CENTURY OF TRENDS PROJECT:

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

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USGS science for a changing world

ACKNOWLEDGEMENTS

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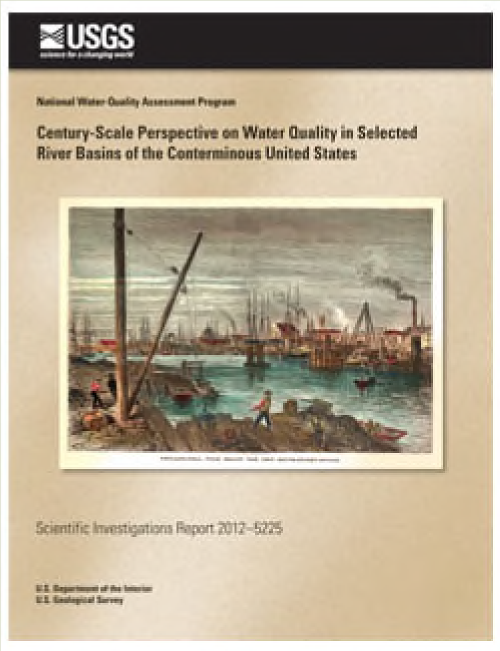
- Whitney Broussard
- Thor Smith
- Donna Myers



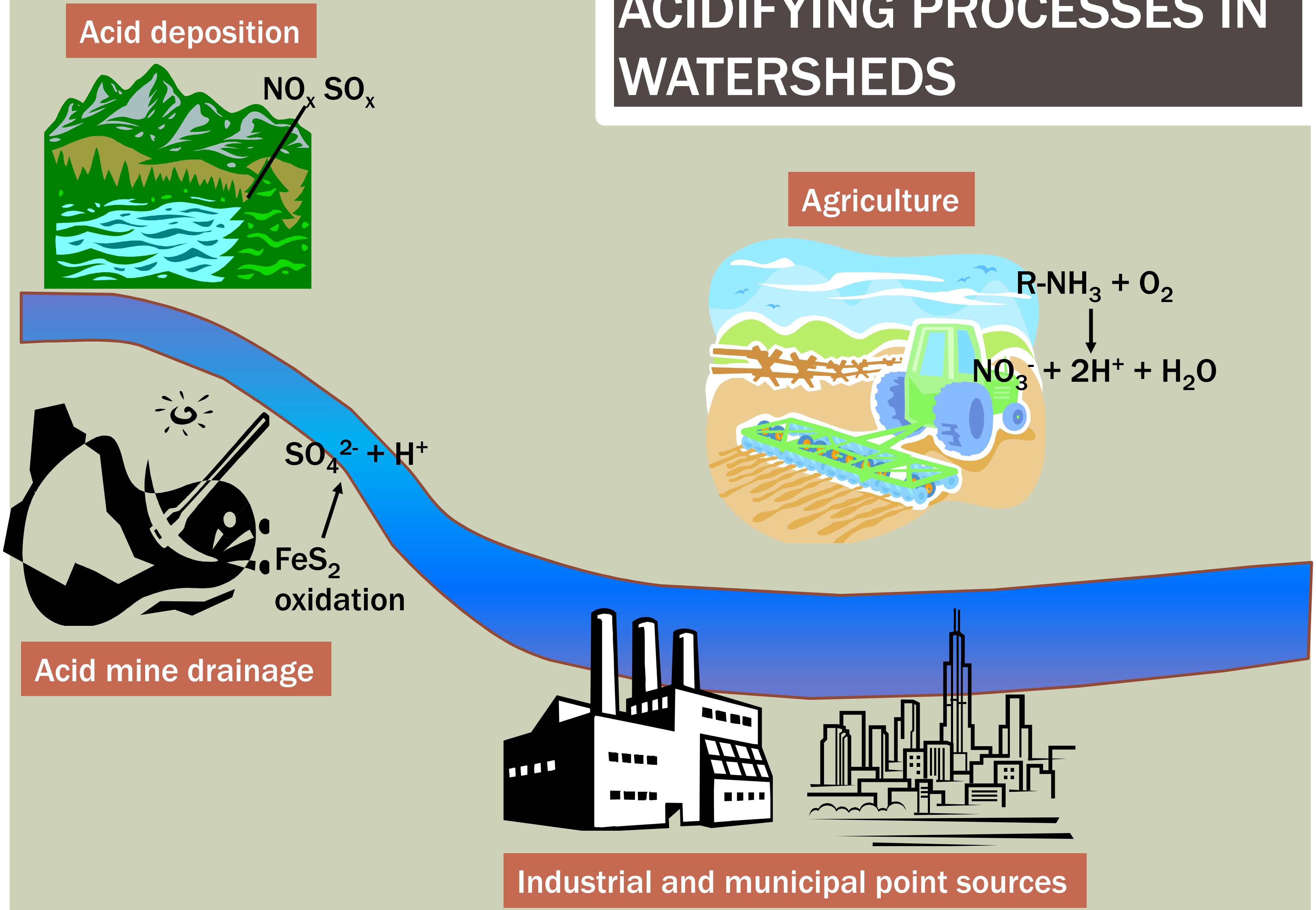
WHY STUDY ALKALINITY TRENDS?

- 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.

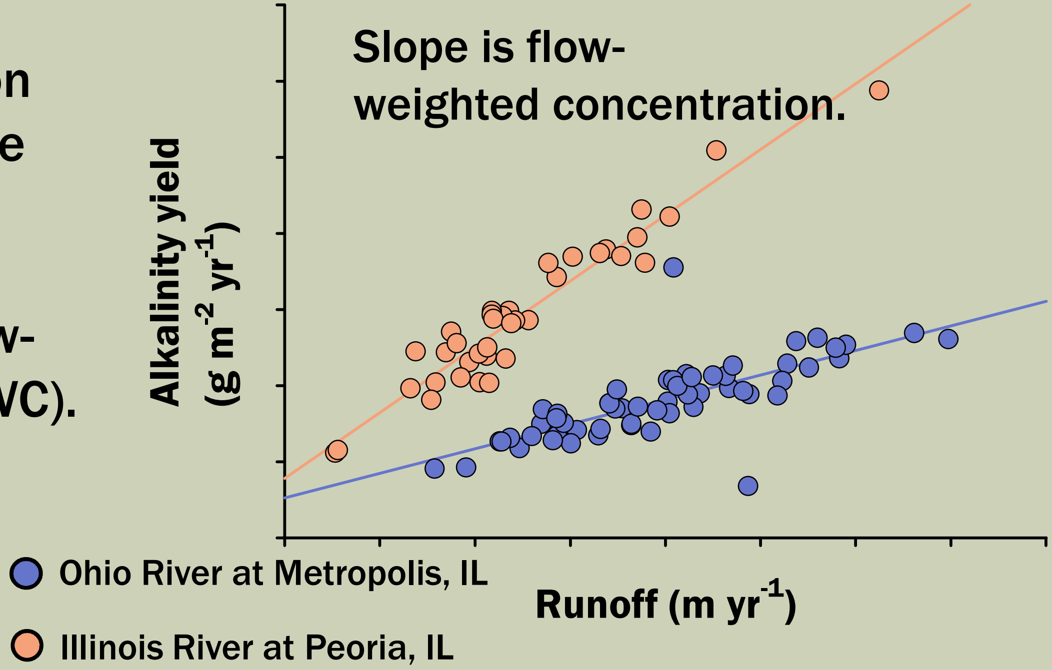
- The underlying causes are not well understood
  - Much more work in small headwaters areas.
  - Large rivers subject to many more processes.

ACIDIFYING PROCESSES IN WATERSHEDS



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).

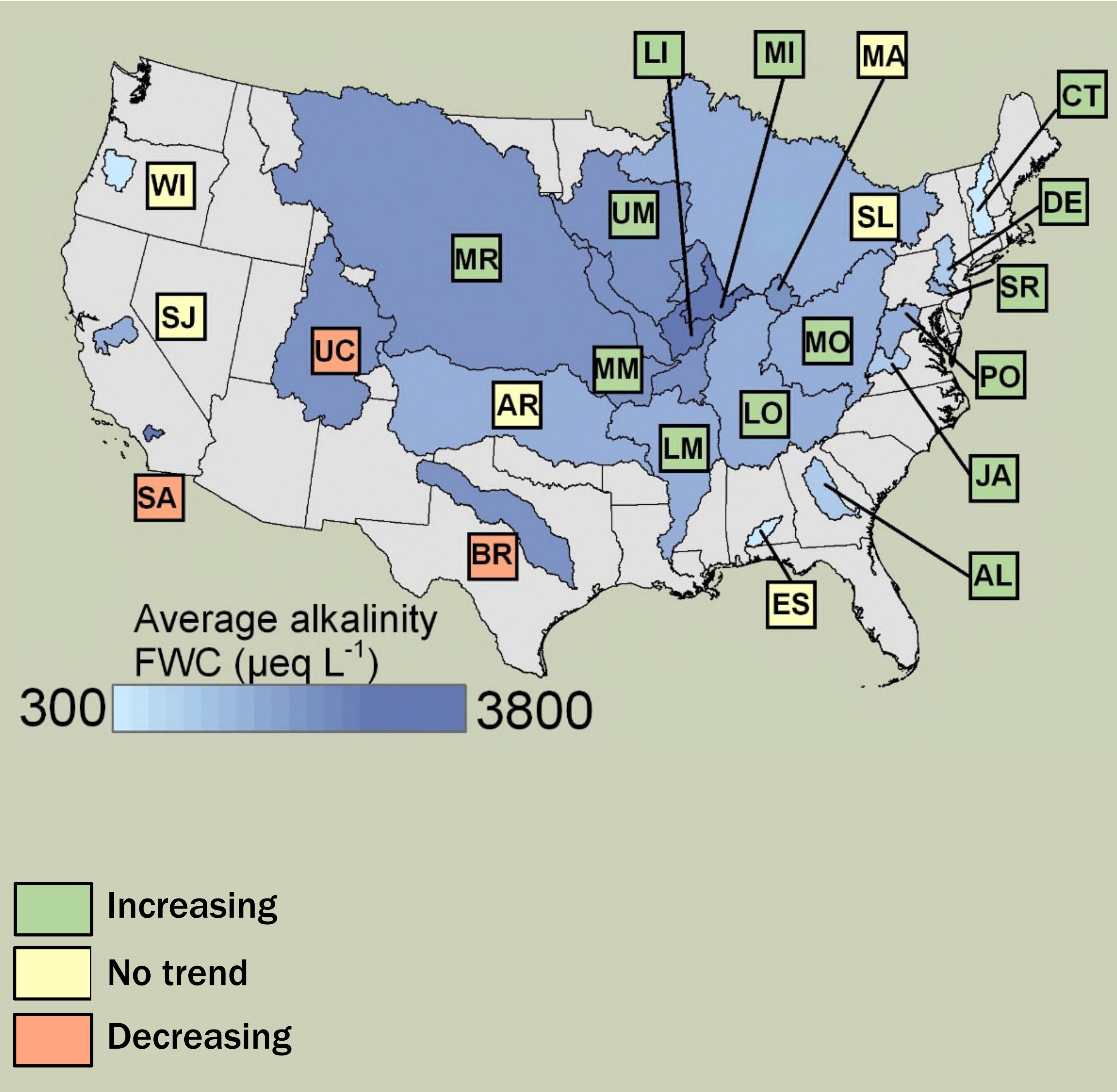


TREND ANALYSIS

- Trends were calculated from the mid 20th century to early 21st 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 INCREASES WERE WIDE-SPREAD .

Alkalinity CONCEN-TRATION increased at 14 of 23 stations examined.

INCREASING FLOW-WEIGHTED CONC. IS WIDE-SPREAD.

	Station	FWC
Eastern Rivers	Connectict	0.28
	Delaware	0.62
	Schuylkill	0.74
	Potomac	0.60
	James	0.39
	Middle Ohio	0.64
	Lower Ohio	0.30
	Maumee	-0.04
	St Lawrence	0.11
Mississippi River Basin	Middle Illinois	0.49
	Lower Illinois	0.24
	Upper Mississippi	0.46
	Missouri	0.42
	Middle Mississippi	0.23
	Arkansas	0.05
	Lower Mississippi	0.32
Western Rivers	Brazos	-0.17
	Colorado	-0.35
	Santa Ana	-0.43
	San Joaquin	0.05
	Willamette	-0.07

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

H_2CO_3
H_2SO_4
HNO_3

→

$CaCO_3$
$CaSiO_3$
$CaMg(CO_3)_2$
$CaMg(SiO_3)_2$

→

HCO_3^- (alkalinity)
NO_3^-
SO_4^-

Ca^{2+}
Mg^{2+}

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CHEMICAL WEATHERING IN THE SOIL MILIEU

Acids + **Weatherable substrates** → **Weathering products**

Acids		Weatherable substrates		Weathering products
				HCO_3^- (alkalinity)
H_2CO_3		$CaCO_3$		NO_3^-
H_2SO_4	→	$CaSiO_3$	→	SO_4^-
HNO_3		$CaMg(CO_3)_2$		Ca^{2+}
		$CaMg(SiO_3)_2$		Mg^{2+}

CATION:ALKALINITY RATIO

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

Higher: Greater influence of HNO_3 + H_2SO_4 weathering

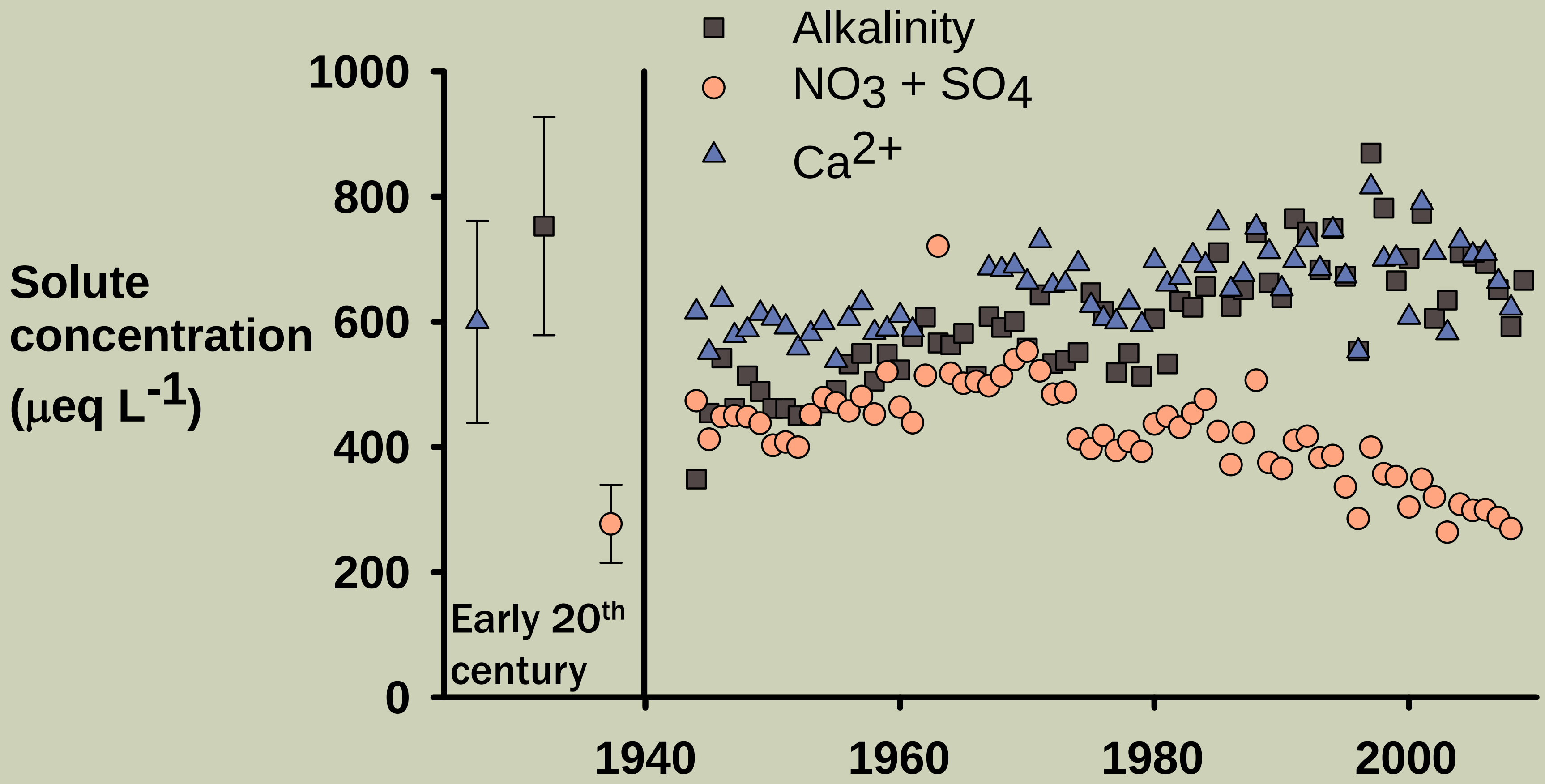
Lower: Lesser influence of HNO_3 + H_2SO_4 weathering

Region	Station	Alkalinity	Ca / Alk	[Ca+Mg] / Alk
Eastern Rivers	Connectict	0.28***	-0.41***	-0.41***
	Delaware	0.61***	-0.51***	-0.56***
	Schuylkill	0.74***	-0.68***	-0.74***
	Potomac	0.6***	-0.07	-0.23**
	James	0.39***	0.01	0.01
	Altamaha	0.25**	0.35**	0.51**
	Escambia	-0.14	0.12	0.05
	Middle Ohio	0.64***	-0.50***	-0.46***
	Lower Ohio	0.3***	-0.36***	-0.30***
	Maumee	-0.04	-0.21*	0.09
	St Lawrence	0.11	-0.47***	-0.40***
Mississippi River Basin	Middle Illinois	0.46***	-0.51***	-0.45***
	Lower Illinois	0.48***	-0.25**	-0.11
	Upper Mississippi	0.46**	-0.23*	-0.07
	Missouri	0.42***	-0.50***	-0.28***
	Middle Mississippi	0.23**	-0.27***	-0.13
	Arkansas	0.05	-0.51***	-0.48***
	Lower Mississisppi	0.32***	-0.57***	-0.31***
Western Rivers	Brazos	-0.17*	-0.12	-0.02
	Colorado	-0.35***	-0.32***	-0.22***
	Santa Ana	-0.43***	-0.09	-0.20*
	San Joaquin	0.06		0.05
	Willamette	-0.11	0.37***	0.38***

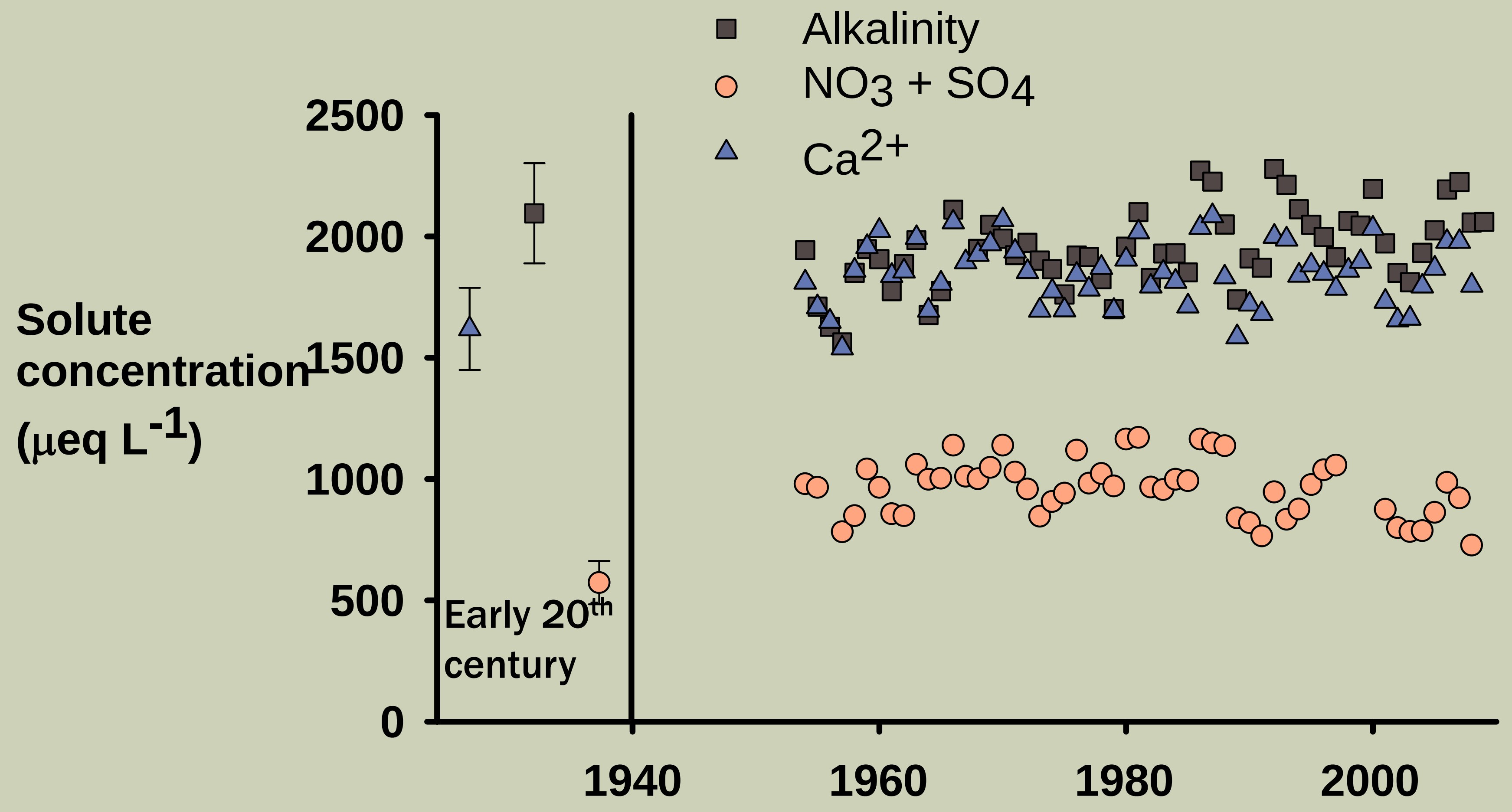
DECREASING CATION : ALKALINITY RATIO IS WIDESPREAD

This result is consistent with recovery from acidification.

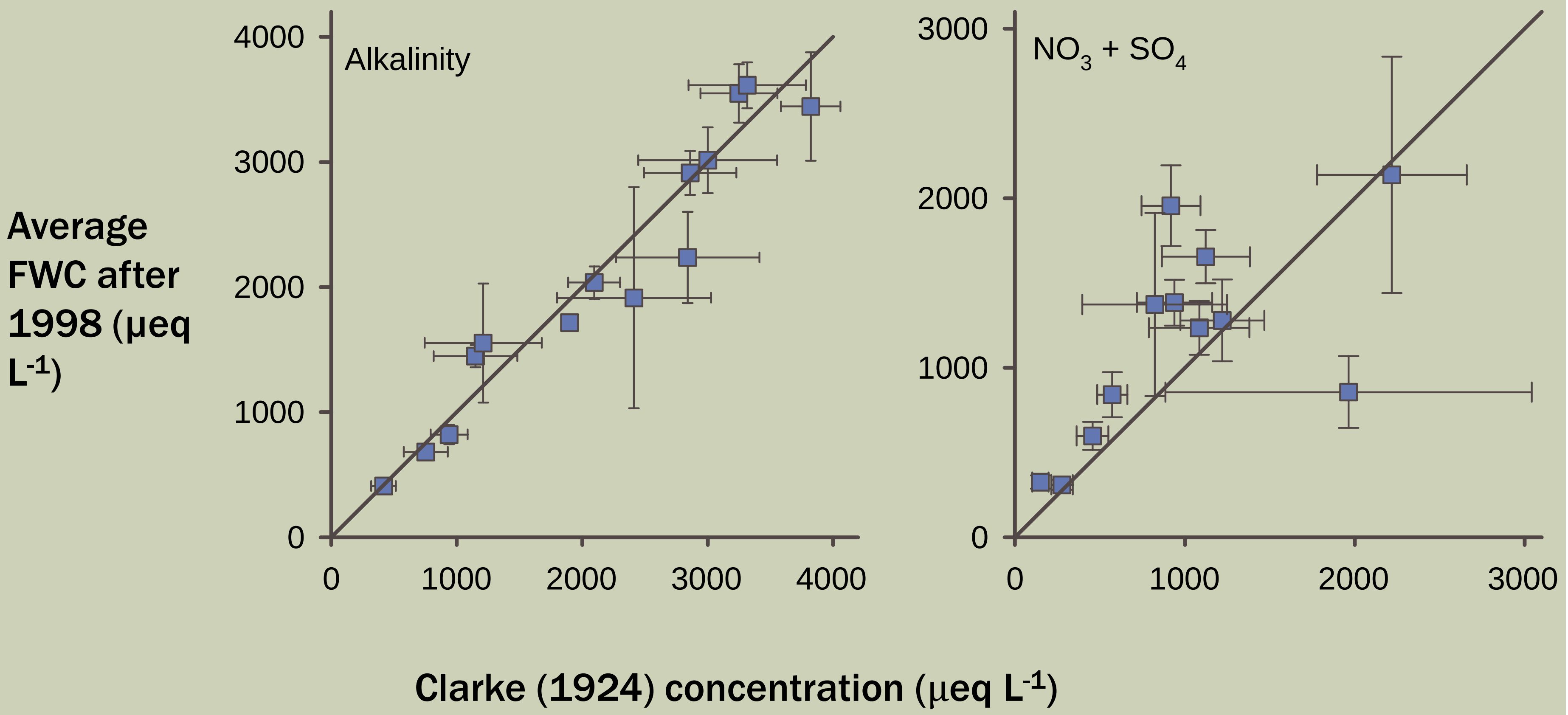
DELAWARE RIVER: RECOVERY FROM ACIDIFICATION



MISSISSIPPI RIVER AT NEW ORLEANS: MIXED MESSAGES



COMPARISON WITH EARLY 20TH CENTURY DATA



CONCLUSIONS

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

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

- Alkalinity in early 21^{st} century is similar to the beginning of the 20^{st} century.

- Heterogeneity is the rule.

CENTURY OF TRENDS PUBLICATIONS (SO FAR)

Stets, E.G., V.J. Kelly, W. Broussard, T. Smith, and C.G. Crawford. (2012). Century-scale perspective on water quality in selected river basins of the conterminous United States. U.S. Geological Survey *Scientific Investigations Report* 2012-5225, 107p.

Stets, E.G., V.J. Kelly, and C.G. Crawford (*In press*). Long-term trends in alkalinity in large rivers of the conterminous US in relation to acidification, agriculture, and hydrologic modification. *Science of the Total Environment*, http://dx.doi.org/10.1016/j.scitotenv.2014.04.054.