

Geothermal solute flux monitoring using electrical conductivity in major rivers of Yellowstone National Park

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Yellowstone National Park

- Yellowstone National Park is well-known for its numerous geysers, hot springs, mud pots, and steam vents
- Yellowstone hosts close to 4 million visits each year
- The Yellowstone Supervolcano is located in YNP

Monitoring the Geothermal System:

1. Management tool
2. Hazard assessment
3. Long-term changes



Monitoring Geothermal Systems

- YNP – difficult to continuously monitor
- 10,000 thermal features
- YNP area = 9,000 km²
- long cold winters

Thermal output from Yellowstone can be estimated by monitoring the chloride flux downstream of thermal sources in major rivers draining the park



River Chloride Flux

- The chloride flux (chloride concentration multiplied by discharge) in the major rivers has been used as a surrogate for estimating the heat flow in geothermal systems ([Ellis and Wilson, 1955](#); [Fournier, 1989](#))
 - “Integrated flux”
 - Convective heat discharge: 5300 to 6100 MW
 - Monitoring changes over time
- Chloride concentrations in most YNP geothermal waters are elevated (100 - 900 mg/L Cl)
- Most of the water discharged from YNP geothermal features eventually enters a major river
 - Madison R., Yellowstone R., Snake R., Falls River
 - Firehole R., Gibbon R., Gardner R.
- Background Cl concentrations in rivers low < 1 mg/L

Dilute Stream water

- snowmelt
- non-thermal baseflow
- low EC (40 - 200 $\mu\text{S}/\text{cm}$)
- Cl < 1 mg/L



Geothermal Water

- high EC (>~1000 $\mu\text{S}/\text{cm}$)
- high Cl, SiO₂, Na, B, As,...
- Most solutes behave conservatively

Mixture of dilute stream water with geothermal water

Historical Cl Flux Monitoring

- The U.S. Geological Survey (USGS) and the National Park Service have collaborated on chloride flux monitoring since the 1970's
- Collected 28 water samples/year/site for Cl analyses
- Difficult to sustain year-after-year
 1. Weather
 2. Funding
 3. Staffing (long-term)
 4. Distance between sample sites
 5. Changing research interests



Electrical Conductivity Monitoring

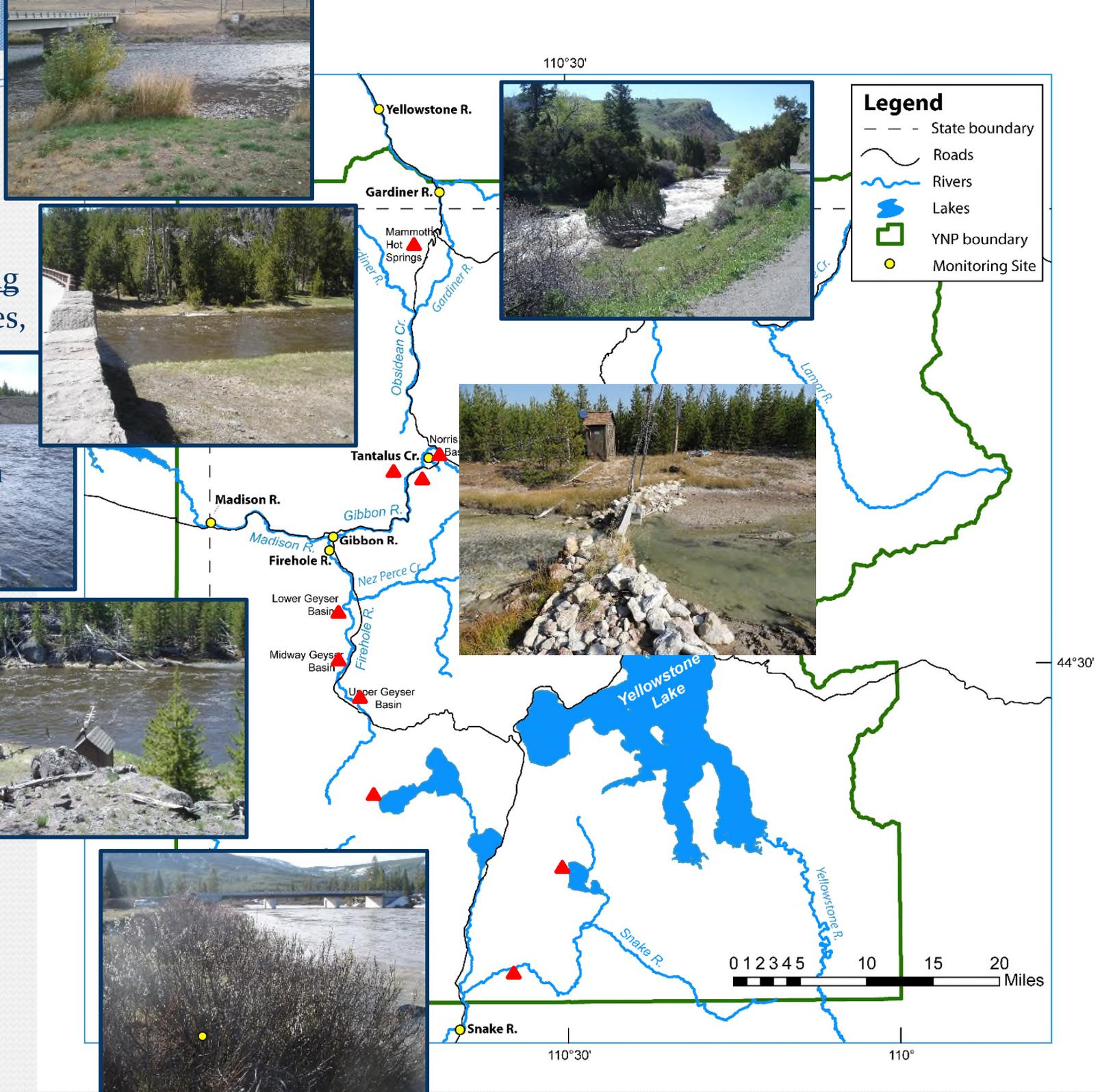
- Beginning in 2010, we developed methods using electrical conductivity as a surrogate for chloride concentrations in major YNP rivers



River Synoptic Sampling

Identify thermal sources, solutes, fate and transport

- Madison R., Gibbon R., Firehole R., Snake R., Yellowstone R. and Gardner R.



EC Monitoring Sites

- Near USGS streamgauge (streamflow every 15 min)
- Continuous electrical conductivity measurements concurrent with streamflow (every 15 min)
 - Low maintenance / checked EC with handheld meter
- Solute Concentrations– Electrical Conductivity Correlations
 - Collect water samples (filtered) and EC under wide range of flow conditions
 - Analyzed for major anions, cations, and trace metals
 - QAQC: Charge Balance and Electrical Conductivity Balance

Cl Flux (g/year) =

Q (m³/s)

(continuous 15 min -
>35,000 measurements/yr)



Cl concentration (mg/L)

(285 samples/year)

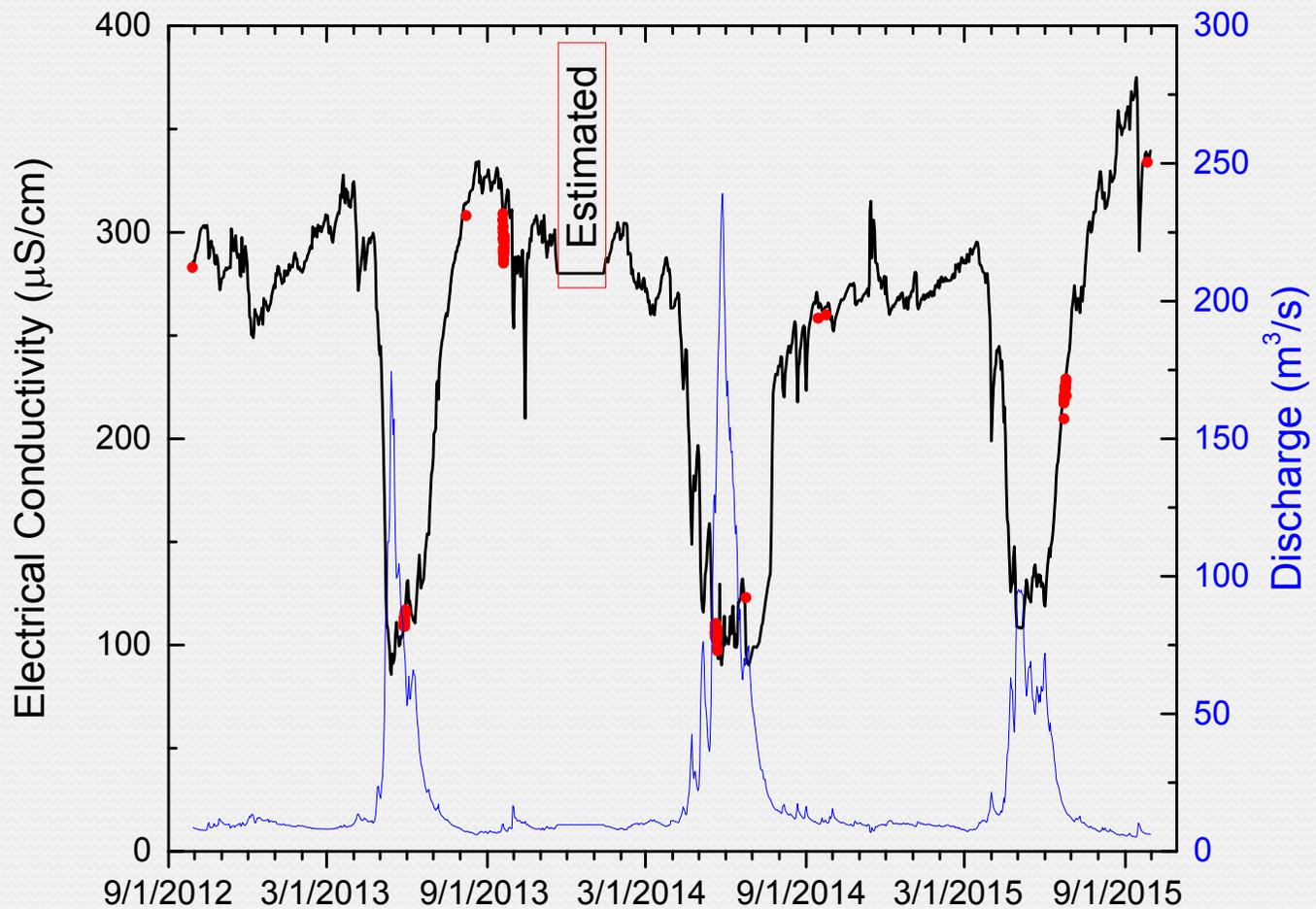
USGS streamgauge

Electrical Conductivity
(continuous 15 min -
>35,000 measurements/yr)

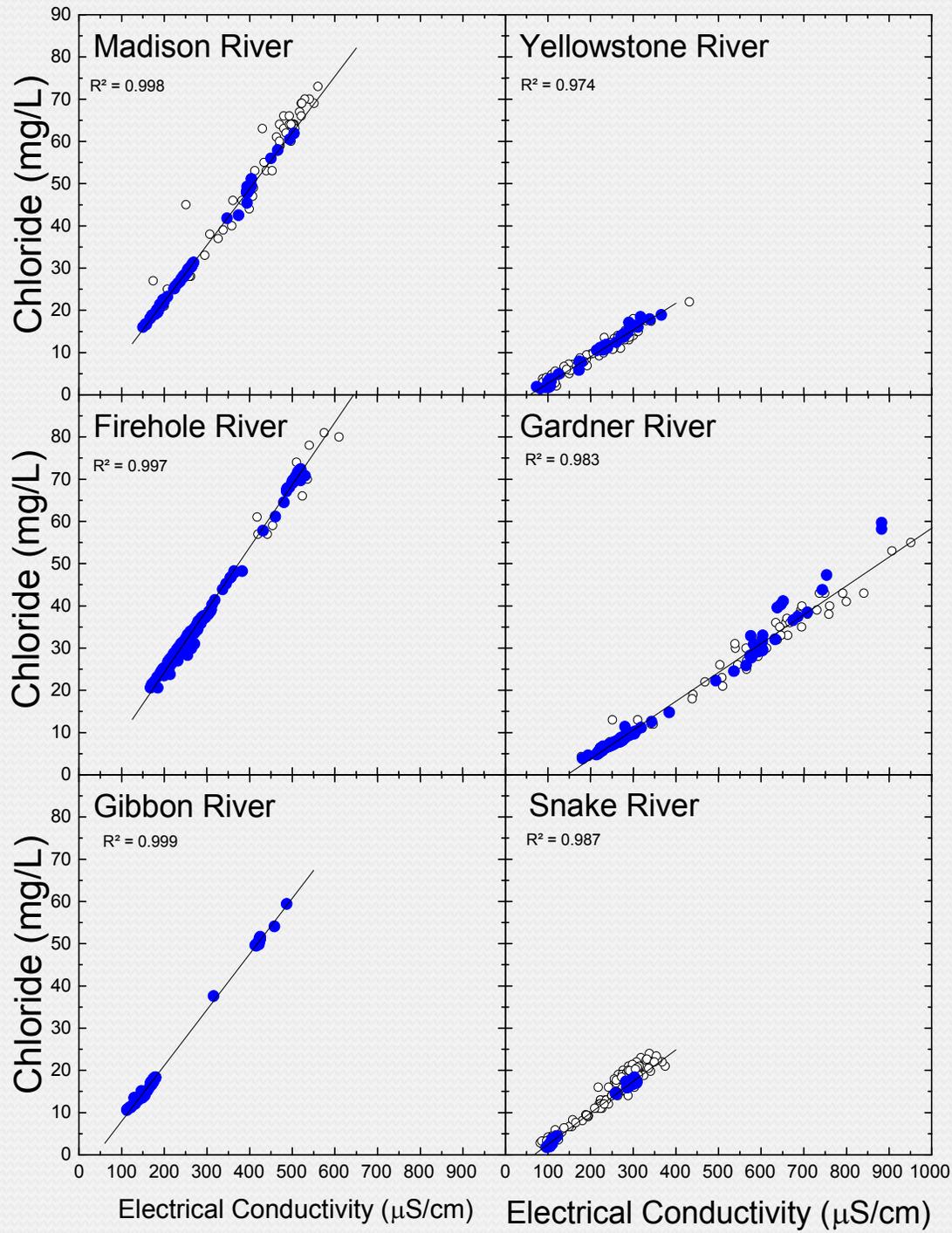
EC - Cl correlation



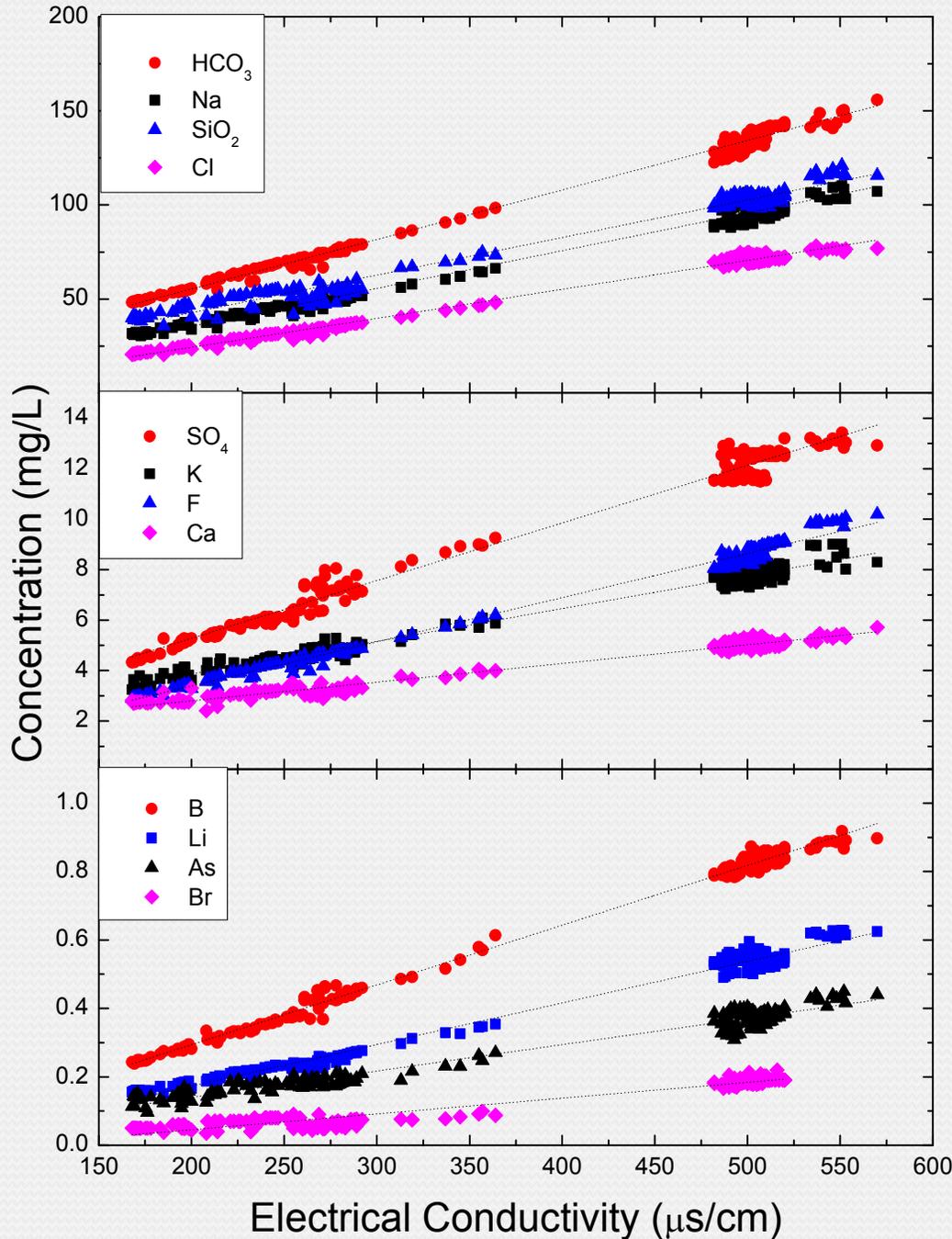
Snake River



Chloride-Electrical Conductivity Correlations



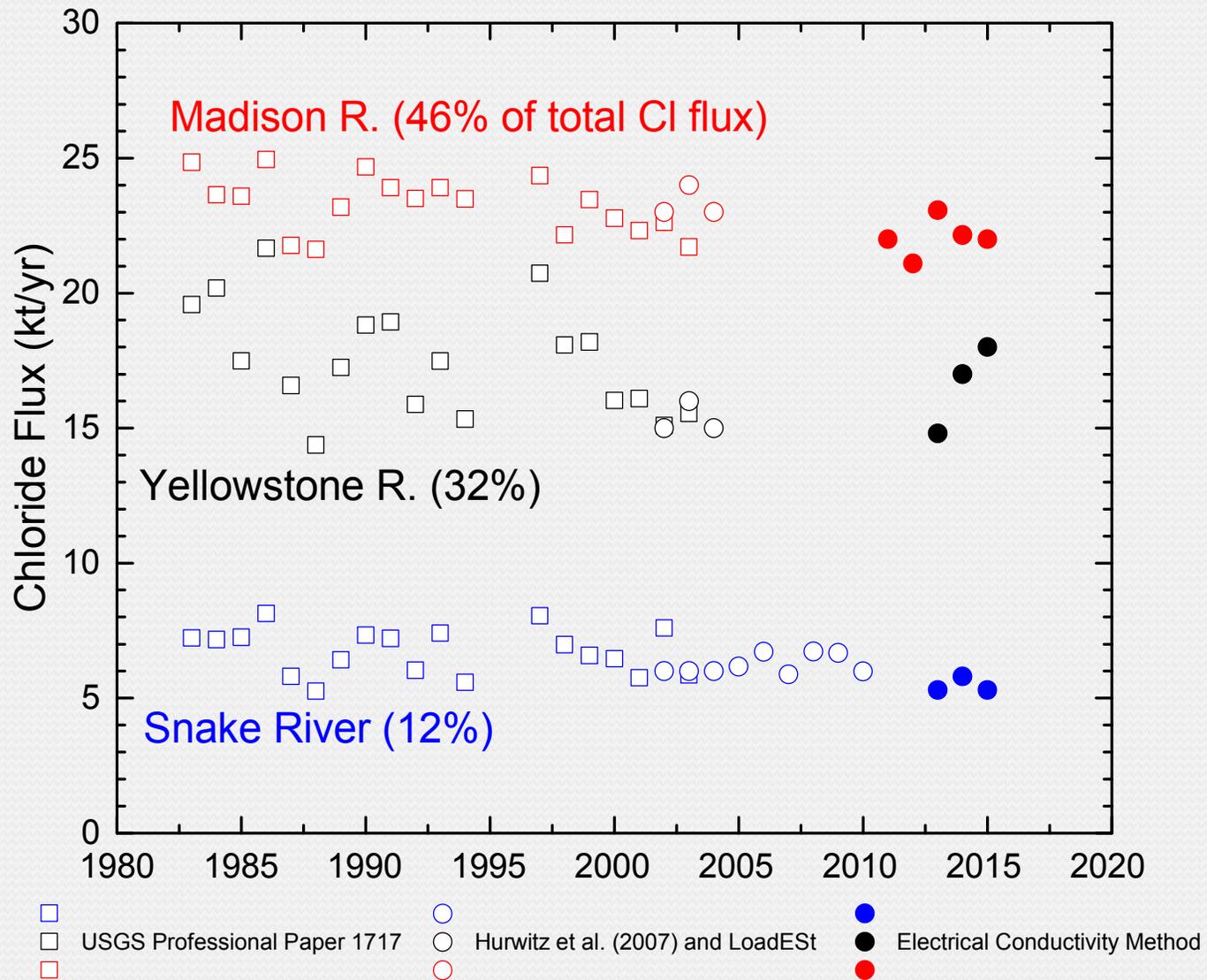
Solute-Electrical Conductivity Correlations

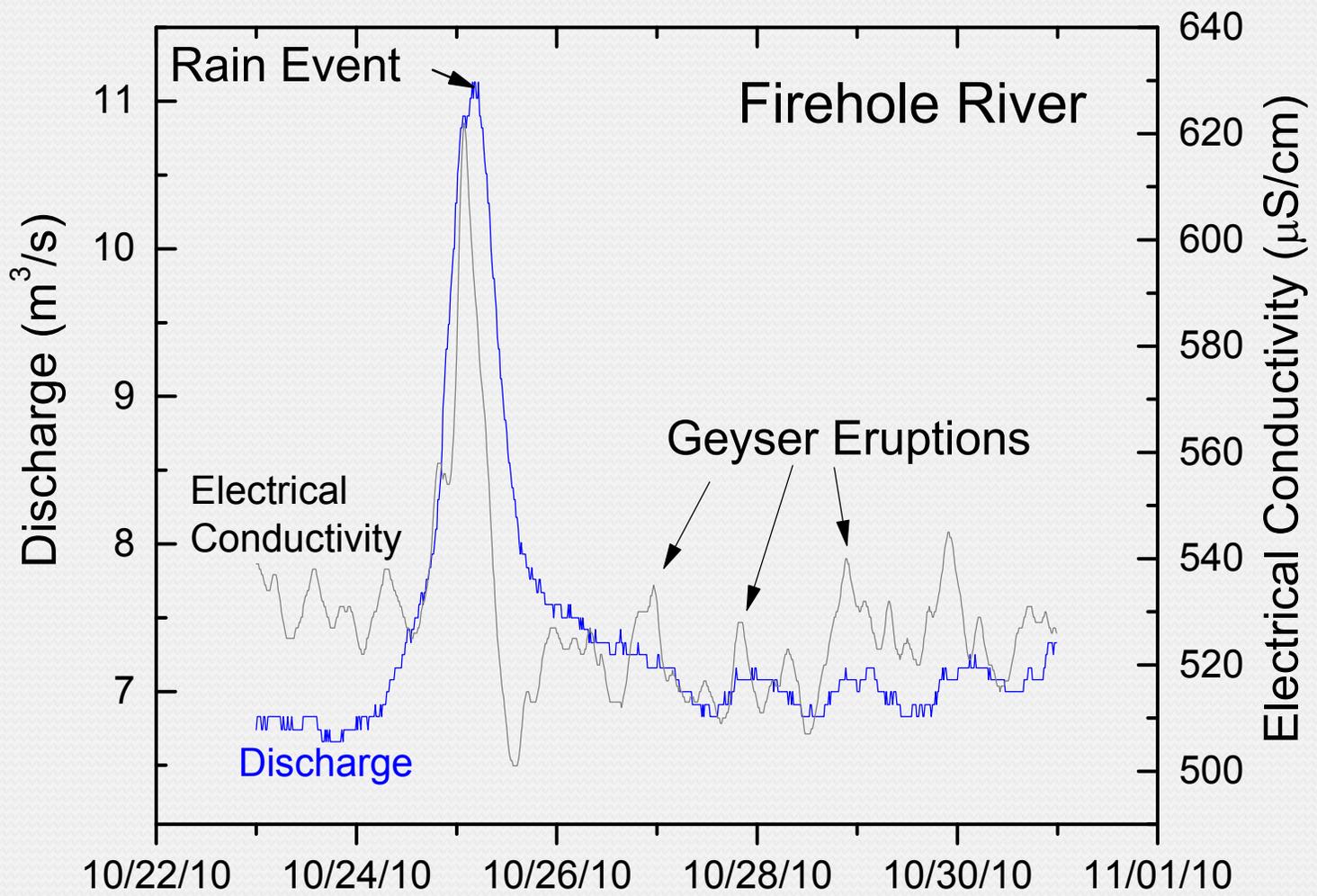


Firehole River

In addition to Cl, 12 other solutes correlate well ($R^2 > 0.95$) with electrical conductivity

Annual Cl Flux





Readily estimate water chemistry at popular swimming holes



Advantages of Continuous Electrical Conductivity Monitoring

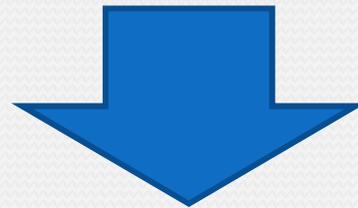
- Primary goal – Cl flux (instantaneous and annual)
- Cost- and labor-effective alternative to previous protocols
- Eliminate data gaps
- High resolution data
 - Depending on river insight into geyser eruptions and the effects of storms
- EC correlates well with several solutes
 - Solute flux leaving the park
 - Estimate concentrations at popular swimming holes

Continuously measure EC

- USGS real-time
(Madison, Firehole, and Yellowstone)
- Data logger
(Snake, Gibbon, Gardner, Tantalus)
- **No monitoring**
(Falls River)

EC-Geothermal Solute

Madison, Firehole, and Yellowstone
Snake, Gibbon, Gardner
Method not developed - Falls River



Chloride (or other solutes) Flux

On my computer only (quarterly)!

**Goal – real time and available to NPS
and other scientists**

Electrical Conductivity (K)

$$\kappa = 1000 \sum \lambda_i m_i$$

where:

λ (ionic molal cond.) is calculated from a series of equations

m is speciated ion concentration

$$\text{where: } \lambda_i = \lambda_0(T) - A(T) \left(\frac{I^{1/2}}{1 + BI^{1/2}} \right)$$

McCleskey, R.B., Nordstrom, D.K., Ryan, J.N., and Ball, J.W., 2012, A New Method of Calculating Electrical Conductivity With Applications to Natural Waters: *Geochimica et Cosmochimica Acta*, v. 77, p. 369-382.

[<http://www.sciencedirect.com/science/article/pii/S0016703711006181>]

$$\kappa_{25} = \frac{\kappa}{1 + \alpha(t - 25 \text{ } ^\circ\text{C})}$$

Non-linear α (ISO 7888): Circumneutral pH
 $\alpha = T_H \alpha_H + T_* \alpha_*$: pH < 4 (Tantulus Cr.)

McCleskey, R.B., 2013, New Method for Electrical Conductivity Temperature Compensation: *Environmental Science & Technology*, v. 47, p. 9874-9881. [<http://dx.doi.org/10.1021/es402188r>]

Electrical Conductivity

Transport Numbers

- The relative contribution of an ion to the overall electrical conductivity

$$t_i = \frac{\lambda_i}{\Lambda} = \frac{\lambda_i m_i}{\sum_{i=1}^n (\lambda_i m_i)}$$

- Transport numbers ($t_i > 10\%$) – Na, Cl, HCO₃, SO₄, Ca
- Despite low t_i , B, SiO₂, As, and F correlate well with EC (Low concentration or uncharged species)
 - Fairly constant solute/Cl ratio in YNP thermal waters
 - Conservative in rivers

