CENTURY OF TRENDS
PROJECT:

LONG-TERM TRENDS IN ALKALINITY IN LARGE RIVERS OF THE CONTIGUOUS U.S.

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ACKNOWLEDGEMENTS

- USGS NAWQA Century of Trends
- Whitney Broussard
- Thor Smith
- Donna Myers
WHY STUDY ALKALINITY TRENDS?

- Indicative of changes in the watershed.
  - Land use.
  - Weathering rate.
  - Acidification.

- Major component of carbonate equilibria
  - Can affect coastal acidification.
  - Implications for river carbon cycling.

- The underlying causes are not well understood
  - Much more work in small headwaters areas.
  - Large rivers subject to many more processes.
Acid deposition

Acid mine drainage

Industrial and municipal point sources

ACIDIFYING PROCESSES IN WATERSHEDS

\[
\text{NO}_x, \text{SO}_x
\]

\[
\text{FeS}_2 \xrightarrow{\text{oxidation}} \text{SO}_4^{2-} + \text{H}^+
\]

\[
\text{R-NH}_3 + \text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}
\]
METHODS

- Data originated from NWIS, STORET, and individual state assessments.
  - Clarke (1924) – Data from first decade of 20th century.

- Water quality data included alkalinity and major ions.

- Used the multiple regression model LOADEST to calculate loads of all constituents.

- Expressed all results as flow-weighted concentration (FWC).
• Trends were calculated from the mid 20\textsuperscript{th} century to early 21\textsuperscript{st} century.
  • Nominally 1950-2010.

• LOADEST run in three-year segments
  • Concentration-discharge based relationship.
  • Running in segments allowed this to change over time.

• Trends detected using nonparametric Kendall correlation on annual flow-weighted concentration.
Alkalinity concentration increased at 14 of 23 stations examined. Alkalinity increases were widespread.
**INCREASING FLOW-WEIGHTED CONC. IS WIDE-SPREAD.**

<table>
<thead>
<tr>
<th>Station</th>
<th>FWC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connectict</td>
<td>0.28</td>
</tr>
<tr>
<td>Delaware</td>
<td>0.62</td>
</tr>
<tr>
<td>Schuylkill</td>
<td>0.74</td>
</tr>
<tr>
<td>Potomac</td>
<td>0.60</td>
</tr>
<tr>
<td>James</td>
<td>0.39</td>
</tr>
<tr>
<td>Middle Ohio</td>
<td>0.64</td>
</tr>
<tr>
<td>Lower Ohio</td>
<td>0.30</td>
</tr>
<tr>
<td>Maumee</td>
<td>-0.04</td>
</tr>
<tr>
<td>St Lawrence</td>
<td>0.11</td>
</tr>
<tr>
<td>Middle Illinois</td>
<td>0.49</td>
</tr>
<tr>
<td>Lower Illinois</td>
<td>0.24</td>
</tr>
<tr>
<td>Upper Mississippi</td>
<td>0.46</td>
</tr>
<tr>
<td>Missouri</td>
<td>0.42</td>
</tr>
<tr>
<td>Middle Mississippi</td>
<td>0.23</td>
</tr>
<tr>
<td>Arkansas</td>
<td>0.05</td>
</tr>
<tr>
<td>Lower Mississippi</td>
<td>0.32</td>
</tr>
<tr>
<td>Brazos</td>
<td>-0.17</td>
</tr>
<tr>
<td>Colorado</td>
<td>-0.35</td>
</tr>
<tr>
<td>Santa Ana</td>
<td>-0.43</td>
</tr>
<tr>
<td>San Joaquin</td>
<td>0.05</td>
</tr>
<tr>
<td>Willamette</td>
<td>-0.07</td>
</tr>
</tbody>
</table>
WHAT CAUSES ALKALINITY INCREASES?

- Increasing weathering rates.
- Increasing sources of weathering products to streams.
- Decreased alkalinity consumption by acidifying processes.
CHEMICAL WEATHERING IN THE SOIL MILIEU

Acids + Weatherable substrates → Weathering products

H₂CO₃  
H₂SO₄  
HNO₃  

CaCO₃  
CaSiO₃  
CaMg(CO₃)₂  
CaMg(SiO₃)₂  

HCO₃⁻ (alkalinity)  
NO₃⁻  
SO₄⁻  
Ca²⁺  
Mg²⁺
CHEMICAL WEATHERING IN THE SOIL MILIEU

Acids + Weatherable substrates → Weathering products

- $\text{H}_2\text{CO}_3$
- $\text{H}_2\text{SO}_4$
- $\text{HNO}_3$

Weatherable substrates:
- $\text{CaCO}_3$
- $\text{CaSiO}_3$
- $\text{CaMg(CO}_3\text{)}_2$
- $\text{CaMg(SiO}_3\text{)}_2$

Weathering products:
- $\text{HCO}_3^-$ (alkalinity)
- $\text{NO}_3^-$
- $\text{SO}_4^-$
- $\text{Ca}^{2+}$
- $\text{Mg}^{2+}$
CHEMICAL WEATHERING IN THE SOIL MILIEU

Acids + Weatherable substrates → Weathering products

$\text{H}_2\text{CO}_3$ $\text{H}_2\text{SO}_4$ $\text{HNO}_3$

$\text{CaCO}_3$ $\text{CaSiO}_3$ $\text{CaMg(CO}_3)_2$ $\text{CaMg(SiO}_3)_2$

$\text{HCO}_3^-$ (alkalinity)

$\text{NO}_3^-$ $\text{SO}_4^-$

$\text{Ca}^{2+}$ $\text{Mg}^{2+}$
CHEMICAL WEATHERING IN THE SOIL MILIEU

Acids + Weatherable substrates → Weathering products

- $\text{H}_2\text{CO}_3$ → $\text{CaCO}_3$
- $\text{H}_2\text{SO}_4$ → $\text{CaSiO}_3$
- $\text{HNO}_3$ → $\text{CaMg(CO}_3\text{)}_2$
- $\text{CaMg(SiO}_3\text{)}_2$

- $\text{HCO}_3^-$ (alkalinity)
- $\text{NO}_3^-$
- $\text{SO}_4^{2-}$
- $\text{Ca}^{2+}$
- $\text{Mg}^{2+}$
CATION:ALKALINITY RATIO

\[
\frac{[\text{Ca}^{2+}+\text{Mg}^{2+}]}{\text{Alkalinity}}
\]

Higher: Greater influence of HNO\textsubscript{3} + H\textsubscript{2}SO\textsubscript{4} weathering

Lower: Lesser influence of HNO\textsubscript{3} + H\textsubscript{2}SO\textsubscript{4} weathering
This result is consistent with recovery from acidification.

<table>
<thead>
<tr>
<th>Station</th>
<th>Alkalinity</th>
<th>Ca / Alk</th>
<th>[Ca+Mg] / Alk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Connecticut</td>
<td>0.28***</td>
<td>-0.41***</td>
<td>-0.41***</td>
</tr>
<tr>
<td>Delaware</td>
<td>0.61***</td>
<td>-0.51***</td>
<td>-0.56***</td>
</tr>
<tr>
<td>Schuylkill</td>
<td>0.74***</td>
<td>-0.68***</td>
<td>-0.74***</td>
</tr>
<tr>
<td>Potomac</td>
<td>0.6***</td>
<td>-0.07</td>
<td>-0.23**</td>
</tr>
<tr>
<td>James</td>
<td>0.39***</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Altamaha</td>
<td>0.25**</td>
<td>0.35**</td>
<td>0.51**</td>
</tr>
<tr>
<td>Escambia</td>
<td>-0.14</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>Middle Ohio</td>
<td>0.64***</td>
<td>-0.50***</td>
<td>-0.46***</td>
</tr>
<tr>
<td>Lower Ohio</td>
<td>0.3***</td>
<td>-0.36***</td>
<td>-0.30***</td>
</tr>
<tr>
<td>Maumee</td>
<td>-0.04</td>
<td>-0.21*</td>
<td>0.09</td>
</tr>
<tr>
<td>St Lawrence</td>
<td>0.11</td>
<td>-0.47***</td>
<td>-0.40***</td>
</tr>
<tr>
<td>Middle Illinois</td>
<td>0.46***</td>
<td>-0.51***</td>
<td>-0.45***</td>
</tr>
<tr>
<td>Lower Illinois</td>
<td>0.48***</td>
<td>-0.25**</td>
<td>-0.11</td>
</tr>
<tr>
<td>Upper Mississippi</td>
<td>0.46**</td>
<td>-0.23*</td>
<td>-0.07</td>
</tr>
<tr>
<td>Missouri</td>
<td>0.42***</td>
<td>-0.50***</td>
<td>-0.28***</td>
</tr>
<tr>
<td>Middle Mississippi</td>
<td>0.23**</td>
<td>-0.27***</td>
<td>-0.13</td>
</tr>
<tr>
<td>Arkansas</td>
<td>0.05</td>
<td>-0.51***</td>
<td>-0.48***</td>
</tr>
<tr>
<td>Lower Mississippi</td>
<td>0.32***</td>
<td>-0.57***</td>
<td>-0.31***</td>
</tr>
<tr>
<td>Brazos</td>
<td>-0.17*</td>
<td>-0.12</td>
<td>-0.02</td>
</tr>
<tr>
<td>Colorado</td>
<td>-0.35***</td>
<td>-0.32***</td>
<td>-0.22***</td>
</tr>
<tr>
<td>Santa Ana</td>
<td>-0.43***</td>
<td>-0.09</td>
<td>-0.20*</td>
</tr>
<tr>
<td>San Joaquin</td>
<td>0.06</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Willamette</td>
<td>-0.11</td>
<td>0.37***</td>
<td>0.38***</td>
</tr>
</tbody>
</table>
DELAWARE RIVER: RECOVERY FROM ACIDIFICATION

Early 20th century
MISSISSIPPI RIVER AT NEW ORLEANS: MIXED MESSAGES

Early 20th century

Solute concentration (μeq L⁻¹)

Alkalinity
NO₃ + SO₄
Ca²⁺
COMPARISON WITH EARLY 20\textsuperscript{TH} CENTURY DATA

Average FWC after 1998 (\(\mu\text{eq L}^{-1}\))

Clarke (1924) concentration (\(\mu\text{eq L}^{-1}\))
CONCLUSIONS

• Alkalinity increases are widespread.
  • Especially Eastern and Central US

• Decreasing cation – alkalinity ratios suggest that recovery from acidification is common.

• Alkalinity in early 21st century is similar to the beginning of the 20th century.

• Heterogeneity is the rule.