Characterizing the Forms of Phosphorus in Lake Superior Sediments and Sources

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Phosphorus in Lake Superior

• Phosphorus frequently limits the productivity of primary producers in aquatic environments

• External inputs of total P to Lake Superior (Chapra, 1977; Weiler, 1978; Chapra and Sonzogni, 1979; Lesh et al 1991)
  • Between 100 and 200 x 10^6 mol P per year
  • 20% is supplied by atmosphere
  • 10% municipal and other sources.
  • 70% is supplied by rivers
  • Erosion from shoreline areas - around 11 x 10^6 metric tons per year (Siebel et al. 1976)

Western arm Lake Superior: external inputs of total P (Matthew & McManus (2003):
• St. Louis River
• Nemadji
• Duluth-Superior Harbor
Sediment Characterization

• Characterize the phosphorus-containing geochemical compartments of Lake Superior western arm sediment
  • Better understand the chemical forms of phosphorus
  • Begin to address their lability in the environment
• Not all the P in the sediments is available - depends on geochemical compartment where P is found.
• Sequential chemical reactions performed to distinguish phosphorus in each compartment
Sequential Chemical Reactions

• **(1) NH₄Cl**: Loosely-bound P, or “exchangeable” P
  - Measures porewater-soluble and loosely-sorbed (i.e. CaCO₃-adsorbed) P
  - Important prior to NaOH step, especially in lakes high in carbonates (improves recovery of nonreactive inorganic P in the NaOH extraction)

• **(2) BD**: Iron-bound P, using NaHCO₃-buffered sodium dithionite (Na₂S₂O₄)
  - For P adsorbed to iron-III oxyhydroxides; released under low redox conditions

• **(3) NaOH**: Aluminum-bound P
  - For amorphous Al(OH)₃ that dissolves under high pH conditions from NaOH
  - Includes some iron-III oxyhydroxides not removed in previous step
  - Also pulls out some sediment organic P

• **(4) Persulfate**: Aluminum-bound P + Labile organic P
  - Persulfate (K₂S₂O₈) digestion of NaOH extract
  - Difference between 3 and 4 equals the labile organic P (LOP) fraction

• **(5) HCl**: Mineral-bound P
Graph of TP

- Talk about TP, lead into fractions
- Replace TP graph with fraction graph (animation)

Total Phosphorus in Sediment Samples - Lake Superior

Sediment Sources to Lake

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<td>Duluth Harbor</td>
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- Mineral Bound
- Aluminum Bound + Labile Org
- Aluminum Bound
- Iron Bound
- Loosely Bound
Source Sediment vs. Lake Bottom Sediment

Lake Superior Sediment Sources P-fractionation (%)

- Loosely Bound: 33.89%
- Iron Bound: 5.14%
- Aluminum Bound: 5.76%
- Aluminum Bound + Labile Org: 0.88%
- Mineral Bound: 54.34%

Lake Superior Bottom Sediments P-fractionation (%)

- Loosely Bound: 1.19%
- Iron Bound: 11.36%
- Aluminum Bound: 7.73%
- Aluminum Bound + Labile Org: 29.62%
- Mineral Bound: 50.10%

Sediment station

- Loosely Bound
- Iron Bound
- Aluminum Bound
- Aluminum Bound + Labile Org
- Mineral Bound
## Lake Superior Sediment Sources - P-fractionation (%)

<table>
<thead>
<tr>
<th>Source</th>
<th>Loosely Bound</th>
<th>Iron Bound</th>
<th>Aluminum Bound</th>
<th>Aluminum Bound + Labile Org</th>
<th>Mineral Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loosely Bound</td>
<td>1.19</td>
<td>11.36</td>
<td>7.73</td>
<td>50.10</td>
<td>29.62</td>
</tr>
</tbody>
</table>

## Lake Superior Bottom Sediments - P-fractionation (%)

<table>
<thead>
<tr>
<th>Bottom Sediments</th>
<th>Loosely Bound</th>
<th>Iron Bound</th>
<th>Aluminum Bound</th>
<th>Aluminum Bound + Labile Org</th>
<th>Mineral Bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom Sediments</td>
<td>0.88</td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
Mineral Bound Phosphorus
• Collect more samples to evaluate the spatial variability
  • What effect does depth have on phosphorus content?
Discussion

**Total Phosphorus vs Lake Depth**

- **P Concentration (mg P/mg)**
- **Lake Depth (m)**

The graph shows a positive correlation between lake depth and total phosphorus concentration. As lake depth increases, the concentration of phosphorus also tends to increase. This suggests that factors associated with lake depth, such as water flow or nutrient input, may influence phosphorus levels.

**Microbial/Chemical Release and P Source**

- Higher P Levels
- Lower P Levels

The data points indicate that microbial or chemical release might be affected by phosphorus source. Further analysis could help identify specific mechanisms or factors contributing to these observations.
Conclusions

• Lake Superior sediment contains large fractions of organic and mineral bound phosphorus compared to Loose, and Al/Fe bound
• Phosphorus-containing sediment is being circulated from sources to bottom sediment in the lake
• Fractions are similar between source and bottom sediment
Future Work

• X-ray diffractometry of mineral compounds
• Organic P fractionation (Yuan et al. 2016)
  • Characterize bioavailability of phosphorus

Acknowledgements

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Dr. Edson Bortoluzzi, Laboratory of Land and Natural Resources, University of Passo Fundo, Brasil
Dr. Tales Tiecher, Soil Department, Federal University of Rio Grande do Sul, Brasil
Acknowledgements
Inorganic fixation of added phosphates at various pH values

Source: Brady (1990)
Organic Phosphorus Fractionation (Yuan et al. 2016)

- Organic P is an important source of potentially bioavailable P (McDowell, 2003; Ahlgren et al. 2007).

- Alkaline phosphatase activity (APA) plays a proeminent role in recycling of organic P (Duhamel et al. 2010)

- Organic P species in sediments:
  - Total microbial P
  - Fulvic-associated P
  - Humic-associate P
- Alkaline phosphatase activity (APA) plays a proeminent role in recycling of organic P (Duhamel et al. 2010).

APA- is a hydrolase enzyme responsible for removing phosphatase groups from many types of molecules, including nucleotides, proteins, and alkaloids.
Deposition of existing lacustric sediments began 11,000 years ago.

Major units:
- Upper unit massive dark gray brown clays deposited after ice retreat.
- Lower unit calcareous varved or massive silty clays deposited while the glacier was still within the lake drainage basin.
- Till deposited during the period of glaciation.
Sediment of Lake Superior (Thomas & Dell (1978))

Glaciolacustrine sediment minerology (Dell 1973):

- Clay minerals (mostly Illite)
- Quartz
- Feldspars
- Calcite and Dolomite (the Lake is surrounded by noncalcareous Precambrian igneous and sedimentary rocks).
- Calcite and Dolomite are origineted from the tills surrounding the lake (derived from Palaeozoic rocks)
Sediment of Lake Superior (Thomas & Dell (1978))

Postglacial sediment (Dell 1973):

• Are non calcareous.
Sediment of Lake Superior (Thomas & Dell (1978))

Sediment composition (Dell 1973):

Mineralogy of clay particles of late-glacial and postglacial sediments:
- Quartz 3-28%, Plagioclase feldspar 4-12%, potash feldspar 3-9%, calcite 0-26% and dolomite 0-15%.

Clay minerals:
- Illite (2:1) 10-41%, Chlorite 2-31%, Kaolinite 1-11%, Vermiculite 0-17% and mixed -layer 7-29%.

* Calcite and Dolomite occurred in the late glacial sediment but were essentially absent in postglacial sequence.
Sediment of Lake Superior (Thomas & Dell (1978))

Sediment organic carbon:
- Range from 0.01-3.85%
- Mean value is 1.70%

Sediment inorganic carbon:
- Mean value is 0.01%

Hakansson (1986)
- There is not net sedimentation of organic matter because the easily resuspendable matter is constantly stirred and decomposed in water phase or transported to more tranquil areas where sedimentation occurs.
External inputs of total P to Lake Superior (Chapra, 1977; Weiler, 1978; Chapra and Sonzogni, 1979; Lesh et al 1991)

- Between 100 and 200 x 10^6 mol P yr^-1
- 70% is supplied by rivers
- 20% is supplied by atmosphere
- 10% municipal and other sources.
Estimating Groundwater Recharge to Buried-Valley Aquifers Underlying the Des Moines and Superior Lobes in Minnesota

Alyssa Witt¹,², William Simpkins², Jared Trost¹, Melinda Erickson¹, Andrew Berg¹, James Stark¹, Robert Tipping³, and Alan Wanamaker²

U.S. Geological Survey, Minnesota WSC¹
Dept. of Geological and Atmos. Sciences, Iowa State University²
Minnesota Geological Survey³
Project

- **Hydrologic Properties of Glacial Confining Units, Minnesota**
  - Administered by the U.S. Geological Survey (Minnesota WSC)
  - Funding provided by the Environment and Natural Resources Trust Fund with USGS Cooperative Matching Funds
Motivation

Glacial Outwash

Till

? Municipalities and Irrigation

Buried-Valley Aquifer

Bedrock
Objective

- Evaluate sustainability of buried-valley aquifers:
  - Estimate aquifer recharge using Darcy’s Law \( Q = -KIA \)
  - Estimate vertical groundwater velocities through the aquitard using hydraulic and geochemical data
Collaborators

• Minnesota Department of Health
• Minnesota Department of Natural Resources
• Minnesota Geological Survey
• Litchfield & Cromwell-Wright High Schools
Glacial lobes and sublobes of Wisconsinan age

Focus of Study
- Cromwell
  Superior lobe
- Litchfield
  Des Moines lobe

(map from Jennings and Johnson, 2011)
Study sites

Cromwell, MN
- Population: 231
- 2 municipal wells
- Pumpage: 6 MGY

Litchfield, MN
- Population: 6,688
- 4 municipal wells
- Pumpage: 340 MGY

MGY = Millions of Gallons per Year
Aquitard
Municipal Well
Continuous core - HSA
1.25-inch wells with transducers
1000 ft.
Mud Rotary
2-in well
3-ft screen
2-in well
Continuous core - HSA
2-in well
Mud Rotary
10-ft screen
1000 ft.
Litchfield Sites: LFO1 and LFO2

LFO1
5 Wells
Max. Depth: 127 ft

LFO2
6 Wells
Max. Depth: 163 ft

- Municipal Wells
Cromwell Sites: CWO1 and CWO2

CWO1
3 Wells
Max. Depth: 340 ft

CWO2
5 Wells
Max. Depth: 130 ft

- Municipal Wells
Litchfield Site - New Ulm Till, Villard Mbr.

49% sand, 33% silt, 18% clay
LFO2 Site

Geology

Depth (ft)

Hydraulic Head (ft) Log K (ms⁻¹)

Geom. Mean: 7.3E-10 ms⁻¹
LFO1

Geology

New Ulm Fm. Deltaic
Till Aquitard
New Ulm Fm.
Villard Mbr.
Buried Valley Aquifer

Hydraulic Head (ft) Log K (ms⁻¹)

0 30 60 90 120

Depth (ft)

1050 1100

-12 -8 -4

Geom. Mean: 2.5E-7 ms⁻¹
Recharge Pathways: Litchfield

Glacial Outwash

Till

Recharge/Age Estimates

LFO1
>30 in/yr
2 Years

LFO2
0.36 in/yr
950 Years

Buried-Valley Aquifer

?
Cromwell Site – Cromwell Formation Till

57% sand, 31% silt, 12% clay
Recharge Pathways: Cromwell Sites

Glacial Outwash

Till

Buried-Valley Aquifer

Slate

Recharge/Age Estimate

11 in/yr
35 Years
Indicators of Groundwater Age

- Anions: evidence of recent water
  - Cl
  - NO$_3$-N
  - Cl/Br Ratio

- $\delta^{18}$O and $\delta^2$H as evidence of glacial-age pore water

- Tritium
LFO1 Site

Geology

0
30
60
90
120
Depth (ft)

New Ulm Fm. Deltaic
Till Aquitard
New Ulm Fm.
Villard Mbr.
Buried Valley Aquifer

Tritium (TU)
0 5 10 15 20
Conclusions

• Litchfield Sites
  – Downward gradient; aquifer recharged from surface
  – Point estimates for recharge range from 0.36 to > 30 in/yr

• Cromwell Sites
  – Upward gradient; aquifer is not recharged from surface
  – More research needed to determine recharge source
Future Work

• Phase I: Modeling (MODFLOW)

• Phase II: Site selection (Wadena lobe till and Des Moines lobe till)

• Phase I & II Report (2019)
Questions?
Figure 6. Potentiometric surface of the bedrock aquifers. Contour interval 40 feet. Supplementary contours with contour interval 20 feet shown in some areas.
Cromwell Cross Sections: Map View
Litchfield: Potential Recharge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LFO2</th>
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<tbody>
<tr>
<td>Till Thickness (x) m</td>
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<tr>
<td>Effective Porosity ($n_e$)</td>
<td>0.25</td>
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<tr>
<td>Hydraulic Conductivity (K) m/s</td>
<td>7.3E-10</td>
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<tr>
<td>Hydraulic Gradient (I)</td>
<td>0.40</td>
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<tr>
<td>Area (A) Km²</td>
<td>20</td>
</tr>
<tr>
<td>Groundwater Age (years)</td>
<td>953</td>
</tr>
<tr>
<td>Recharge (MGY)/(in/yr)</td>
<td>0.49/0.36</td>
</tr>
</tbody>
</table>

\[
\text{Age} = \frac{n_e x}{K I}
\]

\[
\text{Recharge} = -K I A
\]
Litchfield: Potential Recharge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LFO1</th>
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<tr>
<td>Effective Porosity ($n_e$)</td>
<td>0.25</td>
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<tr>
<td>Hydraulic Conductivity (K) m/s</td>
<td>2.5E-7</td>
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<tr>
<td>Hydraulic Gradient (I)</td>
<td>0.29</td>
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<tr>
<td>Area (A) Km²</td>
<td>20</td>
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<td>Groundwater Age (years)</td>
<td>2</td>
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<td>Recharge (MGY)/(in/yr)</td>
<td>122/91</td>
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\[
Age = \frac{n_e x}{K I}
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\[
Recharge = -KIA
\]
### Cromwell Till: Potential Recharge

<table>
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<th>Parameter</th>
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<td>Effective Porosity ((n_e))</td>
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<td>Hydraulic Conductivity ((K)) m/s</td>
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<td>Hydraulic Gradient ((I))</td>
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<td>Area ((A)) Km²</td>
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<tr>
<td>Groundwater Age ((\text{years}))</td>
<td>35</td>
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<tr>
<td>Recharge ((\text{MGY})/(\text{in/yr}))</td>
<td>-3.7/-11</td>
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\[
\text{Age} = \frac{n_e x}{K I}
\]

\[
\text{Recharge} = -KI A
\]
Characterizing Groundwater and Surface-Water Interactions in Selected Northeast Twin Cities Lakes

Chapter A: Statistical Analysis and Field Study

Perry M. Jones, Jared J. Trost, Aliesha Diekoff, Daniel Morel, and Melinda L. Erickson
Background: 2013 Minnesota Legislation
Chapter 137, Article 2, Section 9(b)

“...with the United States Geological Survey to investigate groundwater and surface-water interaction in and around White Bear Lake and surrounding northeast metropolitan lakes, including seepage rate determinations, water quality of groundwater and surface water, isotope analyses, lake level analyses, water balance determination, and creation of a calibrated groundwater-flow model, including a comparison of water levels with lakes bordering the study area. The council shall use the results to prepare guidance for other areas to use in addressing groundwater and surface water interaction issues. “
Statistical Analysis of Lake Levels - Objectives

Short-term (1999-2014) analysis
- Assess lake-level fluctuations across region
- Determine if climatic, landscape, or geologic characteristics (40 variables) can explain lake-level variations

Long-term (1925-2014) analysis
Evaluate temporal relations between precipitation and lake levels
Statistical Lake-Level Analysis

Short-term
96 lakes

Long-term
14 lakes

Selected based on lake-level data
Lake-level variability – based on lake type

Closed-basin Lake
no active surface-water outlet

Turtle Lake

Flow-through Lake
active surface-water outlet

Pleasant Lake

Change in annual mean lake level from 2002 to 2010, in feet

Outflow
Lake levels more stable in urbanized areas

- most urban lakes are flow-through
- most rural lakes are closed-basin

EXPLANATION
- Closed basin lake
- Flow-through lake
Closed-basin lake levels declined more at higher elevations similar to groundwater levels.
Geologic Characteristics vs. Lake-level Change (2002-2010)

Primary Geologic Unit

<table>
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<tr>
<th>Change in annual mean lake level from 2002 to 2010, in feet</th>
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<tbody>
<tr>
<td>Des Moines Lobe</td>
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<tr>
<td>51</td>
</tr>
</tbody>
</table>

Buried Bedrock Valley Under Lake

<table>
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<tr>
<th>Change in annual mean lake level from 2002 to 2010, in feet</th>
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</thead>
<tbody>
<tr>
<td>No</td>
</tr>
<tr>
<td>44</td>
</tr>
</tbody>
</table>
Closed-basin lakes – water levels more variable at high elevations, in Superior Lobe deposits.
Long-term analysis (1925-2014)
White Bear Lake – most variable level

![Graph showing annual lake-level anomalies and precipitation]

- Range in annual lake-level anomalies - 14 lakes
- White Bear Lake
- Valentine Lake
- Precip, 5-yr moving average

Annual lake-level anomaly = mean annual lake level – long-term mean
Statistical Analyses of Lake Levels - Results

Lake type (flow-through/closed-basin), elevation, development, and glacial geology were variables affecting lake-level variability.
Field Assessment of Groundwater and Surface-Water Interactions

Water-quality Analyses – Stable Isotope/Age-dating

Continuous Seismic-Reflection (6 lakes)

White Bear Lake – Shallow and Deep waters

1) Lake-sediment Coring
2) Water Levels – Deep-water Piezometers
3) Seepage-Flux Measurements
Surface-water contribution – Stable Isotopes

Sampled 40 wells
October 2014

Prairie du Chien Group / Jordan Sandstone (PDCJ)

Percentage of Contribution

Groundwater
Surface water

General Groundwater Flow Direction (PDCJ)

White Bear Lake
White Bear Lake – Lake Sediment

No trapped gases

Clays, silts, sands

Trapped gases

Organic Sediments

Trapped Gases

Organic Sediments

P1

P2
Continuous Seismic-Reflection

White Bear Lake

Turtle Lake

Seismic-Reflection Profile Pathlines
- ● Gas-filled sediments
- ○ Low gas sediments in shallow waters
- ○ Low gas sediments in deeper waters

USGS
White Bear Lake – Deepwater Piezometer Nests

**Ice in/out**

1-inch, schedule 40, PVC pipe
1-inch, schedule 40, PVC coupling
1-inch, PVC hose about 2.9 feet long
1-inch galvanized steel coupling
1-inch galvanized steel pipe

**Ice formation/thaw**

2-inch PVC pipe to keep hose straight
Buoy
Lake surface

Lake/ice surface

Well cap
Buoy

Organic-rich sediment
Clay

Sand and gravel

about 6-foot distance between piezometers
3-foot, 10-slot (0.01 inch), wrapped, stainless steel screen

Photo of a deepwater piezometer nest in White Bear Lake.
White Bear Lake – Lake and Piezometer Water Levels, 2014

**Nest P1**

**EXPLANATION**
- White Bear Lake water level elevation
- P1-8.5 water level elevation
- P1-16.5 water level elevation
- P1-19.5 water level elevation

**Nest P3**

**EXPLANATION**
- White Bear Lake water level elevation
- P3-9 water level elevation
- P3-13.5 water level elevation
- P3-18.5 water level elevation
Seepage-Flux Measurements – 2014

Deep water (P1-P4) (March)
lake water outflow
0.04 – 1.0 in/day

Nearshore (August)
groundwater inflow
0.1 - 11.3 in/day

Seepage Flux – in/day
- 0.1 – 0.4
- 0.5 – 1.4
- 1.4 – 5.6
- 5.6 – 11.3
Field Assessment - Results

Stable isotope ratios
- a mixture of surface water and groundwater is reaching Prairie du Chein aquifer in part of NE TMCA

Interactions in White Bear Lake
- Nearshore: Groundwater flows into lake
- Deepwater: Lake water flows into sediments
- Seepage flow rates: Nearshore > Deepwater
Prepared in cooperation with the Metropolitan Council and Minnesota Department of Health


Chapter A of Water Levels and Groundwater and Surface-Water Exchanges in Lakes of the Northeast Twin Cities Metropolitan Area, Minnesota, 2002 through 2015

Available online

http://dx.doi.org/10.3133/sir20165139
Characterizing Groundwater and Surface-Water Interactions in Selected Northeast Twin Cities Lakes

Chapter B: Groundwater-Flow Simulation

Jason L. Roth, Perry M. Jones, Catherine Christenson, Jared J. Trost, Aliesha Diekoff, and Melinda L. Erickson
NE Metro Lakes (NEML) Groundwater-flow Model

Develop groundwater-flow model (tool) to assess

- Groundwater and surface-water interactions in lakes
- Effects of groundwater withdrawals on lake levels

Run eight steady-state MODFLOW model scenarios

- 2003-2013 Average
- Potential future pumping (± 30% pumping)
- Average over five 3-year periods within 2003-13
Presentation Outline

Brief description of MODFLOW model

- Design, extent, and construction
- Calibration data and process
- Simulated scenarios
- Status

Will not present model results – calibration, sensitivity, simulations, and scenarios
Groundwater-flow Model Design

Based on Metro Model 3 (MM3)

- Bedrock Elevations
- Zonation of Bedrock Hydraulic Conductivity
- Edge Boundary Conditions

New configurations/packages

- Discretization
- Quaternary layering
- Updated Recharge
- Lake Package: 8 lakes
- Refined RIV Package: rivers, other lakes, and streams
NEML Model Extents

East - MM3 boundary

North - DNR Level 8 watersheds

West/South - DNR Level 8 watersheds or 5 km perpendicular to river

Encompasses most of North/East Metro GWMA

USGS
NEML Discretization
Based on lake-aquifer interfaces
Horizontal

Uniform 125-meter (m) grid vs. 500-m (MM3)

Vertical Elevations of Layers – 12 layers

Top layer of MM3 - 4 layers
First two layers – 1-3 m thick
Third layer – 1-6 m thick, 1 m thick below deep lakes
Fourth layer bottom – top layer 2 in MM3
Lower layers are MM3 elevations
NEML General Cross-section - Model Layering

Mt Simon
Eau Claire
Wonewoc
Tunnel City
Jordan
St. Lawrence
Prairie du Chein
St. Peter
Quaternary

Quaternary
St. Peter
Prairie du Chein
Jordan
St. Lawrence
Tunnel City
Wonewoc
Eau Claire
Mt Simon
General Schematic – Upper Model Layering

Example of Layering Near Lakes
Quaternary Hydraulic Property Refinement/Zonation

- Minnesota only, using Minnesota Geological Survey data
- Tipping (2012) K-class (textural type)
- Fill-in gaps using Meyer 2007 glacial coverages
UZF Package - Recharge

Soil Water Balance Model

Calibration - monthly runoff (3 watersheds) annual baseflow (1 watersheds)

Output – Monthly recharge (domain), runoff (8 lakes)

Input into NEML Model – 2003-2013 mean recharge values
Lake Package

Used in model for representing 8 lakes

Simulates water balances for lakes

Lake Criteria
Max lake depth > 25 feet
Surface Area > 75 acres
More than 3 miles from model boundary
No major inlets/outlets
Lake-level data in at least 50 percent of months during 2003-2013
Riv Package

Major rivers, streams, and lakes not simulated by Lake Package

Lakes - area greater than 4 model cells

19,088 model cells

Simulated constant head for each cell
Pumping Wells

Modelled with WEL and MNW2 packages

High capacity wells from MDNR Source Water database

900 wells

New wells added since MM3 was produced
Model Calibration - GW Model

Calibration Targets

Sources - USGS, BCWD, RCWD, VCWD, MNDNR
Groundwater levels - 3,733 observation wells
Streamflow - 5 stream gages
Lake Levels – MNDNR – 8 lakes (Lake Package)

PEST – Parameter estimation tool

Observation groups (weighted differently)
- Groundwater levels – 30% initial contribution
- River baseflow – 30% initial contribution
- Lake level – 40% initial contribution
Observation Wells

Well locations with water levels for model calibration

MDNR obwells, USGS/MDNR synoptic studies, other wells (CWI)

3,733 wells
Stream gages

Total Flows over 2003 – 2013

Five stream gages
Steady-state 2003-2013 and Pumping Scenarios

Objective: Assess the impacts of pumping on lake levels and budgets

Three simulations:
- Average 2003 - 2013
- $\pm 30\%$ pumping from existing 900 high-capacity pumping wells in NEML model

Assess change in simulated potentiometric surfaces, lake levels, and lake budgets
Three-year Steady-state Scenarios

Water Level and Precipitation Data from Minnesota Dept. of Natural Resources

White Bear Lake

- 97”
- 95”
- 80”
- 101”
- 100”

Water Level (feet, Ramsey County 1912)

3-year periods scenarios

(Total precipitation over 3-year periods)
Model Status

Steady-state model calibrated for average 2003-2013

Average 2003-2013 simulation completed

Running ± 30% current pumping and 3-year scenarios

Report to be published by January 31, 2017
Questions?
Water Budget Changes from Wetland and Prairie Restoration, Glacial Ridge National Wildlife Refuge, Northwestern Minnesota, 2006–13

Tim Cowdery
Water-Resources Discipline
Mounds View, Minnesota
• Describe the Glacial Ridge project and area
  – What happened at Glacial Ridge
  – What did we study
• Describe how we conceptualized and measured components of the water budget
• Show how flows change as a result of the restoration
• Discuss the implications of those changes
USGS Glacial Ridge Study

• Describe changes in hydrology caused by prairie and wetland restorations
  – Water quantity and quality
  – GW and SW
  – Pre- & post-restoration, annually, seasonally
• Investigate landscape characteristics important to changes (hydrologic benefits)
• Map characteristics to identify areas most likely to produce benefits from restorations
Looking North

Surficial Aquifers

Clayey Till

Buried Aquifer

Restoration Benefits at Glacial Ridge

USGS Project 860797L00
Land-use Changes

• 13% increase in Prairie area (73% change)
  o -7% decrease in Row Crops (-40% change)
  o -3% decrease Small Grains (-39% change)

• 5% increase in Wetland area (53% change)
  o -7% decrease in tame grass (hay, pasture, -24% change)

• 166 km county and private ditches abandoned
Glacial Ridge Restorations

- Restored Wetlands
- Restored Prairies
- Study Area
- Glacial Ridge NWR
- Mass-Balance Basins
- Abandoned Ditches

USGS Project 860797L00
Mass-Balance Measurements

• 15-minute Streamflow at 6 Ditches
  – Total stream outflow
  – Baseflow (GW discharge to ditches)

• Hourly Hydrographs and Precip. at 8 Surf.-Aq. Wells
  – 1 well affected by irrigation, 1 outside SW basins
  – Areal recharge
  – Evapotranspiration

• Synoptic WL Runs (~100 sites, 1–6 per year)
  – Change in GW storage
Net mass balances

- 168 km² (41,561 acres, 31% of the study area)
- Net SW error = total precip. + GW discharge – GW recharge – SW ET – ditch outflow
- Net GW error = GW recharge – GW discharge to ditches – GW ET – Δ storage
Restoration Benefits at Glacial Ridge

Pre-Restoration Average Annual Water Budgets

- Precipitation: 95.2 Mm³, 100%
- SW ET: 56%
- GW recharge: 31%
- Runoff: 13%

Error
SW: 0.8%
Pre-Restoration Average Annual Water Budgets

- Precipitation: 95.2 Mm³, 100%
- Total Evapotranspiration: 79.3 Mm³, 83%
- SW ET: 56%
- GW recharge: 31%
- Runoff: 13%
- GW Discharge to Streams: 14%
- GW ET: 86%
- Δ GW storage: -2.4%

Error:
- SW: 0.8%
- GW: 0.4%
Pre-Restoration Average Annual Water Budgets

- **Precipitation**: 95.2 Mm³, 100%
- **Total Evapotranspiration**: 79.3 Mm³, 83%
- **GW ET**: 86%
- **GW recharge**: 31%
- **Runoff**: 13%
- **Δ GW storage**: -2.4%
- **Error**: SW: 0.8%, GW: 0.4%
- **Total streamflow**: 17.1 Mm³, 18%
- **28.9 Mm³**
Effects of restorations

- 4% more water leaves basins through ET at the expense of ditchflow.
- Ditchflow decreases 23%, runoff 32%.
- Flow through the GW system increased 4% (14% change)
- Peaks are trimmed off of ditchflow, recessions increased.
- Wetland and prairie habitat increased 53% and 73% respectively.
Benefits of restoration for Western Minnesota

- Less downstream flooding
- Lower flood peaks
- More wetland habitat
- Wet habitats last longer
- More prairie habitat
- Greatly improved water quality
Restoration Benefits at Glacial Ridge

USGS Project 860797L00
Summary

- SW and GW form one hydrologic system
- Flow is very shallow
- Ditches short-circuit natural flow
- Most water leaves through ET
- System is interconnected and resilient
- GW buffers rainfall variability for SW
- More will leave through ET after restoration
Water Year 2003 (239 mm)

Total precipitation: 65.6 Mm³ (61% of 2005)

Direct runoff to ditches: 3.8 Mm³ (6%)

Unmeasured losses (eventually leaves basin through ET)

Areal GW recharge: 26.6 Mm³ (41%)

GW discharge to ditches: 5.8 Mm³ (61% of total outflow)

△ GW storage: -9.7 Mm³ (36% of areal recharge)

Unmeasured losses:
SW: runoff to closed basins, aquifer recharge from ditches, ET from ditches
GW: discharge to closed basins, ET from water table
Water Year 2004 (373 mm)

- Total precipitation: 100.8 Mm³ (94% of 2005)
- Direct runoff to ditches: 7.5 Mm³ (7%)
- Total ditch outflow: 13.4 Mm³
- Areal GW recharge: 34.4 Mm³ (34%)
- GW discharge to ditches: 5.9 Mm³ (44% of total outflow)
- Δ GW storage: 10.4 Mm³ (30% of areal recharge)

Unmeasured losses:
- SW: runoff to closed basins, aquifer recharge from ditches, ET from ditches
- GW: discharge to closed basins, ET from water table
Water Year 2005 (373 mm)

Total precipitation: 107.8 Mm³ (100% of 2005)

Direct runoff to ditches: 10.4 Mm³ (10%)

Total ditch outflow: 26.8 Mm³

Areal GW recharge: 40.0 Mm³ (37%)

GW discharge to ditches: 16.4 Mm³ (61% of total outflow)

Δ GW storage: -1.7 Mm³ (4% of areal recharge)

Unmeasured losses: SW: runoff to closed basins, aquifer recharge from ditches, ET from ditches
GW: discharge to closed basins, ET from water table
Reduce, reuse, and recharge to retain local control

Steve Woods
1970s - needed data
1990s - needed knowledge
2010s - need action
What do we do?

- Policy
  (i) groundwater
  (ii) runoff from ag & urban
- Community Engagement to act
Take steps to have a long-term supply that protects property values and attracts businesses without DNR and Met Council tossing curveballs.
We got curious about local governments and spoke with a lot of them via surveys and workshops with MDH and DNR...
Q: If they’re so good... why do needs assessments and reports?
A: they are not all equal

- best in state
- top 10%
- big influencer
- average (for region)
- meets legal minimums
- never charged
- never convicted
So this is how I tell the story to local officials.
Groundwater supplies in some areas...
Groundwater!
A Netflix Original Series
Our 2016 report
Annual Reported Groundwater Use

Years: 1988 to 2012

Billions of Gallons:
- 0
- 50
- 100
- 150
- 200
- 250
- 300
- 350

Graph shows a trend of increasing groundwater use over the years.
APPENDIX C  Groundwater cooperation in Twin Cities Metro Area

Communities are participating in sub-regional workgroups in the Twin Cities Metro Area.
Groundwater levels near Lake Minnetonka communities show a six-decade decline. Long-term continual decline is not sustainable.
Groundwater levels near the City of Shoreview show a long-term increase as recharge is greater than use.
We gave recommendations for reducing locally, allowing reuse where sensible, and enhancing recharge.
Goals: safe and reliable

and under local control
Governments get things done by:

- Regulation
- Incentives
- Projects
- Education
- Taff: ▲ rule, price, ownership, mind
Ask your staff:

Can you show me the long-term trend in our groundwater level?
Ask your staff:

Does our water rate cover the basics **plus** increased coordination, efficiency programs, loss reduction, & meter upgrades?
<table>
<thead>
<tr>
<th>Service</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property tax (co and city)</td>
<td>$4,890</td>
</tr>
<tr>
<td>Cell phone (2-lines)</td>
<td>2,470</td>
</tr>
<tr>
<td>Homeowner insurance</td>
<td>1,320</td>
</tr>
<tr>
<td>Electricity</td>
<td>880</td>
</tr>
<tr>
<td>Natural gas</td>
<td>820</td>
</tr>
<tr>
<td>Internet</td>
<td>710</td>
</tr>
<tr>
<td>Landline/long distance</td>
<td>620</td>
</tr>
<tr>
<td>Garbage/recycle bins</td>
<td>330</td>
</tr>
<tr>
<td>Sanitary sewer</td>
<td>280</td>
</tr>
<tr>
<td>Basic cable</td>
<td>270</td>
</tr>
<tr>
<td>Water</td>
<td>130</td>
</tr>
<tr>
<td>City stormwater fee</td>
<td>90</td>
</tr>
<tr>
<td>Composting bin</td>
<td>85</td>
</tr>
<tr>
<td>Street lighting fee</td>
<td>40</td>
</tr>
</tbody>
</table>
Ask your staff:

Will the rates yield enough once the efficiencies kick in and we sell less water?
The point isn’t to “collect money,”

it’s to take steps to have a long-term supply that protects property values and attracts businesses without DNR and Met Council tossing curveballs.
Support an organization you trust
freshwater.org
Diagram shows approximate proportions of water use in Minnesota. This report focuses on public systems that are the largest user of groundwater. A negligibly small portion of water used returns to groundwater. Values may not add up due to rounding errors. All values are millions of gallons. SOURCES: MN DNR, MDH, US EPA, AWWA.
The Constitutional Amendment

33% Habitat
33% Water
14.25% Parks
19.75% Arts & Culture
Diamond on: people accepting change

- Compatible with current ways
- Fiscal neutral or better
- Visible
- Prestige
The Water Underground
Reframing the local groundwater picture
Monitoring wells in the Bonanza Valley Groundwater Management Area show increasingly large drops in groundwater levels during peak irrigation times. Water levels rebound each winter and spring, but the blue line shows how the drops are worsening as more irrigation wells are added. The dashed line represents what the DNR considers a “warning track.” Crossing it indicates that action is needed soon to reduce use.
2015 Reconnaissance Study of Pesticide Compounds in Community Public Water Supply Wells

Heather Johnson
heather.johnson@state.mn.us
Hydrologist 3

October 18, 2016
Minnesota Water Resources Conference
• Joint project between the Minnesota Department of Agriculture and the Minnesota Department of Health
• Reconnaissance study of Community Public Water Systems (CPWS) 108 wells
• Building off of similar project from 2010
• MDA work funded primarily by pesticide fees and Clean Water Land and Legacy funds
Background

2015 Well Locations
Sample Collection

• Sampling occurred in February and March 2015
• Samples collected by MDH Drinking Water Protection Field engineers
• Water drawn from untreated groundwater pumped from wells through a sample tap
• MDA Laboratory Services performed analysis for pesticides
  – GC-MS/MS
  – LC-MS/MS

• 135 different pesticide and degradates
• All quantified to the nanograms per liter (ng/L)
2015 Pesticide Results

- 19 (out of 135) different pesticide compounds detected
- 72 samples out of 108 locations had at least one pesticide detected (67%)
- Metolachlor ESA most frequently detected (63% of the wells)
- No pesticides measured above applicable drinking water guidance values or standards
Pesticides detected by chemical and chemical type

Herbicide
Herbicide Degradate
Fungicide

Number of Detections

Pesticides

N = 108
75% of sampled wells had three or fewer pesticide compounds detected.

1 well had 9 pesticide and degradeate compounds.

1 well had 10 pesticide and degradeate compounds.
## Findings

<table>
<thead>
<tr>
<th>Groundwater</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetochlor (Harness, Confidence)</td>
</tr>
<tr>
<td>Alachlor (Lasso, Intrro)</td>
</tr>
<tr>
<td>Atrazine (Aatrex,Brawl II)</td>
</tr>
<tr>
<td>Metolachlor (Dual, Magnum)</td>
</tr>
<tr>
<td>Metribuzin (Sencor, Axiom)</td>
</tr>
</tbody>
</table>

Five “commonly detected”, Rarely exceeds health standards
Findings

No parent compound detected

2015 Acetochlor Detections

Estimated Acetochlor Pounds A.I. Sold '96-'15
Findings

No parent compound detected

2015 Alachlor detections
Findings

- **Parent compound found most frequently in this Study (7 times)**
- **4 out of 7 detections were found in southeast MN**
Findings

- **Parent compound detected once**
- **Metolachlor degradates were detected the most often out of the 135 tested**
- **Metolachlor degradates were detected mainly in the southern two thirds of MN**
Findings

- Only one detection from four types of metribuzin was detected
- Metribuzin DADK was detected in the central part of MN
2010 and 2015 Well Locations
2010 and 2015 Pesticide Results

• 2010 Sampling Reconnaissance
  – 83 wells sampled
  – 90 different pesticides and degradates
• 80 of the original locations were sampled again in 2015
• Compared to lowest applicable reference value, no pesticide concentrations were above that value
## Findings – Comparisons between 2010 and 2015

<table>
<thead>
<tr>
<th>Pesticide Analyte</th>
<th>2010 Detection Frequency (n=80)</th>
<th>2015 Detection Frequency (n=80)</th>
<th>2010 Median (ng/L)</th>
<th>2015 Median (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetochlor ESA</td>
<td>19%</td>
<td>21%</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Alachlor ESA</td>
<td>56%</td>
<td>49%</td>
<td>53.5</td>
<td>nd</td>
</tr>
<tr>
<td>Alachlor OXA</td>
<td>10%</td>
<td>13%</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Bentazon</td>
<td>15%</td>
<td>8%</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Metolachlor ESA</td>
<td>70%</td>
<td>70%</td>
<td>65</td>
<td>65.1</td>
</tr>
<tr>
<td>Metolachlor OXA</td>
<td>38%</td>
<td>38%</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

n = 80
Findings

Nitrate and Pesticide Co-Occurrence

Ranges of Nitrate Concentrations (mg/L)
- Black: Not Detected
- Light Pink: ≥0.40 - <3.00
- Red: ≥3.00

Detection Probability

Year
- 2010
- 2015

The chart illustrates the detection probability of pesticide in samples from 2010 and 2015, categorized by nitrate concentrations.
• Pesticides were detected at low levels in 72 out of 108 samples.

• A total of 19 (out of 135 possible) different pesticides and/or pesticide degradates were detected in the 2015 study.

• All detections were well below the MDH or EPA established standards or established health reference values.

• Metolachlor ESA was the most frequently detected compound and was found in 63 percent of the sample wells.
No neonicotinoid pesticides were detected in the sample wells.

80 wells that were sampled both in 2010 and 2015 were compared and overall detection frequency was similar.

– Only alachlor and bentazon showed a greater than five percent decrease in detection frequency between 2010 and 2015.
Summary

- Full report will be available soon on MDA’s and MDH’s website
- Contact heather.johnson@state.mn.us for a copy

Report Acknowledgements

David Rindal, Anna Schliep, Todd Johnson, MDH
Brennon Schaefer and Dylan Timm, MDA
Community Public Water Systems
MDH field engineers
MDA Laboratory Services
MDH Public Health Laboratory
Extra slides
Pesticide Monitoring Regions (PMRs)

- Monitoring and data analysis completed for 10 Pesticide Monitoring Regions (PMRs)
2015 Median Combined Metolachlor and Degradate Concentrations, MDA Groundwater Monitoring Wells and Community Public Water Supply Wells

Numbers above the bars are number of samples collected.
### Findings

<table>
<thead>
<tr>
<th>Pesticide compounds detected in greater than 10% of samples</th>
<th>2015 Detection and Frequency (n=108)</th>
<th>2015 Median (ng/L)</th>
<th>2015 Maximum (ng/L)</th>
<th>Reference Value (ng/L)</th>
<th>Value Type</th>
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</thead>
<tbody>
<tr>
<td>Acetochlor ESA</td>
<td>21 (19%)</td>
<td>nd</td>
<td>1,460</td>
<td>300,000</td>
<td>HRL&lt;sub&gt;11&lt;/sub&gt;</td>
</tr>
<tr>
<td>Alachlor ESA</td>
<td>49 (45%)</td>
<td>nd</td>
<td>3,130</td>
<td>60,000</td>
<td>RAA&lt;sub&gt;15&lt;/sub&gt;</td>
</tr>
<tr>
<td>Alachlor OXA</td>
<td>12 (11%)</td>
<td>nd</td>
<td>111</td>
<td>60,000</td>
<td>RAA&lt;sub&gt;15&lt;/sub&gt;</td>
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<tr>
<td>Metolachlor ESA</td>
<td>68 (63%)</td>
<td>27.3</td>
<td>3,690</td>
<td>800,000</td>
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<tr>
<td>Metolachlor OXA</td>
<td>36 (33%)</td>
<td>nd</td>
<td>996</td>
<td>800,000</td>
<td>HRL&lt;sub&gt;11&lt;/sub&gt;</td>
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</table>
## Findings – Comparisons between 2010 and 2015

<table>
<thead>
<tr>
<th>Common Name</th>
<th>2010 Detection Frequency (n=80)</th>
<th>2015 Detection Frequency (n=80)</th>
<th>2010 Median (ng/L)</th>
<th>2015 Median (ng/L)</th>
<th>2010 90th percentile (ng/L)</th>
<th>2015 90th percentile (ng/L)</th>
<th>2010 Maximum (ng/L)</th>
<th>2015 Maximum (ng/L)</th>
<th>Reference Value (ng/L)</th>
<th>Value Type†</th>
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<tr>
<td>2,4-D</td>
<td>1%</td>
<td>0%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>14.4</td>
<td>nd</td>
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<td>RA_{14}</td>
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<td>21%</td>
<td>nd</td>
<td>nd</td>
<td>85</td>
<td>96</td>
<td>2,180</td>
<td>1,460</td>
<td>300,000</td>
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<td>6%</td>
<td>nd</td>
<td>nd</td>
<td>54</td>
<td>nd</td>
<td>71</td>
<td>81</td>
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<td>1,270</td>
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<td>32.4</td>
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<td>Atrazine</td>
<td>5%</td>
<td>4%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>90</td>
<td>81</td>
<td>3,000</td>
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<td>DACT Atrazine*</td>
<td>6%</td>
<td>na</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>na</td>
<td>104</td>
<td>na</td>
<td>3,000</td>
<td>HRL</td>
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<tr>
<td>DEDI Atrazine*</td>
<td>na</td>
<td>5%</td>
<td>na</td>
<td>nd</td>
<td>na</td>
<td>na</td>
<td>83</td>
<td>3,000**</td>
<td>Parent HRL_{MCL}</td>
<td></td>
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<tr>
<td>Desethylatrazine</td>
<td>5%</td>
<td>4%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>90</td>
<td>81.7</td>
<td>3,000**</td>
<td>Parent HRL_{MCL}</td>
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<td>nd</td>
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<td>nd</td>
<td>nd</td>
<td>8</td>
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<td>76.2</td>
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<tr>
<td>Clopyralid</td>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>928</td>
<td>200,000</td>
<td>RA_{14}</td>
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<tr>
<td>Dimethenamid ESA</td>
<td>2%</td>
<td>1%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>19</td>
<td>13.3</td>
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<tr>
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<td>1%</td>
<td>0%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>15</td>
<td>nd</td>
<td>300,000</td>
<td>RAA_{13}</td>
</tr>
<tr>
<td>Imazapyr</td>
<td>0%</td>
<td>1%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>18.3</td>
<td>900,000</td>
<td>RA_{14}</td>
</tr>
<tr>
<td>Metalaxyl</td>
<td>0%</td>
<td>1%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>9.57</td>
<td>20,000</td>
<td>RA_{14}</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>1%</td>
<td>1%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>80</td>
<td>56</td>
<td>300,000</td>
<td>HRL_{11}</td>
</tr>
<tr>
<td>Metolachlor ESA</td>
<td>70%</td>
<td>70%</td>
<td>65</td>
<td>64</td>
<td>694</td>
<td>582</td>
<td>6,170</td>
<td>3,690</td>
<td>800,000</td>
<td>HRL_{11}</td>
</tr>
<tr>
<td>Metolachlor OXA</td>
<td>38%</td>
<td>37%</td>
<td>nd</td>
<td>nd</td>
<td>89</td>
<td>155</td>
<td>2,120</td>
<td>996</td>
<td>800,000</td>
<td>HRL_{11}</td>
</tr>
<tr>
<td>Metribuzin DADK</td>
<td>0%</td>
<td>1%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>607</td>
<td>10,000</td>
<td>10,000</td>
<td>RAA_{12}</td>
</tr>
<tr>
<td>Picloram</td>
<td>1%</td>
<td>0%</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>155</td>
<td>nd</td>
<td>300,000</td>
<td>RA_{14}</td>
</tr>
<tr>
<td>Common Name</td>
<td>2015 Detection and Frequency (n=108)</td>
<td>2015 Median (ng/L)</td>
<td>2015 75th percentile (ng/L)</td>
<td>2015 90th percentile (ng/L)</td>
<td>2015 Maximum (ng/L)</td>
<td>Reference Value (ng/L)</td>
<td>Value Type†</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------------------------------------</td>
<td>--------------------</td>
<td>----------------------------</td>
<td>-----------------------------</td>
<td>---------------------</td>
<td>------------------------</td>
<td>-------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetochlor ESA</td>
<td>21 (19%) nd</td>
<td>86</td>
<td>90</td>
<td>1,460</td>
<td></td>
<td>300,000</td>
<td>HRL11</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Alachlor ESA</td>
<td>49 (45%) nd</td>
<td>178</td>
<td>1,365</td>
<td>3,130</td>
<td>60,000</td>
<td>RAA15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alachlor OXA</td>
<td>12 (11%) nd</td>
<td>nd</td>
<td>35.2</td>
<td>111</td>
<td>60,000</td>
<td>RAA15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td>7 (6%) nd</td>
<td>nd</td>
<td>nd</td>
<td>92.9</td>
<td>3,000</td>
<td>HRLMCL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEDI Atrazine</td>
<td>6 (6%) nd</td>
<td>nd</td>
<td>nd</td>
<td>182</td>
<td>3,000*</td>
<td>Parent HRLMCL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desethylatrazine</td>
<td>7 (6%) nd</td>
<td>nd</td>
<td>nd</td>
<td>88.2</td>
<td>3,000*</td>
<td>Parent HRLMCL</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyatrazine</td>
<td>3 (3%) nd</td>
<td>nd</td>
<td>nd</td>
<td>44.7</td>
<td>20,000</td>
<td>HBV05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentazon</td>
<td>9 (8%) nd</td>
<td>nd</td>
<td>nd</td>
<td>56.2</td>
<td>30,000</td>
<td>HBV14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromacil</td>
<td>2 (2%) nd</td>
<td>nd</td>
<td>nd</td>
<td>76.2</td>
<td>30,000</td>
<td>HBV14</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Clopyralid</td>
<td>1 (1%) nd</td>
<td>nd</td>
<td>nd</td>
<td>928</td>
<td>200,000</td>
<td>RA14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dimethenamid ESA</td>
<td>2 (2%) nd</td>
<td>nd</td>
<td>nd</td>
<td>34.3</td>
<td>300,000*</td>
<td>RAA13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imazapyr</td>
<td>3 (3%) nd</td>
<td>nd</td>
<td>nd</td>
<td>57</td>
<td>900,000</td>
<td>RA14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metalaxyl</td>
<td>1 (1%) nd</td>
<td>nd</td>
<td>nd</td>
<td>9.57</td>
<td>20,000</td>
<td>RA14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor</td>
<td>1 (1%) nd</td>
<td>nd</td>
<td>nd</td>
<td>56</td>
<td>300,000</td>
<td>HRL11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor ESA</td>
<td>68 (63%) 27.3</td>
<td>183</td>
<td>574</td>
<td>3,690</td>
<td>800,000</td>
<td>HRL11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor OXA</td>
<td>36 (33%) nd</td>
<td>nd</td>
<td>26.7</td>
<td>134</td>
<td>996</td>
<td>800,000</td>
<td>HRL11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metribuzin DADK</td>
<td>1 (1%) nd</td>
<td>nd</td>
<td>nd</td>
<td>607</td>
<td>10,000</td>
<td>RAA12</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
## Chloride/Bromide Comparisons

### Pesticides Detected with Chloride and Bromide Results

<table>
<thead>
<tr>
<th></th>
<th>Pesticides Detected with Chloride and Bromide Results</th>
<th>No Pesticides Detected with Chloride and Bromide Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Samples</td>
<td>72</td>
<td>35</td>
</tr>
<tr>
<td>Number of Pesticide Detections in 108 samples</td>
<td>236</td>
<td>0</td>
</tr>
<tr>
<td>Maximum $[\text{Cl}^-]/[\text{Br}^-]$</td>
<td>11,760</td>
<td>2,445</td>
</tr>
<tr>
<td>90\textsuperscript{th} Percentile $[\text{Cl}^-]/[\text{Br}^-]$</td>
<td>1,270</td>
<td>449</td>
</tr>
<tr>
<td>Mean $[\text{Cl}^-]/[\text{Br}^-]$</td>
<td>811</td>
<td>241</td>
</tr>
<tr>
<td>Median $[\text{Cl}^-]/[\text{Br}^-]$</td>
<td>490</td>
<td>122</td>
</tr>
</tbody>
</table>
Historical Trends & Spatial Distribution of Antibiotics in Minnesota Lakes & Rivers

Jill F. Kerrigan\textsuperscript{1}, Daniel R. Engstrom\textsuperscript{2}, Kyle Sandberg\textsuperscript{1}, Timothy LaPara\textsuperscript{1}, and William A. Arnold\textsuperscript{1}

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\textsuperscript{2}St. Croix Watershed Research Station, Science Museum of Minnesota
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Kyle Sandberg
Daniel Engstrom

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LacCore.org
National Lacustrine Core Facility

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Acadia Stephan
Robert Rudin III

Financial Support

Environment and Natural Resources Trust Fund
background
antibiotics
lifestyle → environment

hand soaps
cocaine
detergents
pharmaceuticals
DEET

environment
animals
atmosphere
ground water
soil
sediment

fragrances
surface water
22,700 TONS

(about 50% is for human consumption)
The presence of antibiotics is of concern because they are...

persistent and effective at low concentrations
Antibiotic resistant genes (Superbugs...)
different production dates

old VS new
different origins

natural vs synthetic
different uses

human vs agriculture
A portion of the antibiotic taken is undigested by the body.
Part I.

historical trends
Sediment cores can be used to determine historical trends of antibiotics in a water body.
Sediment cores can be used to determine historical trends of antibiotics in a water body.
Sediment cores can be used to determine historical trends of antibiotics in a water body.
sediment core can be used as a historical record for antibiotic usage

1. Determine **the date** of sediment layers at various depths
sediment core can be used as a historical record for antibiotic usage

1. Determine the date of sediment layers at various depths

2. Measure the amount of antibiotics sorbed to the sediment
sediment core can be used as a historical record for antibiotic usage

1. Determine the date of sediment layers at various depths

2. Measure the amount of antibiotics sorbed to the sediment

antibiotic deployment
experimental procedure
Lake Pepin

large watershed & receives multiple waste discharges

Duluth Harbor

Lake Sediment Core Sampling Locations

Lake Pepin
Lake Winona

small watershed & approx. 63% of in flow is wastewater effluent
Younger sediment at the top (current level)

Older sediment deeper in the core (historical levels)
Extruding in 4 – 8 cm intervals
Subsamples were taken for antibiotic, and dating analysis
# Major Classification of Antibiotics and General Use

<table>
<thead>
<tr>
<th>Sulfonamides</th>
<th>Fluoroquinolones</th>
<th>Tetracyclines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfachloropyridazine</td>
<td>Ofloxacin</td>
<td>Tetracycline</td>
</tr>
<tr>
<td>Sulfadiazine</td>
<td>Norfloxacin</td>
<td>Oxytetracycline</td>
</tr>
<tr>
<td>Sulfadimethoxine</td>
<td>Ciprofloxacin</td>
<td>Chlortetracycline</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Enrofloxacin</td>
<td>Doxycycline</td>
</tr>
<tr>
<td>Sulfamethazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfapyridine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Macrolides</th>
<th>β-Lactamases</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erthyromycin</td>
<td>Penicillin G</td>
<td>Trimethoprim</td>
</tr>
<tr>
<td>Tylosin</td>
<td>Penicillin V</td>
<td>Carbadox</td>
</tr>
<tr>
<td>Roxithromycin</td>
<td>Amoxicilin</td>
<td>Lincomycin</td>
</tr>
</tbody>
</table>

- Fluoroquinolones: Ciprofloxacin, Norfloxacin, Ofloxacin, Enrofloxacin
- β-Lactamases: Penicillin G, Penicillin V, Amoxicilin
- Others: Trimethoprim, Carbadox, Lincomycin
Sediment Extraction

(Internal Standard & Isotope Dilution)

Accelerated Solvent Extraction (ASE) → Solid Phase Extraction (SPE) → UPLC-MS/MS Analysis
results
different production dates

old VS new
Sulfapyridine

- Sulfonamide drug - synthetic
- Synthesized in 1937
- No longer prescribed or manufactured as of Dec 1990
Ofloxacin

- Fluoroquinolone - synthetic
- Approved by the FDA in 1990
- World Health Organization List of Essential Medicines
different origins

natural vs synthetic
Lincomycin

- natural product
- Discovered in the early 1960s
- Rarely used today – typically for patients that are allergic to penicillin
- Appears to be naturally produced throughout past century
- Human influence may have increase its presence circa 1980
different uses

human vs agriculture
Number of antibiotics detected in each Minnesota lake
(Note: non-detected classes of antibiotics are not shown)

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Duluth Harbor</th>
<th>Lake Pepin</th>
<th>Lake Winona</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Human</td>
<td>Agric.</td>
<td>Both</td>
</tr>
<tr>
<td>SAs</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>FQs</td>
<td>--</td>
<td>--</td>
<td>2</td>
</tr>
<tr>
<td>TCs</td>
<td>--</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Others</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

SAs: sulfonamides  -  FQs: fluoroquinolones  -  TCs: tetracyclines

*detected throughout the core, but not in recent years

**natural production?
Number of antibiotics detected in each Minnesota lake
(Note: non-detected classes of antibiotics are not shown)

primarily see **human use** antibiotics in these wastewater impacted lakes…

<table>
<thead>
<tr>
<th>Lake Winona</th>
<th>Antibiotic</th>
<th>Human</th>
<th>Agric.</th>
<th>Both</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAs</td>
<td>3</td>
<td>2*</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>FQs</td>
<td>--</td>
<td>--</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>TCs</td>
<td>1</td>
<td>--</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

*detected throughout the core, but not in recent years

<table>
<thead>
<tr>
<th>Lake Pepin</th>
<th>Antibiotic</th>
<th>Human</th>
<th>Agric.</th>
<th>Both</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAs</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>FQs</td>
<td>--</td>
<td>--</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TCs</td>
<td>--</td>
<td>1</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Others</td>
<td>1*</td>
<td>1**</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

**natural production?**

…with a few exceptions

SAs: sulfonamides - FQs: fluoroquinolones - TCs: tetracyclines
Part I. Take Home Messages

Sediment cores can provide historical record for select antibiotics

Wastewater effluent appears to be primary source of antibiotics in these Minnesota Lakes

The degree of anthropogenic impact had a great affect on the number of antibiotics detected and their concentration
Part II.

spatial trends
Minnesota and Mississippi River
Surface Sediment Sampling Locations

Mississippi River

Minnesota River

Surface Sediment Sampling Locations

Mississippi & Minnesota River

Mississippi River

Minnesota River
Trimethoprim. Pollution *increases moving downstream* of both rivers with increasing anthropogenic inputs.
Ofloxacin. Both agriculture and human use of the antibiotic was likely detected in these rivers.
Sulfadimethoxine. Low levels were detected only in the Minnesota River.
Sulfamethazine appears to have traveled from the agriculture impacted Minnesota River to the Mississippi River.
Part II. Take Home Message

Varying spatial distribution of antibiotics were observed due to anthropogenic uses, i.e. run-off of agriculture fields vs. wastewater effluent.
Questions?