

# **KEY FINDINGS**

The 2008 MCES Empire Wastewater Treatment Plant (WWTP) diversion drastically reduced chloride concentrations and loads in the Vermillion River.

Chloride concentrations were increasing before the effluent diversion, decreased sharply immediately after effluent diversion and have been slowly increasing since. The persistent increase in chloride indicates that watershed factors are affecting chloride in the river independent of the effects of the Empire WWTP effluent.

Prior to the Empire WWTP diversion the primary source of chloride to the river was household water softening passed through the wastewater treatment plant. After the diversion the primary source of chloride is unknown. Livestock excreta, household water softening, synthetic fertilizer, and de-icing salt are all likely sources.

# INTRODUCTION

The Metropolitan Council Environmental Services (MCES) is committed to stewardship of Twin Cities streams and tributary rivers and works with its partners to maintain and improve waterbody health and function. These efforts are supported by the collection and analysis of high-quality, long-term data.

In 2014, Comprehensive Water Quality Assessment of Select Metropolitan Area Streams described statistical water quality trends for streams and tributary rivers in the Twin Cities. At that time, data were insufficient to analyze chloride trends. By 2019, our monitoring work provided sufficient data for statistical trend analysis. Meanwhile, concern about chloride pollution has increased for watershed managers and the general public. This memo includes information about chloride sources and timing of chloride runoff and addresses the following questions:

- How has in-stream chloride changed over time?
- How have upland watershed activities impacted in-stream chloride over time?
- What can monitoring data tell us about chloride sources and pathways in the watershed?

This memo provides data and analyses from the Vermillion River with state and regional context about chloride pollution. This information has prompted questions from MCES staff and will likely prompt questions from readers. This memo is intended to initiate a dialog about regional chloride dynamics and inspire action to alleviate chloride pollution. Please contact us to discuss potential future partnerships if you are interested in continuing this work.

## CHLORIDE POLLUTION IN TWIN CITIES WATERS

Chloride concentrations have been rapidly rising in many Twin Cities waterbodies over the past two decades. In the Twin Cities, 40 lakes and streams are impaired for aquatic life due to chloride contamination and an additional 41 waterbodies are high risk for chloride impairment. A recent study by MCES indicated an increasing trend for chloride concentrations in the Mississippi, Minnesota, and St. Croix Rivers during the recent 30 years.2 Thirty percent of Twin Cities shallow aquifer monitoring wells have chloride concentrations that exceed the Minnesota state water quality standard.3

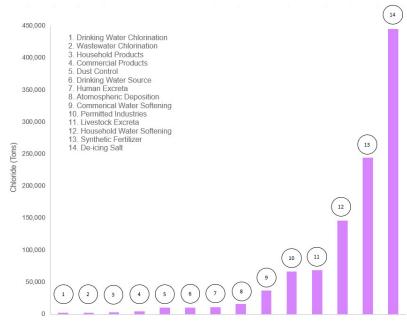


Figure 1: Major chloride sources and their annual chloride contributions to the environment in Minnesota.

Chloride is a permanent water pollutant, there is no easy way to remove it with existing technology. It is toxic to fish,

aquatic bugs, and amphibians. Chronic toxicity is indicated by samples above 230 mg/L, acute toxicity by samples above 860 mg/L.<sup>4</sup>

Chloride pollution in Minnesota has multiple sources.<sup>5</sup> The four largest are livestock excreta, household water softening, synthetic fertilizer and de-icing salt (Figure 1).

<u>Livestock Excreta:</u> Research found elevated chloride in seepage from earthen-lined manure storage and high chloride levels in groundwater downgradient of manure storage<sup>6</sup>, but there is little research investigating effects of livestock feedlots or manure application practices on chloride levels in water.

<u>Household water softening</u>: More than 70% of the drinking water used in the Twin Cities comes from groundwater<sup>7</sup> and many groundwater users soften their water with chloride salts. The chloride waste from the water softening process enters surface and groundwater through wastewater treatment plants or residential subsurface treatment systems.<sup>8</sup>

<u>Synthetic fertilizer</u>: Chloride is associated with macronutrients like potassium. The most common potassium source in Minnesota is potash fertilizer, potassium chloride.<sup>9</sup> Plants consume the potassium and release the chloride into surface and groundwater.

<u>De-icing salt</u>: Approximately 402,000 tons of de-icing salt is annually applied in the Twin Cities.<sup>10</sup> De-icing salt is carried by melting ice and snow into surface and groundwater.

Climate change is creating a warmer, wetter climate in Minnesota and the effects are most significant during the coldest months. An altered winter freeze-thaw cycle will have unpredictable effects on chloride use and pollution dynamics.

## STREAM AND WATERSHED DESCRIPTION

The Vermillion River is located in the southeast metropolitan area and is a tributary to the Mississippi River. It drains approximately 312 square miles of agricultural areas, forest, wetlands, grasses, and urban areas through portions of Scott, Dakota, and Goodhue counties. Watershed groundwater-surface water interactions are complex with some gaining and some losing reaches. The dynamics of groundwater contributions to the monitoring station are not well understood. (Figure 2).

The Vermillion River watershed is a total of 199,474 acres, 49% of the land use is agricultural. About 24% of the land is developed urban land, including the cities of



Figure 2: Map of Vermillion River Watershed

Farmington, Hampton, Coates, and Vermillion, the majority of Elko New Market and Hastings, and portions of Burnsville, Apple Valley, Lakeville, Rosemount and Red Wing. The rest of the land is forest and grassland.<sup>11</sup>

To protect the Vermillion River, in 2008 Empire Wastewater Treatment Plant (WWTP) effluent was permanently diverted from the Vermillion River to the Mississippi River. The redirection of the Empire WWTP effluent dramatically changed the water quality of the river, especially at low flows. Consequently, 2008 is an important break point in the analyses in this memo and we omitted 2002-2007 when investigating monthly concentration and monthly load calculation patterns later in this memo.

Approximately 10% of the Vermillion River watershed is roadways, based on an analysis completed by the Minnesota Pollution Control Agency (MPCA). The MPCA found that watersheds with 18% roadway density or higher are more likely to have chloride concentrations above water quality standards. As a concentration of the concent

Two segments of the Vermillion River, from just west of highway 3 to the confluence with the south branch of the Vermillion River near highway 52 and from just east of highway 52 to the dam at Hastings, are at risk of being impaired for aguatic life use due to excess chloride (Figure 2).

Vermillion River chloride pollution sources likely include livestock excreta, household water softening, synthetic fertilizer, and de-icing salt.

<u>Livestock Excreta:</u> The Vermillion River watershed has 87 registered feedlots with a total of 12,700 animal units (AUs) in the monitored part of the watershed.

Household Water Softening: During parts of the study period there were four domestic wastewater treatment plants in the watershed that discharged to the Vermillion River; currently there are only two: Hampton and Vermillion. In 2008, Vermillion River chloride pollution from household water softening was reduced when the MCES Empire WWTP effluent was diverted to the Mississippi River. In 2011, Elko New Market decommissioned their WWTP, sending wastewater to the MCES Empire WWTP, further decreasing household water softening chloride pollution to the Vermillion River. Some household wastewater in the watershed is also treated by residential subsurface treatment systems. The chloride waste from the water softening process has

the potential to enter surface and groundwater through wastewater treatment plants or residential subsurface sewage treatment systems.<sup>14</sup>

<u>Synthetic Fertilizer:</u> Chloride may come from agricultural and urban application of potash fertilizer. <sup>15</sup> This source of chloride is not well understood in the watershed.

<u>De-icing Salt:</u> De-icing salt is primarily applied between December and March and would likely runoff during melt events from February through April.

## **FINDINGS**

# **Annual Chloride Dynamics 2002-2019**

#### **Chloride Concentration**

MCES and Dakota County Soil and Water Conservation District collected 394 chloride samples between 2002 and 2019. The ambient concentrations are plotted with the annual median concentration (Figure 3). Ambient concentration describes the conditions experienced by aquatic organisms in the river. These values are affected by precipitation, flow, and watershed factors, including those caused by human activity. The timing of the Empire WWTP diversion is shown with a vertical line near the beginning of 2008.

The ambient concentrations and annual median concentrations were trending upward between 2002-2007 before the significant drop in 2008 due to the re-routing of Empire WWTP effluent from the Vermillion River to the Mississippi River. Since 2008, annual median chloride concentrations have been slowly increasing again.

**Ambient concentration:** The mass of chloride divided by the total volume of water in a stream at a specific time. This value represents the instantaneous amount of chloride in the stream water.

Annual Median Concentration: This is the 'typical' concentration observed in the stream during the year. It is the center of our observed data and is not affected by extreme high or low concentrations.

## **Precipitation and Streamflow**

Ambient concentrations are often closely tied to rainfall and resulting flow conditions in the river. Higher streamflow can lower pollutant levels through dilution, and lower streamflow can increase pollutant levels through concentration.

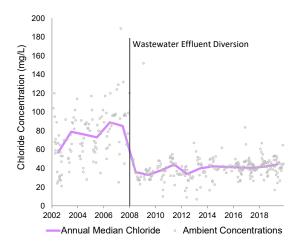


Figure 3: Annual Median and Ambient Chloride Concentrations of the Vermillion River

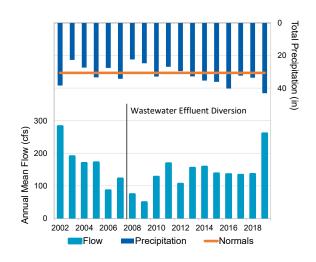


Figure 4: Annual Mean Flow and Precipitation for the Vermillion River

Figure 4 shows annual total precipitation and the 1981-2010 National Weather Service Climate Normal precipitation at Minneapolis-St. Paul airport<sup>16</sup> with Vermillion River annual mean flows. Flow is usually higher in

years with greater rainfall. Annual mean flow in the Vermillion River generally decreased from 2002 through 2009, then increased in 2010 and 2011 and have during the remainder of the assessment period.

There is a slight decrease in annual mean flow after the 2008 Empire WWTP effluent diversion to the Mississippi River.

Annual Mean Flow: The average of all daily flows for the year.

#### Streamflow and Chloride Concentration

Figure 5 shows annual median chloride concentration and annual median flow values, representing typical conditions for each year. There is a general inverse relationship between flow and concentration before the 2008 Empire WWTP effluent diversion. After 2008 chloride has a more direct relationship with flow. However, there is variability in concentration that does not vary perfectly with flow. This means that factors other than flow impact chloride conditions in the river.

In order to see how non-flow factors such as watershed practices may have affected chloride concentrations, we used the R-QWTREND model.

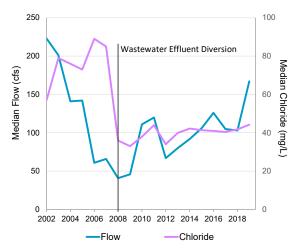


Figure 5: Annual Median Flow and Chloride Concentration in the Vermillion River

#### Chloride Trends

R-QWTREND is a statistical model specifically designed to investigate pollutant trends, which tests potential trends (increase or decrease in concentration) against a no-trend model (no increase or decrease in concentrations). This model removes the variability of annual flow and seasonality from the statistical analysis. If the model does not show a statistically significant trend for a given time period, there is not sufficient evidence to claim that concentrations are increasing or decreasing. If increasing or decreasing concentrations cannot be described, then concentrations are assumed to be stable.

R-QWTREND analysis shows that changes of the flow-adjusted chloride concentration in the Vermillion River can be best represented by a statistically significant three-trend model (p = 0) over the assessment period of 2002 to 2019. (Table 1 and Figure 6). Chloride concentration increased gradually from 2002 to 2008. In March 2008, effluent from the Empire WWTP was diverted from Vermillion River to the Mississippi River, resulting in a 62% decrease in flow-adjusted chloride concentration. From

2009 - 2019, chloride increased, but at a slower pace than before the diversion.

Table 1: Statistical Trend for Chloride Concentration in the Vermillion River

Trend Period	Concentration range (mg/L)	Change in Conc (%)	Change Rate (mg/L/yr)	p	Trend
2002 - 2007	64.9 - 89.1	37%	4.04	0.0046	1
2008	89.1 - 33.4	-62%	-55.7	0	4
2009 - 2019	33.4 - 45.4	36%	1.09	0.0002	1

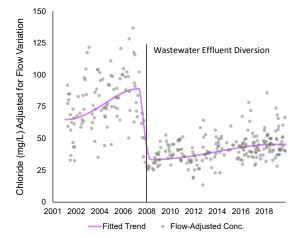


Figure 6: Flow-Adjusted Trends for Chloride Concentration in the Vermillion River

Chloride concentrations were increasing before the effluent diversion, decreased sharply immediately after effluent diversion and have been slowly increasing since the effluent diversion. The persistent increase in chloride indicates that watershed factors are affecting chloride in the river independent of the effects of the Empire WWTP effluent.

Additional data from 2020 and into the future has the potential to impact the significance and the direction of the recent trend period.

**Pollutant trend:** An analysis that shows the direction of change (improving vs. declining water quality) in a pollutant over time. This study examined changes in flow-adjusted chloride concentration from 2002 – 2019, allowing us to look at human-caused influences in chloride concentrations.

**Flow-adjusted concentration:** An adjustment to ambient concentration that removes variability of annual flow and seasonality mathematically, for use in statistical analysis.

## **Chloride Loads**

Figure 7 illustrates annual chloride loads and annual mean flow. The annual loads for chloride decreased significantly in 2008-2009 due to the removal of Empire treated effluent from the river. The magnitude of annual loads after 2009 are much smaller than pre-diversion loads and generally follow the pattern of the annual mean flows.

The increase in chloride loads in years of higher flow could be due to the increased flushing of salt that had built up in watershed lakes and groundwater during drier years, when pollutants are less likely to be mobilized.

# **Seasonal Chloride Dynamics 2008 – 2019**

Seasonal chloride dynamics were investigated only for the period after the Empire WWTP diversion to eliminate the confounding effect of that diversion on seasonal patterns.

# **Chloride Concentration and Streamflow**

Figure 8 shows monthly median chloride concentration and monthly median flow values, representing typical conditions in each month. Seasonal changes can influence monthly median flow and monthly median chloride concentration. Monthly median flow was highest from April through June while median ambient chloride concentration was highest in January and February. There seems to be only a slight relationship between monthly median flow and median ambient chloride concentration over the analysis period.

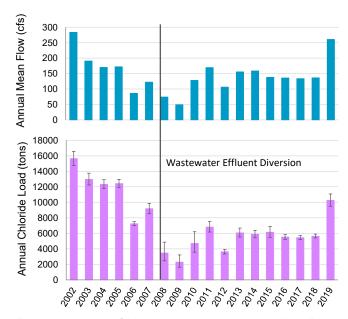


Figure 7: Annual Chloride Loads in the Vermillion River (Error bars = 95% Confidence Interval)

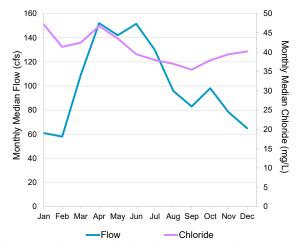


Figure 8: Monthly Median Flow and Median Ambient Chloride Concentrations in the Vermillion River

## **Chloride Load**

Chloride load is seasonally dynamic (Figure 9). The highest chloride load occurs from March through July, with loads gradually decreasing in subsequent months. Chloride loads calculated with Flux32 were compiled as monthly averages for 2008 – 2019. Figure 9 uses a line to indicate maximum and minimum values for each month. The bottom of each box represents the first quartile, the top represents the third quartile, and the line in the middle of the box represents the median monthly chloride load.

From 2008-2019, higher monthly loads occur in the spring and early summer, possibly due to de-icing salt and synthetic fertilizer runoff coupled with the higher flows occurring during that period.

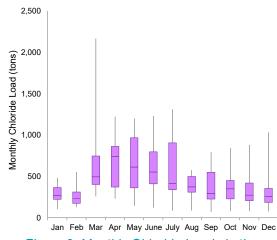


Figure 9: Monthly Chloride Loads in the Vermillion River

# **LIMITATIONS**

The analyses described in this memo identify changes in chloride concentrations in the river, but they do not identify the cause of those changes, other than the abrupt decrease in chloride concentration and load after the 2008 Empire WWTP diversion. MCES has suggested hypotheses about causes of changing chloride dynamics but additional information or research is needed to identify specific changes in watershed management, climactic changes, or any other factors which may have affected concentration in the river.

During some winter months in from 2002 – 2019, hazardous ice conditions precluded sample collection. This data gap possibly biases our understanding of seasonal and annual chloride dynamics. The Flux load calculation method changed in 2016.

# **RECOMMENDATIONS & NEXT STEPS**

Chloride pollution reduction projects and initiatives are most effective when guided by data collection and analysis. In order to support the Vermillion River Joint Powers Organization and partners to prioritize resources to understand chloride dynamics and mitigate chloride pollution, MCES provides the following recommendations:

- Calculate or compile the watershed water and chloride budgets including but not limited to livestock excreta, fertilizer use, household water softening and de-icing salt application.
- Investigate the potential for stormwater runoff to enter shallow groundwater. Groundwater-surface
  water interactions are complex in the watershed with some gaining and some losing reaches. The
  dynamics of groundwater contributions to the monitoring station and the effects on chloride pollution
  timing and concentration are not well understood.
- Pursue a home water softener upgrade incentive program or centralized water softening.
- Monitor upstream chloride and flow to better identify chloride sources to the Vermillion River.
- Update flow and load duration curves from 2014 Comprehensive Water Quality Assessment of Select Metropolitan Area Streams. This analysis calculates the likelihood of a chloride standard exceedance for a particular flow. Load duration curves should be updated for 2008 – 2019, the period after the MCES WWTP effluent diversion.

 Implement chloride mitigation and management BMPs including trainings to minimize de-icing salt use and synthetic fertilizer runoff.

We are aware that not all watershed organizations have the time, capacity, or resources to take these or other future next steps. MCES may have the ability to assist with future data collection, data analysis or other technical advice. Please contact us to discuss the potential of future partnerships if you are interested in continuing this work. Please contact us for additional technical information or information on field, laboratory and data analysis methods. Method documentation is also available as part of the Comprehensive Water Quality Assessment of Select Metropolitan Area Streams report, Introduction and Methodologies section, available on the Council website at <a href="https://metrocouncil.org/streams">https://metrocouncil.org/streams</a>.



<sup>1</sup> Minnesota Pollution Control Agency. Chloride 101. <a href="https://www.pca.state.mn.us/water/chloride-101">https://www.pca.state.mn.us/water/chloride-101</a>>

<sup>3</sup> Minnesota Pollution Control Agency. Chloride 101. <a href="https://www.pca.state.mn.us/water/chloride-101">https://www.pca.state.mn.us/water/chloride-101</a>>

<sup>5</sup> Overbo and Heger, n.d. Estimating annual chloride use in Minnesota. Water Resources Center. <wrc.umn.edu/chloride>

<sup>6</sup> Minnesota Pollution Control Agency. 2001. Effects of Liquid Manure Storage Systems on Groundwater Quality. <a href="https://www.pca.state.mn.us/sites/default/files/rpt-liquidmanurestorage.pdf">https://www.pca.state.mn.us/sites/default/files/rpt-liquidmanurestorage.pdf</a>

<sup>8</sup> Minnesota Pollution Control Agency. Chloride 101. <a href="https://www.pca.state.mn.us/water/chloride-101">https://www.pca.state.mn.us/water/chloride-101</a>>

- <sup>9</sup> Rehm, G. and M. Schmitt. 1997. Potassium for crop production. Minnesota Extension Service. Minneapolis: University of Minnesota.
- <sup>10</sup> Minnesota Pollution Control Agency. <a href="https://www.pca.state.mn.us/water/chloride-101">https://www.pca.state.mn.us/water/chloride-101</a>>
- <sup>11</sup> Metropolitan Council. 2014. Vermillion River. In Comprehensive water quality assessment of select metropolitan area streams. St. Paul: Metropolitan Council.
- <sup>12</sup> Minnesota Pollution Control Agency. 2020. Draft Statewide Chloride Management Plan <a href="https://www.pca.state.mn.us/water/draft-statewide-chloride-management-plan">https://www.pca.state.mn.us/water/draft-statewide-chloride-management-plan</a>
- Minnesota Pollution Control Agency. 2016. Twin Cities Metropolitan Area Chloride Management Plan. <a href="https://www.pca.state.mn.us/sites/default/files/wq-iw11-06ff.pdf">https://www.pca.state.mn.us/sites/default/files/wq-iw11-06ff.pdf</a>
- 14 Minnesota Pollution Control Agency. Chloride 101. <a href="https://www.pca.state.mn.us/water/chloride-101">https://www.pca.state.mn.us/water/chloride-101</a>
- <sup>15</sup> USGS. 2015. Methods for Evaluation Potential Sources of Chloride in Surface Waters and Groundwaters of the Conterminous United States.
- <sup>16</sup> Minnesota Department of Natural Resources. 2020. *Minneapolis/St. Paul Climate Data Normals and Averages.* <a href="https://www.dnr.state.mn.us/climate/twin\_cities/normals.html">https://www.dnr.state.mn.us/climate/twin\_cities/normals.html</a>>

<sup>&</sup>lt;sup>2</sup> Metropolitan Council Environmental Services, 2018. Regional Assessment of River Quality in the Twin Cities Metropolitan Area. <a href="https://metrocouncil.org/Wastewater-Water/Services/Water-Quality-Management/River-Monitoring-Analysis/Regional-Assessment-of-River-Quality-(2).aspx">https://metrocouncil.org/Wastewater-Water/Services/Water-Quality-Management/River-Monitoring-Analysis/Regional-Assessment-of-River-Quality-(2).aspx</a>

<sup>&</sup>lt;sup>4</sup> Minnesota Administrative Rules. *Minnesota Water Quality Standards for Protection of Waters of the State*. Minn. Rules 7050.0218 and Minn. Rules7050.0222. < https://www.revisor.mn.gov/rules/7050/>

Metropolitan Council, 2013. Municipal Water Use in the Seven-County Twin Cities Metro Area. <a href="https://metrocouncil.org/Wastewater-Water/Planning/Water-Supply-Planning.aspx">https://metrocouncil.org/Wastewater-Water/Planning/Water-Supply-Planning.aspx</a>