassays with minimum or no sediment. Thus, the criteria would logically correspond to bioavailable , i.e., dissolved, concentrations. Table 3.14 shows Ecological Effects Quotient (EEQ) for both total and dissolved concentrations. EEQ is defined as a ratio of measured concentration and water quality criterion (dimensionless). Thus, EEQ is greater than one if the criterion is exceeded. When the total concentration is considered, all the sites would fail to meet the criteria except for zinc. When the dissolved concentration is considered, the acute toxicity criteria are generally kept. However, the values show the problems with chronic toxicity for lead and cadmium.

Table 3.14. Ecological effects quotient: total concentration (dissolved concentration) / criterion. Oak Creek watershed.

Station	**Cd**		**Cu**		**Zn**	
	99.5%	**99.9%**	**99.5%**	**99.9%**	**99.5%**	**99.9%**
RI-23	2.9 (0.8)	0.8 (0.2)	1.1 (0.4)	1.0 (0.4)	0.3 (0.1)	0.4 (0.2)
RI-24	5.1 (1.4)	1.6 (0.4)	1.1 (0.4)	0.9 (0.3)	0.3 (0.2)	0.5 (0.2)
RI-25	2.9 (0.8)	0.7 (0.2)	1.3 (0.5)	0.9 (0.3)	0.3 (0.1)	0.4 (0.2)
RI-26	5.1 (1.4)	2.4 (0.6)	1.1 (0.4)	1.0 (0.4)	0.6 (0.3)	0.8 (0.4)
RI-27	5.7 (1.5)	0.7 (0.2)	1.0 (0.4)	0.9 (0.3)	0.3 (0.1)	0.4 (0.2)

Station	**Pb (pre-1987)**		**Pb (post-1987)**	
	99.5%	**99.9%**	**99.5%**	**99.9%**
RI-23	34 (7.1)	2.2 (0.5)	9.5 (2.0)	0.8 (0.2)
RI-24	41 (8.5)	2.6 (0.5)	11 (2.3)	0.9 (0.2)
RI-25	38 (7.8)	2.4 (0.5)	8.6 (1.8)	0.6 (0.1)
RI-26	37 (7.7)	2.3 (0.5)	9.7 (2.0)	0.8 (0.2)
RI-27	44 (9.2)	2.9 (0.6)	11 (2.3)	0.9 (0.2)

Menomonee River

Summary of Monitoring Programs

The Menomonee River watershed has been given greater attention by monitoring agencies than the Oak Creek watershed. The STORET system contains information on 66 stations. However, many of these stations were monitored only for limited time and/or a limited number of parameters were analyzed. There are 11 locations on the Menomonee River, 4 of them in the estuary portion of the stream, and 9 locations on various tributaries such as Little Menomonee River, Underwood Creek (the PRR reference sites), Noyes Creek, Honey Creek and Schoonmaker Creek. Most of these locations were monitored in 1970s. A separate monitoring program is carried out by MMSD at 9 locations, 4 of them in the river estuary. MMSD stations are sampled regularly once to four times a month during non-winter months from 1980. The program was expanded in 1985 when new stations were added. Not all parameters were analyzed for every sample, though. For example, heavy metal content was not measured at all during 1987-1989 years.

Figure 3.6 shows the location of the monitoring stations that were in operation for at least two years as monitored by USGS, WI DNR, or MMSD. This section summarizes water quality in key locations (see Table 3.15). The river estuary was excluded from the water quality analysis. Further analysis in following section were conducted on MMSD data only due to insufficient length of record available through STORET.

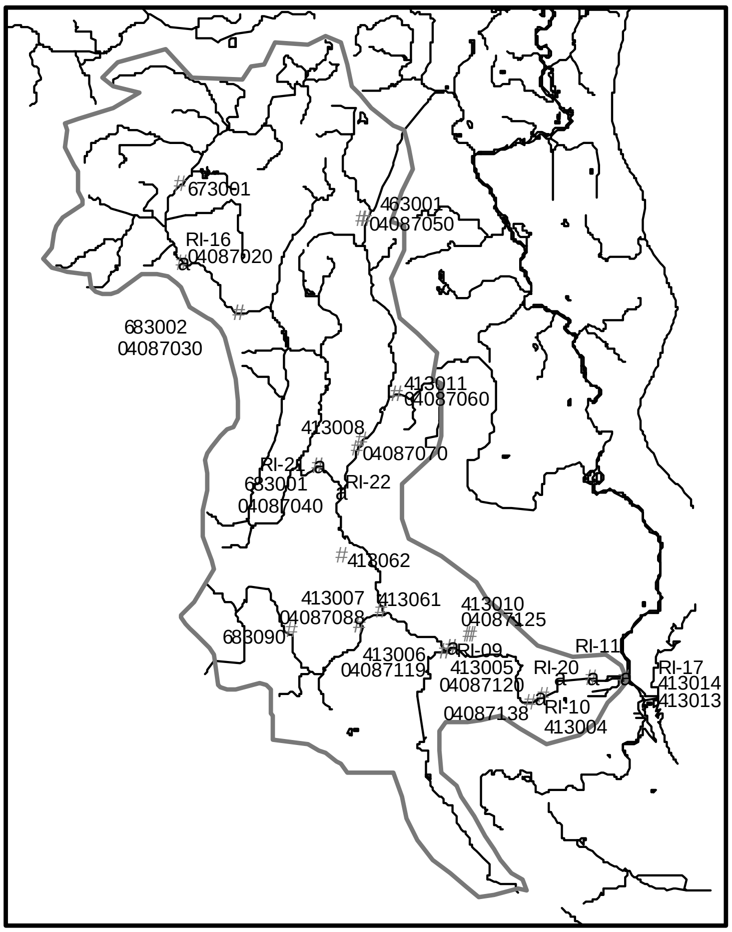

Figure 3.6. Location of water quality monitoring stations in the Menomonee River watershed.

Table 3.15. List of selected water quality stations. Menomonee River watershed.

Station number	Name	Period of record	Agency
04087020*	Menomonee River near Menomonee Falls	1973-1974	USGS
RI-16	County Line Road	1982-1997	MMSD
683001	Menomonee River @ 124th St	1975-1977	DNR
04087040*	Menomonee River @ Butler	1975-1977	USGS
RI-21	127th Street Ext.	1985-1997	MMSD
RI-22	Hampton Avenue	1985-1997	MMSD
413062	Menomonee River @ Currie P Golf CRS	1975-1977	DNR
413061	Menomonee R @ North Ave Bridge	1975-1977	DNR

413005 04087120 RI-09	Menomonee River @ 70th St Bridge Menomonee River @ Wauwatosa North 70th Street	1975-1994 1992-1996 1981-1997	DNR USGS MMSD
413004 RI-10	Menomonee R AB 27th Street, Falk Corp. Falk Dam	1975-1977 1980-1988	DNR MMSD

* ... limited water quality data

Table 3.16. Summary of water quality data-conventional pollutants [mg/l]. Menomonee Rvr watershed. average [range]

Station number	**BOD_5**	**DO**	**$N\text{-}NH_{3+4}$**	**$N\text{-}NO_{3+2}$**	**TP**	**SS**	**Cl**
RI-16	2.5 [0.5-7.8]	8.6 [1.6-17.6]	1.1^{TKN} [0.06-2.7]	1.11 [0.03-3.4]	0.13 [0.01-1.1]	14 [2-132]	96 [6-653]
683001	NA	9.8 [2.6-14.1]	0.95 [0.10-12.0]	1.87 [0.0-4.6]	0.602 [0.13-1.80]	117 [2-1444]	155 [30-1100]
RI-21	2.3 [0.4-6.2]	10.1 [3.6-17.0]	0.85^{TKN} [0.11-4.70]	0.59 [0.03-2.70]	0.10 [0.01-4.0]	23 [2-248]	102 [3-373]
RI-22	2.5 [1-8.6]	9.6 [3.8-17]	0.86^{TKN} [0.06-3.30]	0.62 [0.03-2.00]	0.11 [0.01-0.8]	28 [3-368]	99 [1-429]
413062	NA	9.1 [5.0-13.4]	1.11 [0.02-9.80]	1.81 [0.9-4.0]	0.537 [0.13-1.45]	36 [2-330]	153 [50-380]
413061	NA	11.1 [4.6-16.5]	0.86 [0.02-7.1]	1.60 [0.3-2.9]	0.414 [0.12-1.0]	39 [3-546]	155 [55-700]
413005	5.5 [0-22]	11.7 [6.7-19.5]	0.34 [0.005⌫-4.7]	1.08 [0.1⌫-5.0]	0.373 [0.02⌫-2.1]	157 [1⌫-2100]	188 [1⌫-2800]
04087120	5.4 [1.0⌫-22]	NA	0.08 [0.005⌫-0.42]	0.73 [0.1-1.5]	0.172 [0.02-0.81]	94 [2⌫-720]	132 [0.1-1000]
RI-09	2.9 [0.8-9.0]	11.6 [1.0-20.0]	0.80^{TKN} [0.14-7.1]	0.69 [0.03-2.80]	0.09 [0.01-1.6]	21 [0-349]	134 [2-946]
413004	NA	9.3 [3.8-13.9]	0.39 [0.01⌫-3.3]	1.09 [0-4.7]	0.376 [0.02⌫-1.74]	91 [0-804]	171 [25-1800]
RI-10	3.4 [2.0-14.0]	10.9 [2.5-20.0]	0.92^{TKN} [0.09-6.20]	0.78 [0.05-7.10]	0.15 [0.01-2.0]	21 [3-341]	121 [11-680]

⌫ ... value is a detection limit NA ... not analyzed ^{TKN} ... Total Kjeldahl nitrogen

Table 3.7 summarizes the results of water quality analyses for conventional pollutants. The minima oxygen levels at some stations are lower than 1 Day Minimum Criterion of 3 mg DO/l. Table 3.17 shows the percentage of samples at selected sites that fail the oxygen criteria. The oxygen level is generally better than in Oak Creek. The worst situation is at station RI-16 where 2% and 15.7% of samples have DO less than 3 mg/l and 6 mg/l, respectively.

Table 3.17. Percentage of samples below oxygen level criteria. Menomonee River watershed.

Station number	RI-16	RI-21	RI-22	RI-09	RI-10
P(DO < 6 mg/l)	15.7 %	2.3 %	5.5 %	0.9 %	4.5 %
P(DO < 3 mg/l)	2.0 %	0.0 %	0.0 %	0.2 %	0.8 %

The flow in Menomonee River is measured by USGS at two stations: 04087030 (Menomonee River at Menomonee Falls, RI-16) and 08047120 (Menomonee River at Wauwatosa, RI-09, RI-10). Limited flow measurements are available from USGS station 04087040 for 1974-1977 period. This location corresponds to the location of monitoring sites RI-21 and RI-22. The flow in station 04087040 was related to the flow in station 04087030 through simple regression $\log q = a \log q' + b$, where $q = Q / Area$ is the unit flow [cfs/mi^2], Q is the flow [cfs], *Area* is the watershed area [mi^2], and a and b are the regression coefficients. The regression coefficients are $a = 0.953$ and $b = 0.00944$ (with $R^2 = 0.96$). Figure 3.7 shows the relationship between unit flows in evaluated stations and the regression line. The estimated flow was then used for statistical analyses of dependencies on flow.

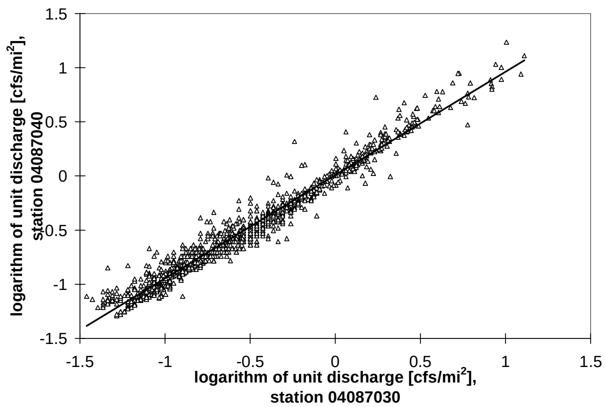

Figure 3.7. Relationship between unit flows [cfs/mi^2] for stations 04087030 and 04087040.

Nitrogen and phosphorus concentrations correlate positively with flow, although the results are not so conclusive as for the Oak Creek watershed. Figures 3.8 and 3.9 show the trends for phosphorus and nitrate concentration at monitoring station RI-21. Similar relationships were found for other monitoring stations. Both nitrogen and phosphorus concentrations are substantially higher than those in Oak Creek. One can also see an improvement in water quality since 1977 when comparing measurements for the same location (e.g., stations 683001 ad RI-21, Table 3.7).

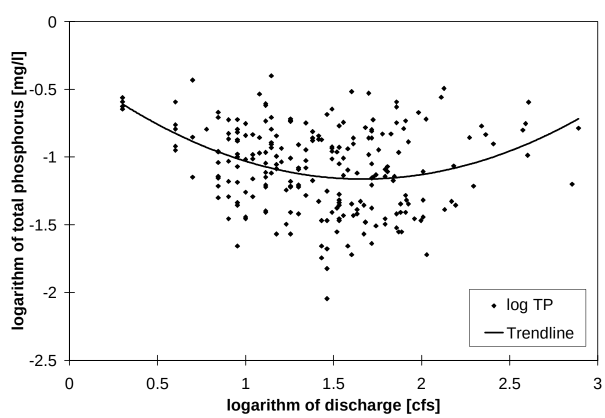

Figure 3.8. Phosphorus concentration versus flow at monitoring site RI-21. Log-log scale.

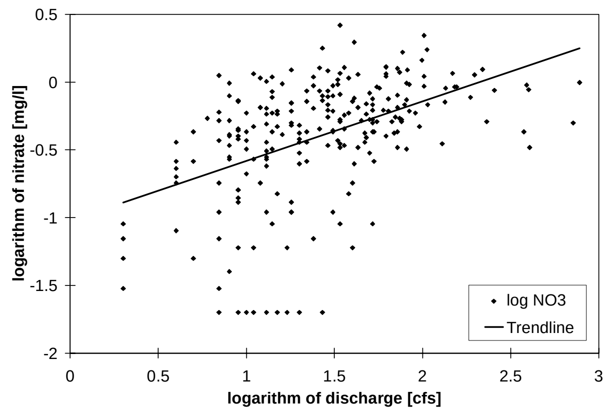

Figure 3.9. Nitrate concentration versus flow at monitoring site RI-21. Log-log scale.

Evaluation of Heavy Metals

The heavy metal concentrations (Table 3.18) are significantly higher than those reported for reference streams and most of the stations in the Oak Creek watershed. The maximum concentration often reaches hundreds of μg/l for copper, lead, and zinc. The high concentrations appear even in the most upstream station already found in commercial area with many small businesses located around the stream. On the other hand, the concentration of zinc steadily increases from upstream to downstream (MMSD stations).

It should be noted that many cadmium measurements were found below the detection limit for almost all monitoring stations. All MMSD monitoring stations except for station RI-10 have only two to four values measured above the detection limit. This makes it almost impossible to conduct any statistical analyses. Thus, the values presented in this or the next section are only the best estimate. No other conclusion concerning the water quality can be made than that concentrations are not detectable in most cases. The detail discussion on toxicity and water quality criteria for heavy metals is included in the following section.

Table 3.18. Summary of water quality data - heavy metals [μg/l]. Menomonee River watershed. average [range]

Station Number	Cd	Cr	Cu	Pb	Ni	Zn	Hg
RI-16	2.2 [0.1⌫-9.0]	NA	11.1 [2.0-321]	46.3 [1.0-550]	NA	13.5 [5.0-284]	NA
683001	0.9 [0.2⌫-4]	9.25 [3⌫-34]	31.9 [3⌫-69]	14.4 [3⌫-49]	26.3 [20⌫-44]	88.1 [30-220]	0.236 [0.2⌫-0.4]
RI-21	2.0 [0.1⌫-6.0]	NA	10.5 [2.0-63]	35.9 [1.0-339]	NA	20.4 [4.1-150]	NA
RI-22	2.0 [0.1⌫-5.0]	NA	10.6 [2.0-89]	36.2 [1.0-363]	NA	23.9 [3.3-350]	NA
413062	0.2⌫	6.30	9.0	9.0	20⌫	30.0	0.300

	[0.2⌫]	[4-9]	[5-13]	[4-14]	[20⌫]	[20-40]	[0.2⌫-0.4]
413061	0.2*⌫	6.30 [5-8]	8.0 [5-11]	21.0 [12-30]	20⌫ [20⌫]	50.0 [30-70]	0.2⌫ [0.2⌫]

Table 3.18 contd.

413005	1.3 [0.2⌫-7]	19.9 [3⌫-100]	43.3 [3⌫-110]	104 [3⌫-550]	27.8 [20⌫-140]	113 [10⌫-320]	0.212 [0.2⌫-0.4]
04087120	1.0 [1⌫-2]	5.14 [1⌫-19]	12.3 [3⌫-51]	13.8 [1-50]	NA	53.9 [10⌫-260]	NA
RI-09	2.3 [0.1⌫-4.8]	NA	9.8 [2.0-65]	41.1 [1.0-420]	NA	23.9 [5.0-236]	NA
413004	2.1 [0.3-10]	29.3 [3⌫-106]	45.9 [3⌫-161]	84.2 [3⌫-700]	24.9 [20⌫-64]	163.1 [50-440]	0.340 [0.2⌫-0.9]
RI-10	3.73 [3.0-19]	NA	10.8 [3.0-69]	73.7 [8.0-420]	NA	31.1 [5.0-160]	NA

⌫ ... value is a detection limit   * ... measured only once   NA ... not analyzed

With respect to the record period and the number of available measurements, only MMSD data will be used for detail evaluation of toxicity within this section. The analyses are limited to stations RI-09, RI-10, RI-16, RI-21, and RI-22 (i.e., the river estuary is excluded). As described previously, toxicity of heavy metals is strongly influenced by hardness (see Equation 3.1 on page 8). Figure 3.10 compares the distribution of measurements in these stations. On 5% confidence level, the means of measurements can be equal regardless of station. The only exception is the station RI-16 where the distribution differs from stations RI-09 and RI-10. The hardness tends to decrease slightly as water flows downstream. The average hardness is 340 mg $CaCO_3$/l for the upstream (RI-16), 325 mg $CaCO_3$/l for the middle (RI-21, RI-22), and 320 mg $CaCO_3$/l for the downstream (RI-09, RI-10) stations. Figure 3.11 shows the changes of hardness with flows. There is a greater range of values during low flows than during high flows. there seems to be a limit of 200 mg $CaCO_3$/l associated with high flows.

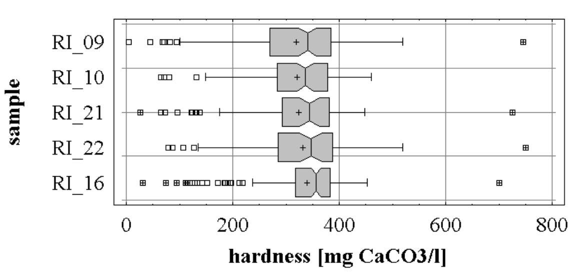

Figure 3.10. Box-and-Whisker plot of hardness in the Menomonee River watershed monitoring sites.

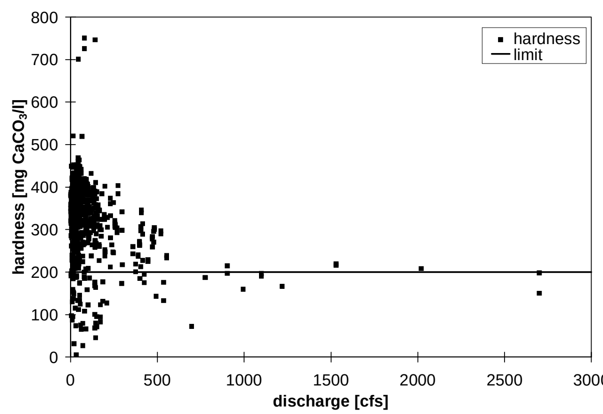

Figure 3.11. Hardness versus discharge. Menomonee River watershed.

Water quality criteria for Menomonee River are summarized in Table 3.19. These criteria are compared with values with 0.5% and 0.1% exceedance (99.5% and 99.9% probability) estimated from log-probability charts using the same procedure as described for the Oak Creek watershed. The characteristic values for total concentration are given in Table 3.20. The measurements of lead are divided into two groups: before 1987 and after 1987, since the concentration significantly decreased over the monitoring period as the ban of leaded gasoline was implemented.

Table 3.19. Water quality criteria for heavy metals [μg/l] in Menomonee River. .

Toxicity	mg $CaCO_3$/l	Cd	Cu	Pb	Zn
Acute	320	15	53	360	314
	325	15	54	366	318
	340	16	56	388	330
Chronic	320	2.8	32	14	284
	325	2.9	32	14	288
	340	3.0	34	15	299

Table 3.20. Characteristic values for water quality evaluation -- total conc. [μg/l]. Menomonee River watershed.

Station	Cd		Cu		Zn	
	99.5%	99.9%	99.5%	99.9%	99.5%	99.9%
RI-16	8.9	17.8	57	90	95	191
RI-21	8.3	15.1	62	95	158	251
RI-22	6.6	12.6	63	96	331	794
RI-09	5.0	8.3	76	126	138	213
RI-10	18.6	29.5	64	100	241	400

s

Station	Pb (pre-1987)		Pb (post-1987)	
	99.5%	99.9%	99.5%	99.9%
RI-16	648	1073	96	177
RI-21	629	990	82	141
RI-22	551	859	138	253
RI-09	519	842	75	129
RI-10	449	694	NA	NA

Table 3.21. Ecological effects quotient: total concentration (dissolved concentration) / criterion.. Menomonee River watershed.

Station	Cd		Cu		Zn	
	99.5%	99.9%	99.5%	99.9%	99.5%	99.9%
RI-16	3.0 (0.8)	1.1 (0.3)	1.7 (0.6)	1.6 (0.6)	0.3 (0.1)	0.6 (0.3)

RI-21	2.9 (0.8)	1.0 (0.3)	1.9 (0.7)	1.8 (0.7)	0.6 (0.3)	0.8 (0.4)
RI-22	2.3 (0.6)	0.8 (0.2)	1.9 (0.7)	1.8 (0.7)	1.2 (0.5)	2.5 (1.1)
RI-09	1.8 (0.5)	0.6 (0.2)	2.4 (0.9)	2.4 (0.9)	0.5 (0.2)	0.7 (0.3)
RI-10	6.6 (1.8)	2.0 (0.5)	2.0 (0.8)	1.9 (0.7)	0.8 (0.4)	1.3 (0.6)

Table 3.21. contd.

Station	**Pb (pre-1987)**		**Pb (post-1987)**	
	99.5%	**99.9%**	**99.5%**	**99.9%**
RI-16	43 (8.9)	2.8 (0.6)	6.4 (1.3)	0.5 (0.1)
RI-21	44 (9.2)	2.7 (0.6)	5.7 (1.2)	0.4 (0.1)
RI-22	39 (8.0)	2.3 (0.5)	9.7 (2.0)	0.7 (0.1)
RI-09	37 (7.8)	2.3 (0.5)	5.4 (1.1)	0.4 (0.1)
RI-10	32 (6.7)	1.9 (0.4)	NA	NA

Table 3.21 shows the EEQ for both total and dissolved concentrations. The data on dissolved metals concentration are scarce for the Menomonee River. The MMSD analyzes only total concentration. Limited data is available for two locations on the Menomonee River from USGS and WI DNR. However, when the dissolved concentration was measured, the total concentration was not analyzed. Thus, it was assumed that a relationship between dissolved and total concentration in Menomonee River is similar to that in Oak Creek.

Although the EEQ for cadmium is relatively high, we cannot make definite conclusion about exceedance of criteria. It has been mentioned in the previous section that most cadmium measurements were reported as ‘data below the detection limit’ (see page 21). Copper is of concern in all locations on the Menomonee River. Even when dissolved concentration is compared with the criterion, the EEQ is close to 1.0. The concentration of lead after 1987 is low enough to satisfy the criterion for acute toxicity. However, the criterion for chronic toxicity is exceeded 2-3 times.

CHAPTER 4

ECOLOGICAL RISK ASSESSMENT

Overview of the Modified WERF Methodology

Novotny and Witte (1997) provided the extension of the WERF risk characterization methodology that was outlined previously by Parkhurst et al. (1996). This extension is designed to allow the application of the methodology to estimating the toxicological-ecological impacts of *stormwater*. The ecological impacts of stormwater include the degradation of aquatic habitat by flow, as well as the toxicological-ecological impacts on water quality. The overall ecological state of the receiving water body can be ascertained using a biological evaluation, such as that outlined in the *Rapid Bioassessment Protocol* methodology (Plafkin et al., 1989, Barbour et al., 1997). However, biological assessment procedures of this type are based on the application of multiple indices calling for subjective judgment. The toxicological-ecological component of the overall ecological risk assessment lends itself more readily to numerical expression.

Tier 1: Screening Level

In the screening-level approach, the probability of injury to the indigenous biota from concentration exceeding the criterion value is multiplied by the exceedance probability of the criterion by the concentration in the receiving water body. The corresponding joint probability function can be approximated as follows:

$$p = p_1 p_2 p_{ww} \alpha \qquad \textbf{(4.1)}$$

where p is the overall joint probability of adverse toxicological-ecological effect, p_1 is the safety factor incorporated in the numeric criteria from the 96-hour bioassays using the US EPA procedure (this factor has a value of about 0.001), p_2 is the probability of exceedance of the water quality criterion (which should consider the biological availability effects as expressed in the water effect ratio, WER), p_{ww} is the probability of wet-weather flow (for the Central United States, this probability is about 0.065), and α is a factor that considers the effect of the difference between the 96-hour duration of the test exposure and the expected duration of storm events (for an average storm of 9-hour duration, $\alpha = 0.3$).

Although the application of Eq. 4.1 does remove some of the excess of the conservative nature of a naive application of the water quality criteria, it still overestimates the toxicological risk by orders of magnitude. This can be shown by the application of the more accurate, tier-2 level assessment procedure, which is outlined next.

Tier 2: Risk Quantification for Stormwater Discharges

The more accurate (and conceptually cleaner) tier-2 procedure, as outlined in the WERF methodology by Parkhurst et al. (1996) and modified for stormwater discharges as outlined by Novotny and Witte (1997), removes the consideration of the water quality criteria completely. Instead, it is based on a direct consideration of the joint probability of two probability functions: (1) the probability density function of the event mean concentrations (EMC) adjusted for the appropriate dilution ratio (DR) and WER effects, f(EMC) = pdf(EMC x DR/WER), and (2) the risk function g(R|EMC), which gives the value of the probability that an organism will be adversely affected by the exposure to the given stormwater EMC (as modified by DR and WER), and considering also the effects of water hardness on the LC_{50} values. The joint probability, again taking into account the probability of wet-weather events, is

$$h(R,C) = p_{ww} \, \mathrm{f(EMC)\; g(R|EMC)} \tag{4.2}$$

Put in words, the joint probability function of Eq. 4.2 gives the probability that (1) a wet-weather event will occur, (2) a particular EMC will occur in the stormwater (given that there is a wet-weather event), and (3) an indigenous organism will be adversely impacted (given that there is a wet-weather event and given that the adjusted EMC is equal to that particular value). The integration of Eq. 4.2 over all concentrations, as summarized in Fig. 4.1, will then yield the total risk that the stormwater discharges will be adverse to the indigenous aquatic life, *r*.

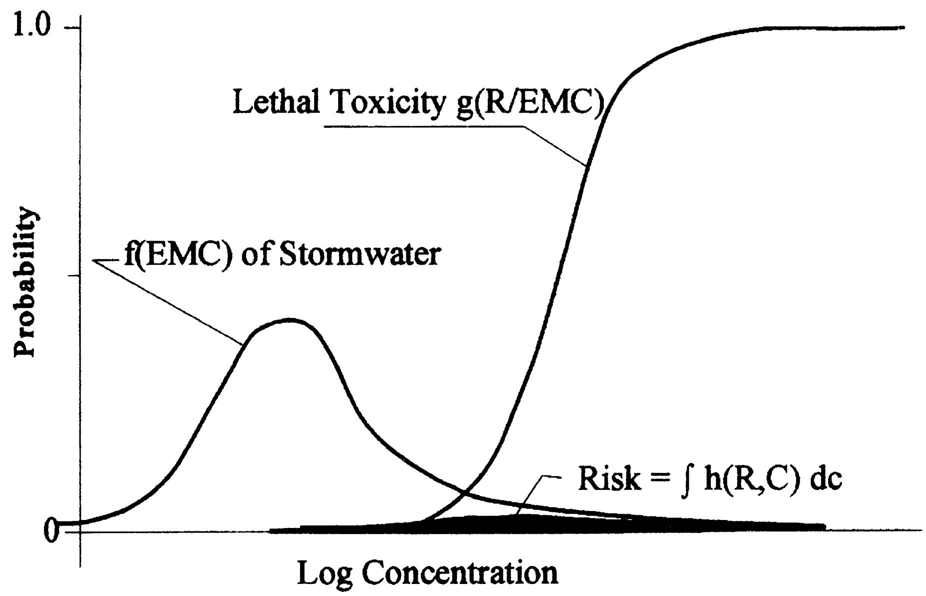

Figure 4.1. Tier-2 ecological risk assessment for stormwater impacts (from Novotny and Witte, 1997).

The *r* value, however, expresses the total risk due to one stressor only. Therefore, the total risk due to all the relevant stressors will be

$$R = \sum r_i \tag{4.3}$$

The stressors may exert a combined effect on organism (additive), they may interfere one with another (antagonism), or their overall effect may be greater than when acting alone (synergism) (Mason, 1991). An example of an additive interaction is the combined toxicity of zinc and cadmium to fish, though their toxicity is synergistic to algae. Calcium (hardness) is antagonistic to heavy metals.

Oak Creek

The ecological risk to aquatic biota was calculated for selected heavy metals (see Chapter 3). Cadmium was excluded from analysis because of the small number of values measured above the detection limit. It would be impossible to fit the distribution to such data set. The data for copper, lead (both before and after 1987), and zinc were statistically analyzed. A certain proportion of measurements is reported as *data below detection limit*. This does not mean that the concentration is zero, only that it is somewhere between zero and the detection limit.

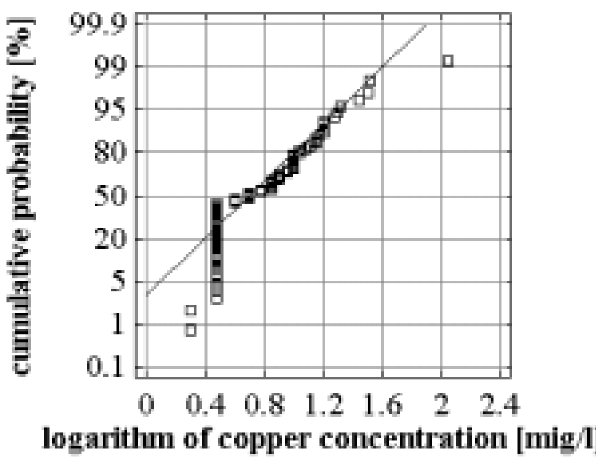

Figure 4.2. Log-normal distribution of copper concentration for site RI-23. Oak Creek.

The data follow log-normal distribution (Figure 4.2). The mean and the standard deviation for those monitoring sites with measurements less than detection limit were estimated from quantile plot, as long as median was above the detection limit. The results are summarized in Table 4.1. The total concentration reported by MMSD has been transformed to the dissolved concentration using the ratios determined from our monitoring program (see Table 3.10)

Table 4.1. The mean and standard deviation of fitted log-normal distribution for dissolved concentrations [log µg/l].

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-23	0.309 0.358	1.06 0.449	0.093 0.603	0.674 0.464
RI-24	0.312 0.316	1.07 0.426	0.006 0.602	0.761 0.426
RI-25	0.262 0.344	1.04 0.422	0.016 0.602	0.724 0.403
RI-26	0.252 0.374	1.05 0.410	-0.092 0.626	0.686 0.454
RI-27	0.277 0.336	1.06 0.440	-0.053 0.630	0.657 0.460

The acute toxicity has been calculated using the methodology described previously. The spreadsheet developed in Excel for risk calculation is described in detail in Technical Memo #1 (Bartošová, 2000). The Gumbel distribution has been used to fit the toxic response curve for copper while the normal distribution has been used to fit the toxic response curve for lead and zinc. The results are summarized in Table 4.2. The chronic toxicity is approximated by using the Acute-To-Chronic ratio (ACR). This ratio has been estimated for given hardness from EPA water quality criteria. The GMAVs were recalculated using ACR and the values were fitted the selected distributions. The chronic toxicity risk is summarized in Table 4.3.

Table 4.2. The acute toxicity risk to aquatic biota. Oak Creek watershed.

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-23	1.9 E-07	3.0 E-04	2.9 E-05	3.1 E-06
RI-24	7.7 E-08	4.1 E-04	3.2 E-05	4.6 E-06
RI-25	1.6 E-07	3.7 E-04	3.3 E-05	2.7 E-06
RI-26	5.4 E-07	3.6 E-04	2.7 E-05	4.5 E-06
RI-27	1.3 E-07	4.1 E-04	3.1 E-05	4.1 E-06

Table 4.3. The chronic toxicity risk to aquatic biota. Oak Creek watershed.

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-23	4.7 E-06	1.2 E-02	1.9 E-03	1.7 E-05
RI-24	2.9 E-06	1.6 E-02	2.0 E-03	2.6 E-05
RI-25	4.5 E-06	1.5 E-02	2.1 E-03	1.6 E-05
RI-26	1.1 E-05	1.5 E-02	1.7 E-03	2.4 E-05
RI-27	3.9 E-06	1.6 E-02	1.9 E-03	2.2 E-05

Both acute and toxic risks are in the same order of magnitude for all stations within each parameter. There is an order of magnitude improvement in both acute and chronic toxicity from lead after 1987 year. The chronic toxicity represents a bigger problem than the acute toxicity, especially for lead.

Menomonee River

The ecological risk to aquatic biota was calculated for selected heavy metals. Cadmium was excluded from analysis because of the small number of values measured above the detection limit. The data for copper, lead (both before and after 1987), and zinc were statistically analyzed.

The data follow log-normal distribution (Figure 4.3). The same procedure as described for the Oak Creek watershed has been used to find the mean and the standard deviation of measurements. The results are summarized in Table 4.4. The total concentration reported by MMSD has been transformed to the dissolved concentration using the ratios determined from our monitoring program (see Table 3.10)

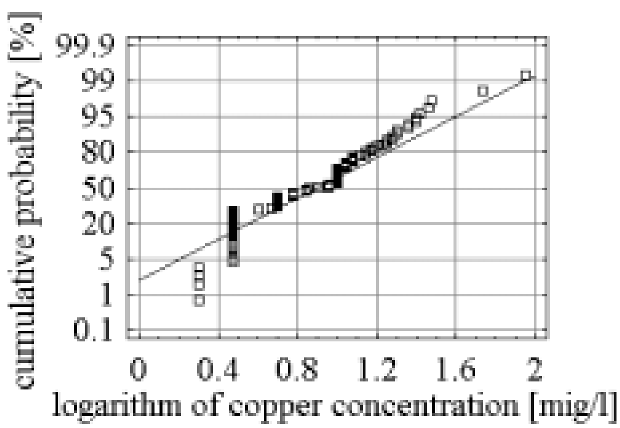

Figure 4.3. Log-normal distribution for copper concentration at site RI-22. Menomonee River.

Table 4.4. The mean and standard deviation of fitted log-normal distribution for dissolved concentrations [log μg/l].

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-16	0.192 0.503	1.03 0.426	-0.031 0.517	0.493 0.424
RI-21	0.324 0.473	1.13 0.383	0.041 0.461	0.701 0.462
RI-22	0.309 0.479	1.10 0.374	0.146 0.510	0.795 0.442
RI-09	0.263 0.479	0.98 0.409	-0.205 0.458	0.836 0.421
RI-10	0.267 0.486	1.02 0.368	NA	0.899 0.501

The acute toxicity has been calculated using the methodology described previously. The Gumbel distribution has been used to fit the toxic response curve for copper while the normal distribution has been used to fit the toxic response curve for zinc and lead. The results are summarized in Tables 4.5 and 4.6.

Table 4.5. The acute toxicity risk to aquatic biota. Menomonee River watershed.

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-16	2.1 E-05	4.0 E-04	1.8 E-06	9.9 E-07
RI-21	3.0 E-05	5.0 E-04	1.8 E-06	6.8 E-06
RI-22	3.2 E-05	4.4 E-04	3.5 E-05	8.8 E-06
RI-09	2.3 E-05	3.5 E-04	7.4 E-06	8.7 E-06
RI-10	2.9 E-05	3.5 E-04	NA	3.4 E-05

Table 4.6. The chronic toxicity risk to aquatic biota. Menomonee River watershed.

Station Number	Cu	Pb <1987	Pb >1987	Zn
RI-16	1.6 E-04	1.6 E-02	1.5 E-03	6.2 E-06
RI-21	2.3 E-04	1.9 E-02	1.6 E-03	3.5 E-05
RI-22	2.4 E-04	1.7 E-02	2.5 E-03	4.6 E-05
RI-09	1.8 E-04	1.5 E-02	8.3 E-04	4.6 E-05
RI-10	2.2 E-04	1.5 E-02	NA	1.5 E-05

Similarly to the results for the Oak Creek watershed, both acute and toxic risks are in the same order of magnitude for all stations within each parameter. The improvement in toxicity from lead after 1987 year reaches 2 orders of magnitude for acute toxicity and 1 order of magnitude for chronic toxicity. The acute toxicity from zinc is approximately 1 order of magnitude lower than the chronic one. The same is true for ecological risk from copper.

The risks (both chronic and acute) from copper calculated for the Menomonee River are two orders of magnitude higher than those for the Oak Creek. The risks from lead and zinc are at the same level for both watersheds, with the exception of acute risk from lead after 1987 which is one order of magnitude higher for Oak Creek than for Menomonee River.

CHAPTER 5

CONCLUSIONS

The water quality of two investigate watersheds has been evaluated. The Oak Creek watershed is a rural, rapidly developing watershed. The Menomonee River watershed is mostly developed. Traditional approach to water quality suggests possible chronic toxicity problems with cadmium and lead for both watersheds. The ecological effect quotients are close to 1.0 for copper at several monitoring sites on Menomonee River, both for acute and chronic toxicity. The acute toxicity criterion for zinc is exceeded only at one site on Menomonee River.

The acute and chronic toxicity risks have been calculated using modified WERF methodology. The chronic toxicity calculated does not include the effect of contaminated sediment, only the water column concentration. The release of pollutants from the contaminated sediment further affects the biotic community. Chronic effects of lead represent the highest risk to aquatic biota in both watersheds (10^{-3}). Copper is also a pollutant of concern (chronic toxicity risk of 10^{-4}) in Menomonee River. Both acute and chronic risks from copper calculated for the Menomonee River are two orders of magnitude higher than those for the Oak Creek.

Potential risk (10^{-5}) is caused by copper (acute toxicity, Menomonee River) and zinc (chronic toxicity, both watersheds). The risks from lead and zinc are at the same level for both watersheds, with the exception of acute risk from lead after 1987 which is one order of magnitude higher for Oak Creek than for Menomonee River.

CHAPTER 6

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