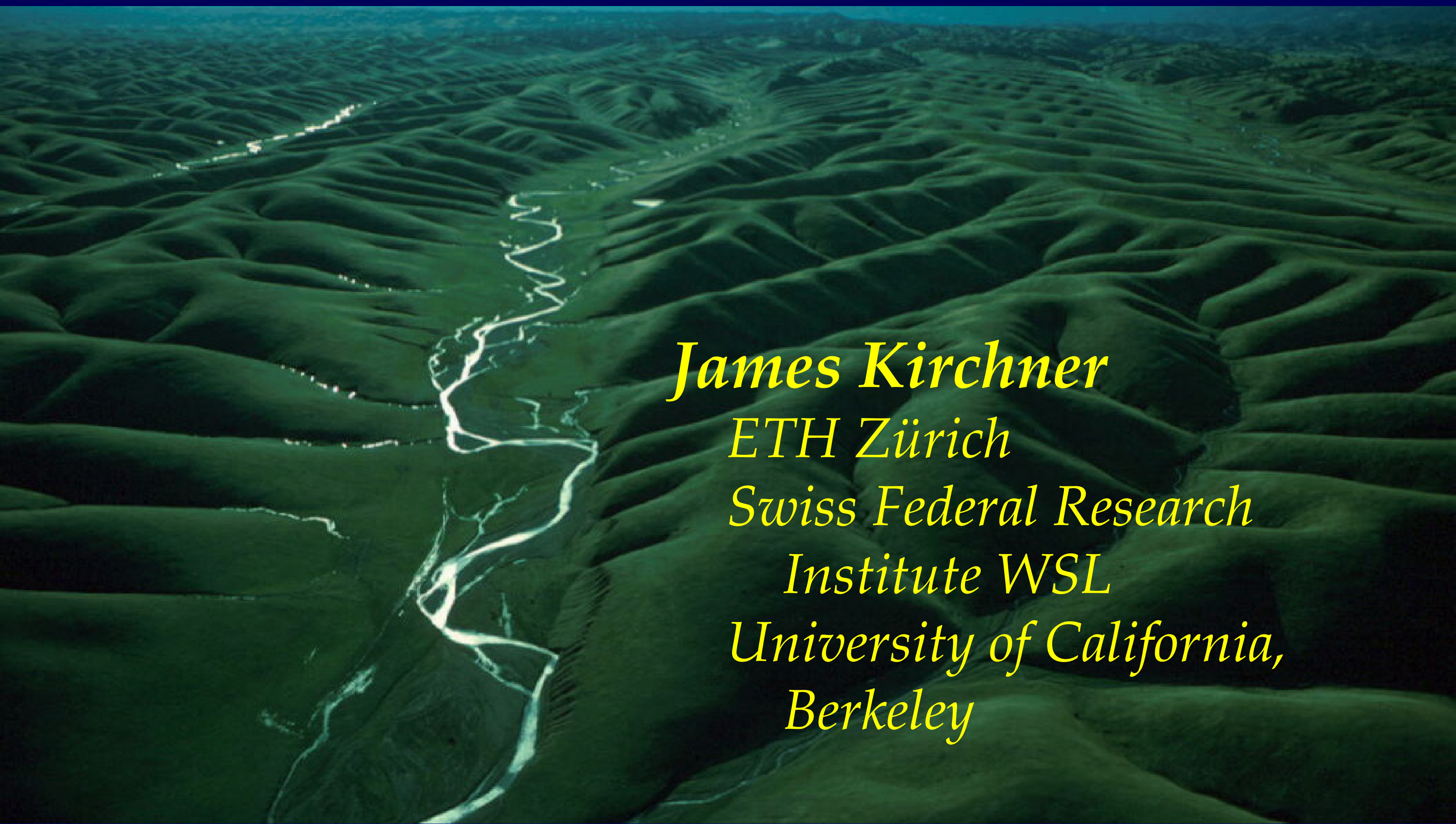
# *Water quality on time scales from hours to decades: diurnal cycles, fractal spectra, non-self-averaging, and challenges for trend detection*



***James Kirchner***

*ETH Zürich*

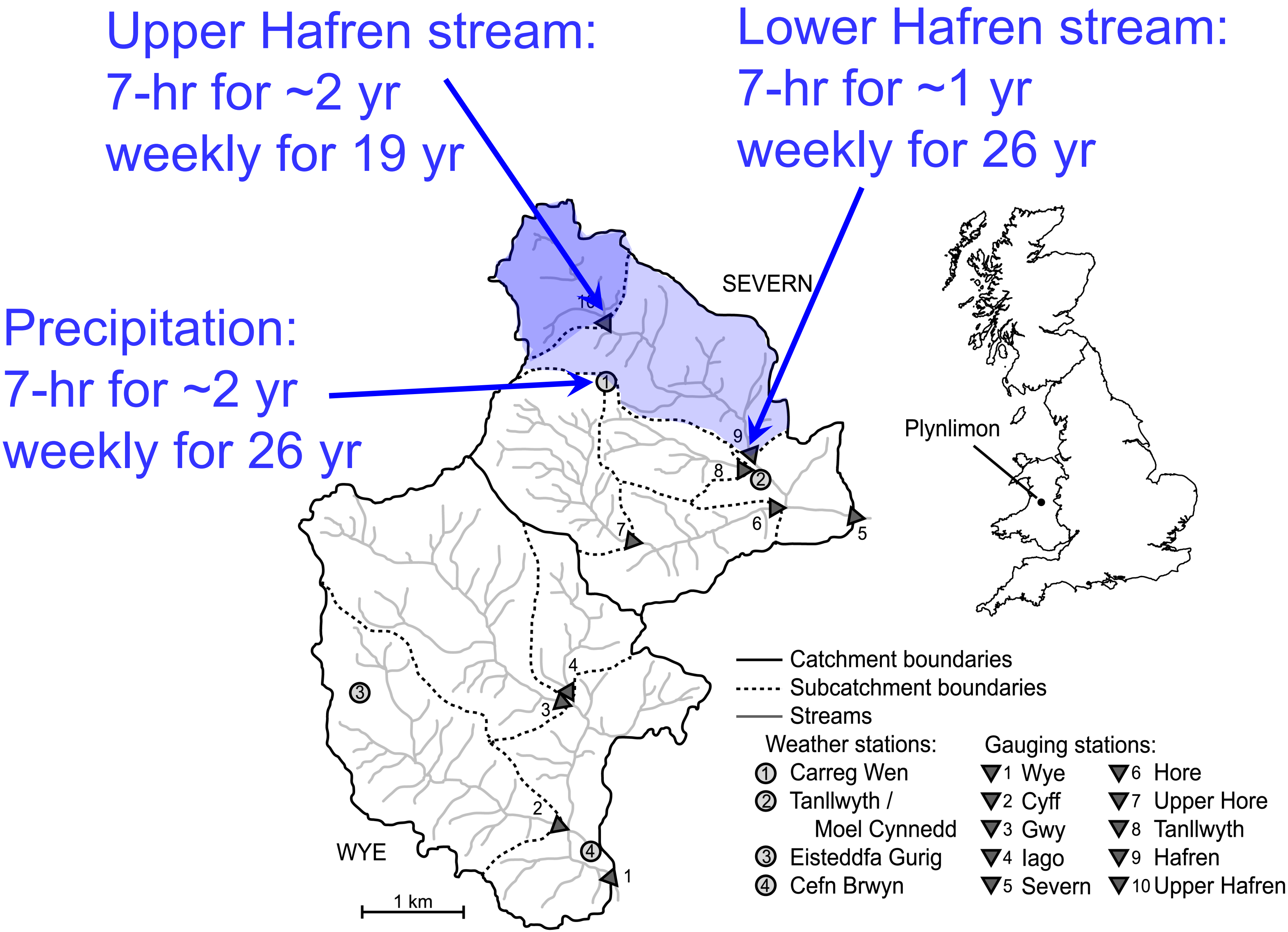
*Swiss Federal Research Institute WSL*

*University of California, Berkeley*

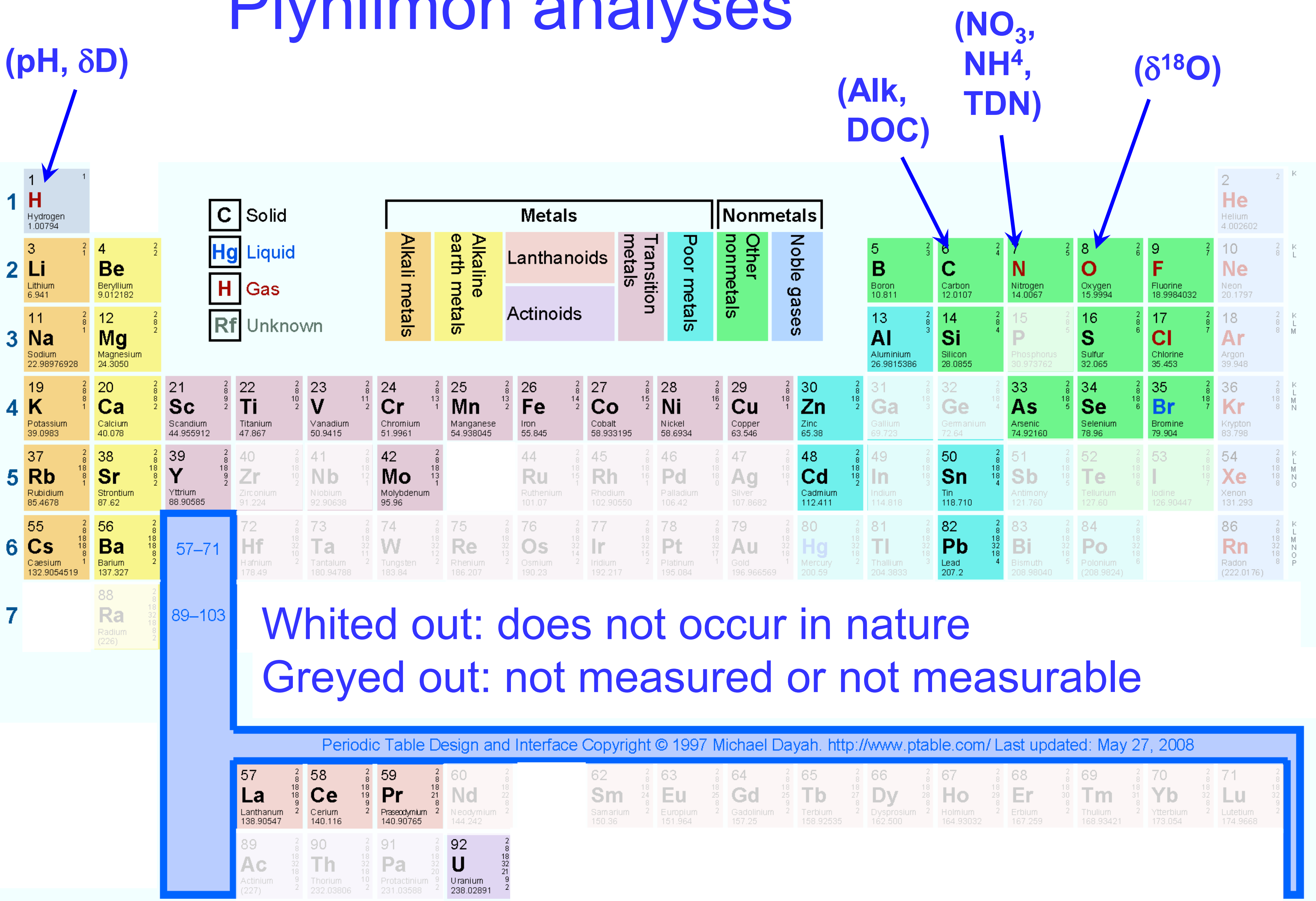
# Plynlimon hydrochemical data set, unique worldwide:

Precipitation and stream flow
- two small catchments in Wales
- sampled ***every 7 hours for 1-2 years***
- analyzed for ***~everything*** (present at ≥ ppt)
  45 analytes from $H^+$ to U
- ***24-30 years of weekly analyses*** are also available (same analytes and same sites)

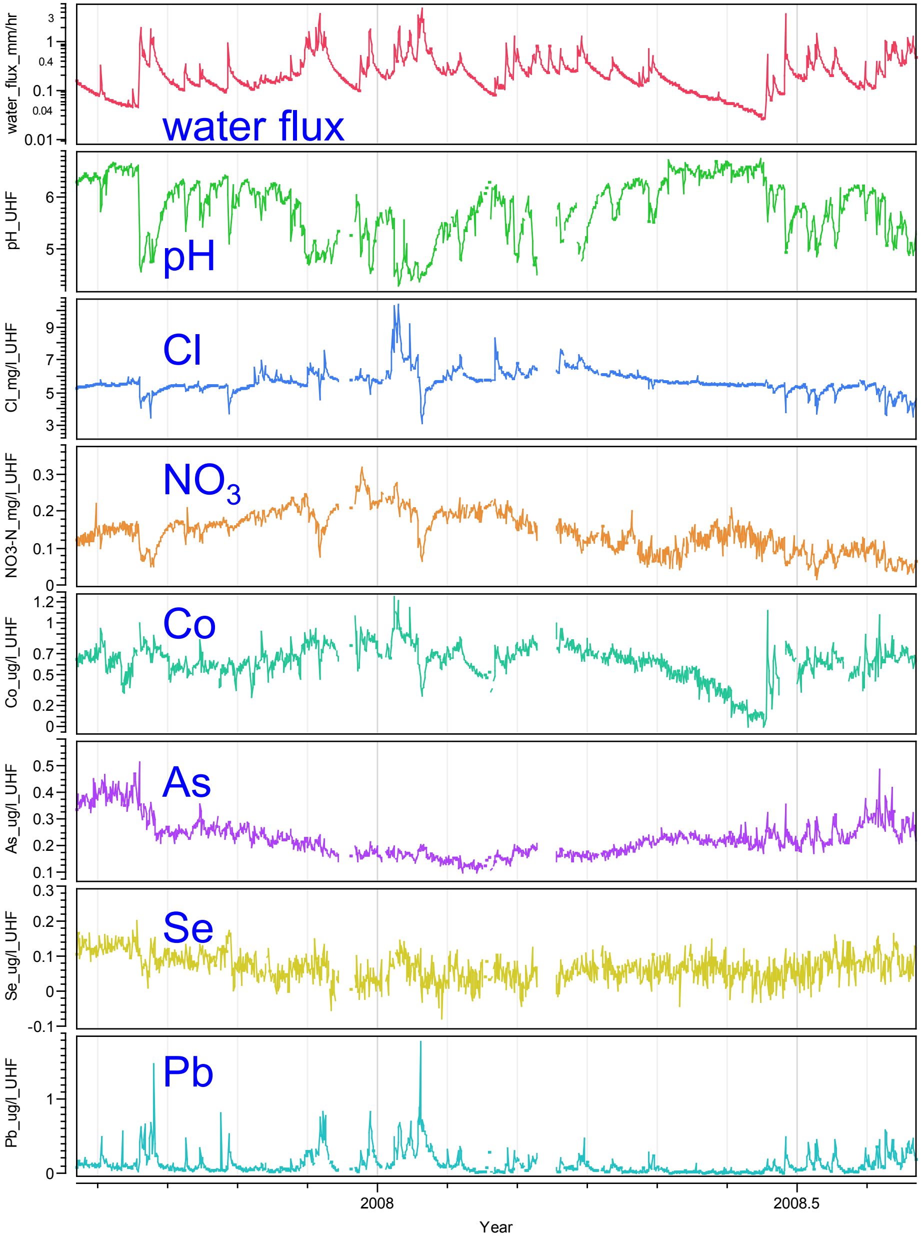
The guy who made it happen:
***Colin Neal***
***Centre for Ecology and Hydrology, UK***


Upper Hafren stream:
7-hr for ~2 yr
weekly for 19 yr
Lower Hafren stream:
7-hr for ~1 yr
weekly for 26 yr
Precipitation:
7-hr for ~2 yr
weekly for 26 yr
SEVERN
WYE
Plynlimon
1 km
Catchment boundaries
Subcatchment boundaries
Streams
Weather stations:
1 Carreg Wen
2 Tanllwyth / Moel Cynnedd
3 Eisteddfa Gurig
4 Cefn Brwyn
Gauging stations:
1 Wye
2 Cyff
3 Gwy
4 Iago
5 Severn
6 Hore
7 Upper Hore
8 Tanllwyth
9 Hafren
10 Upper Hafren

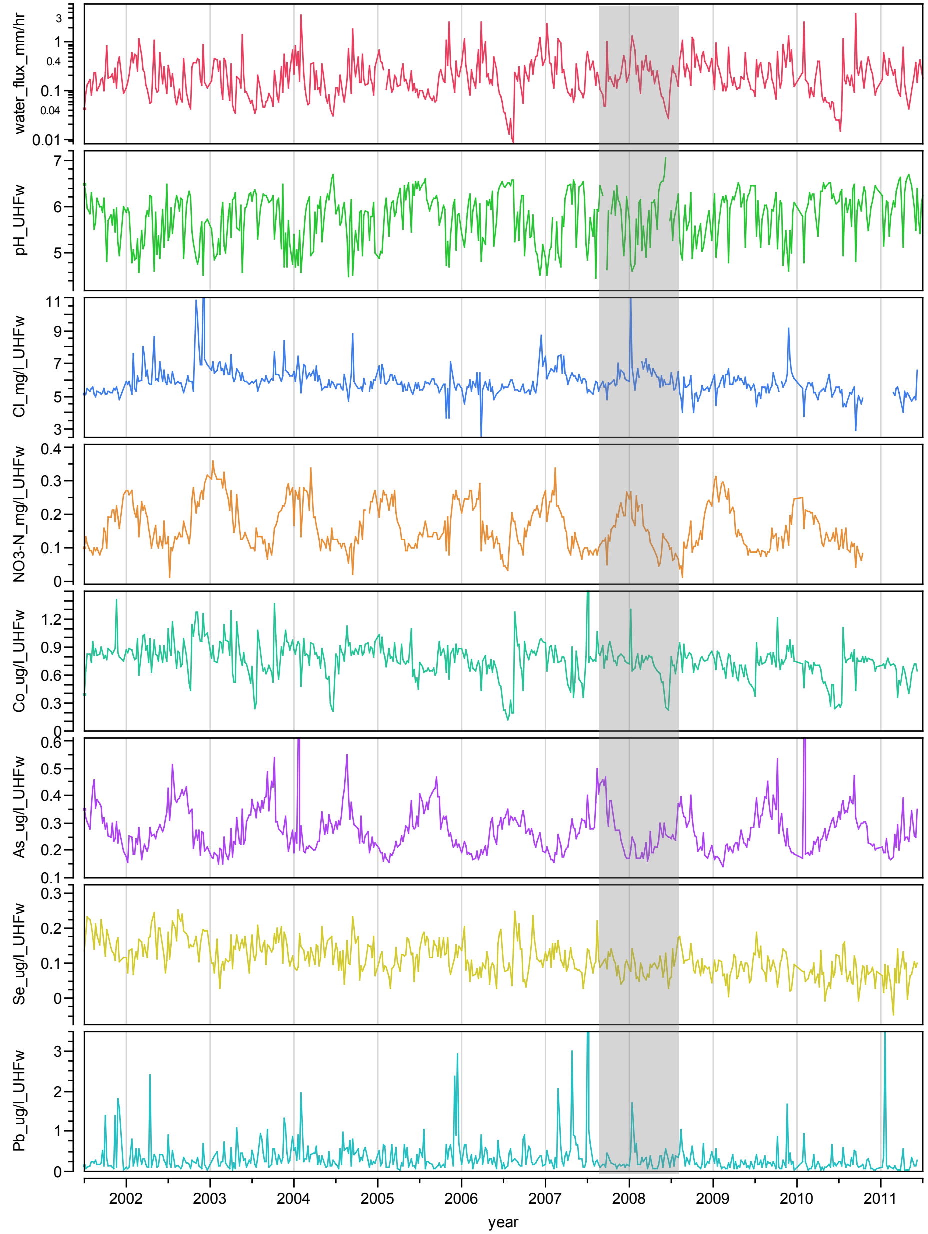
# Plynlimon analyses



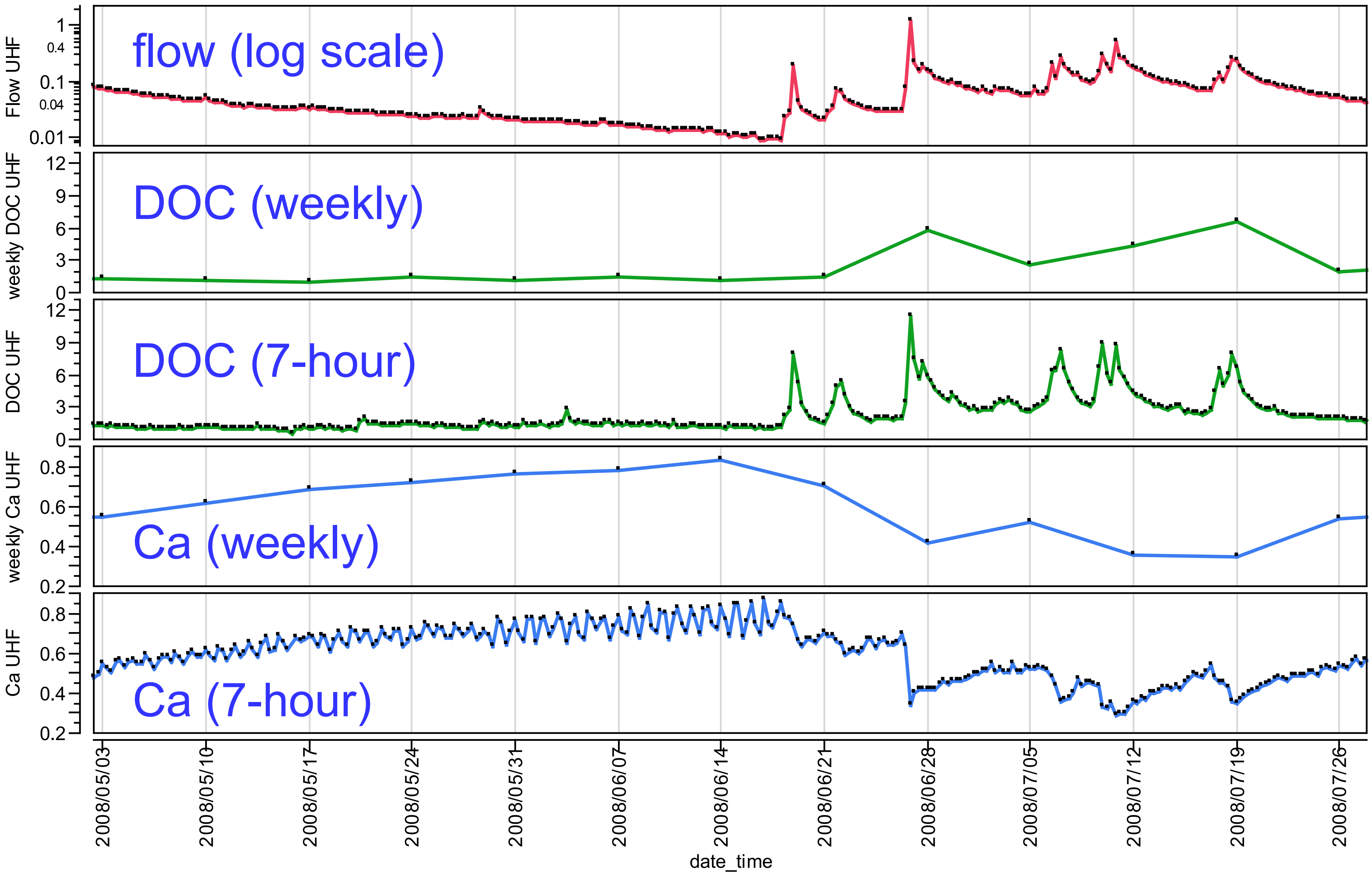
# Every 7 hours for a year
# (*half* of the high-freq. record)



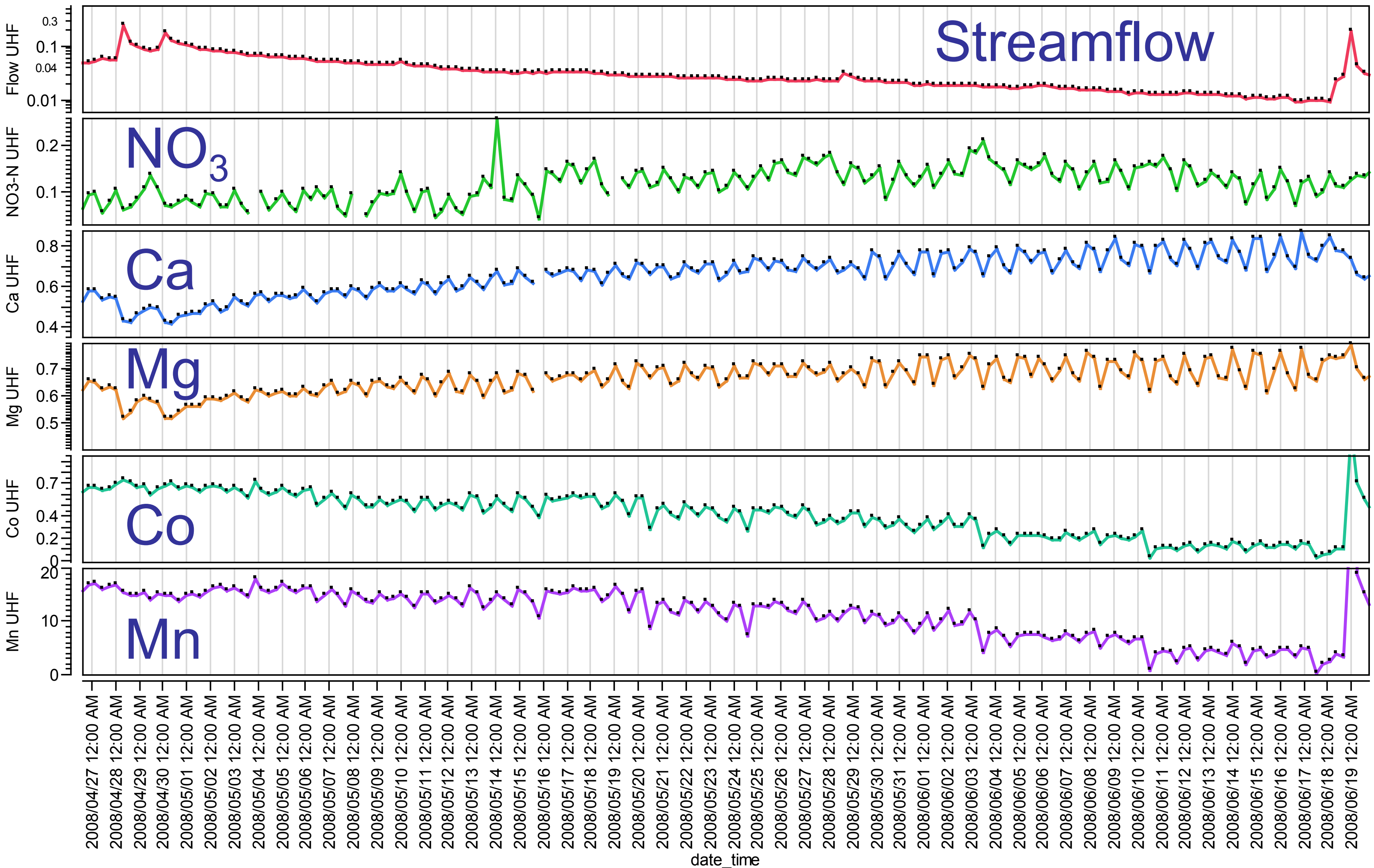

# Every 7 days for a decade
# (*1/2-1/3* of the long-term record)



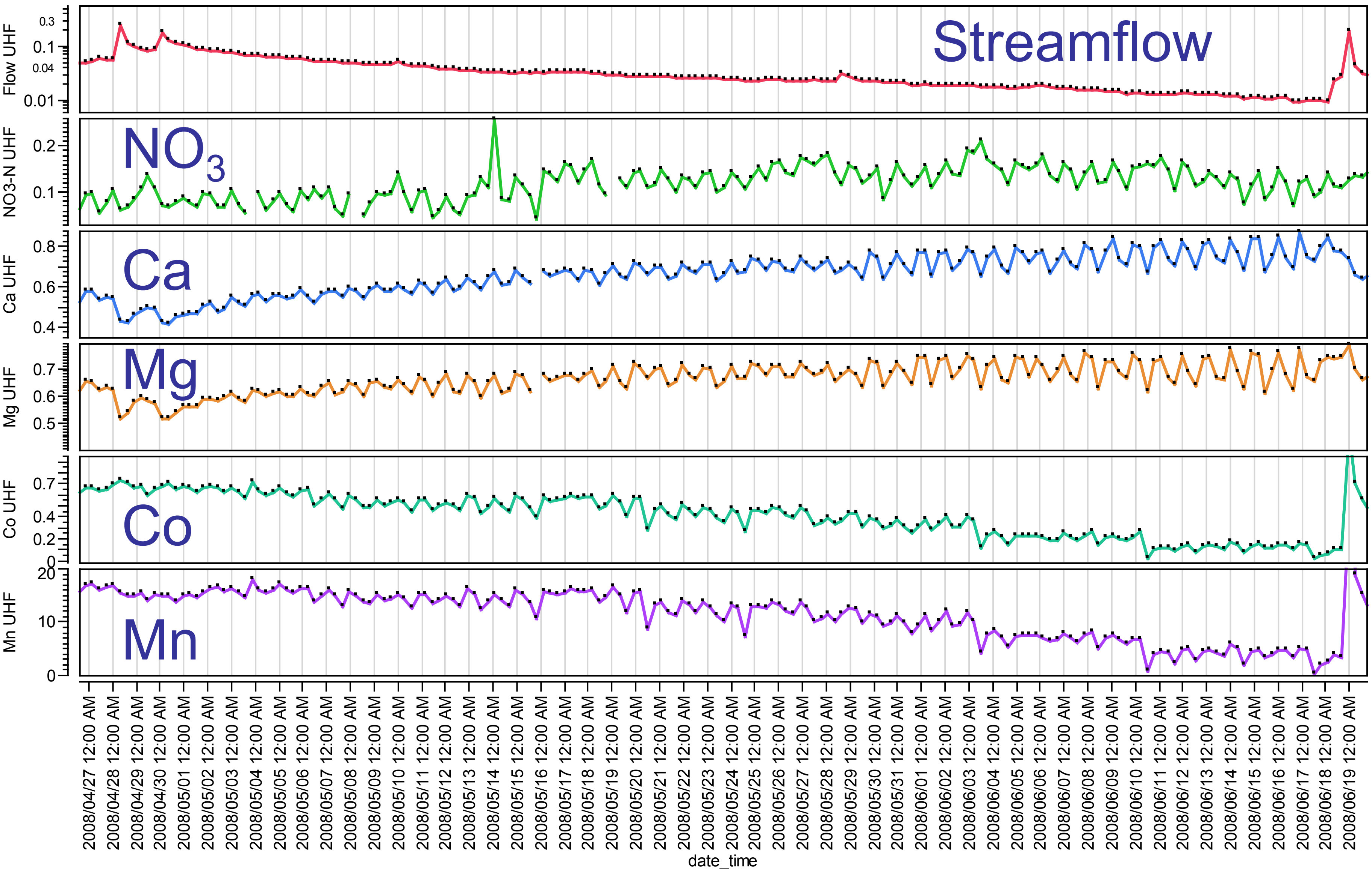
# High-frequency sampling reveals interesting dynamics!

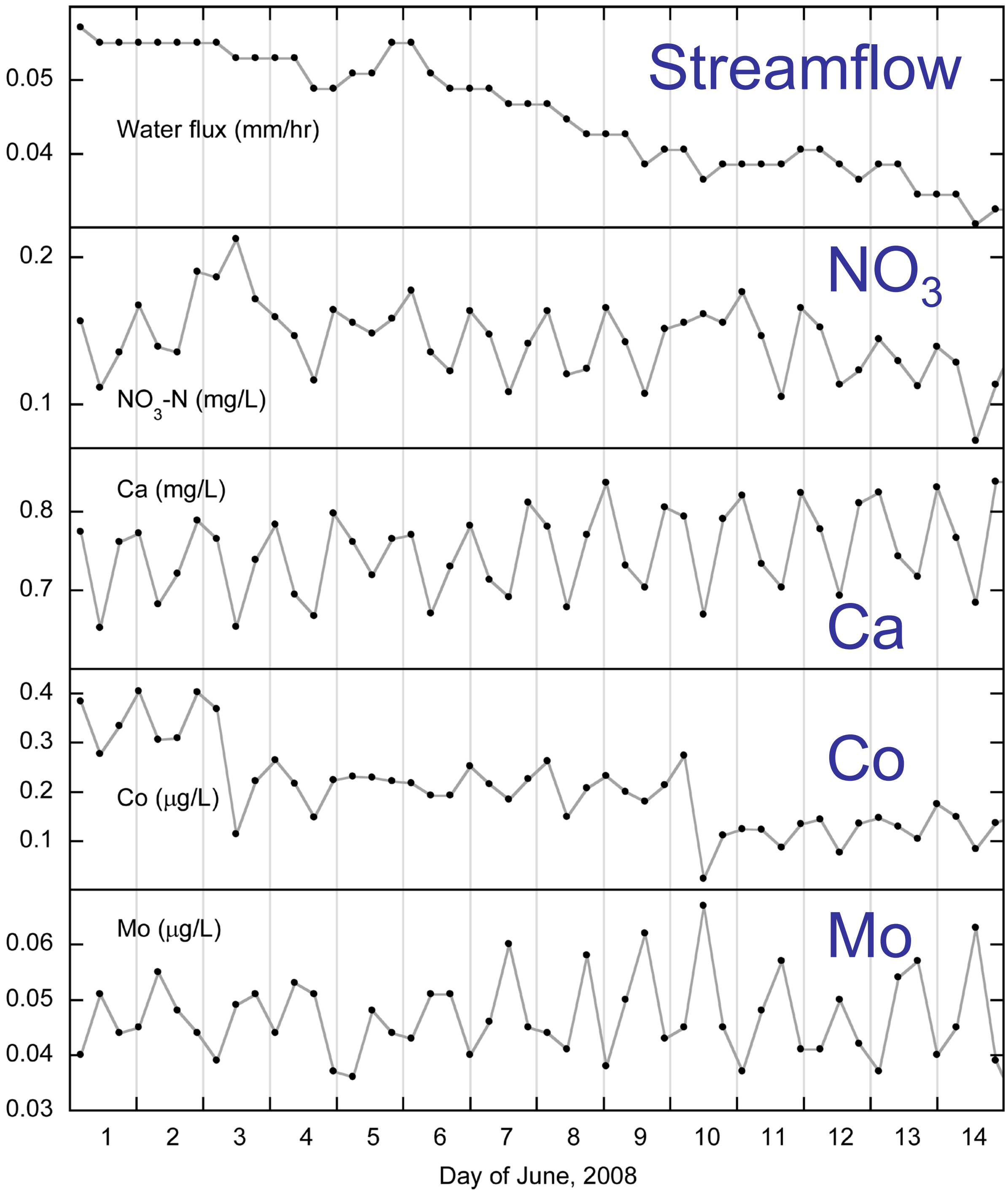


# During low-flow periods: daily cycles in ~32 elements (out of 45!).



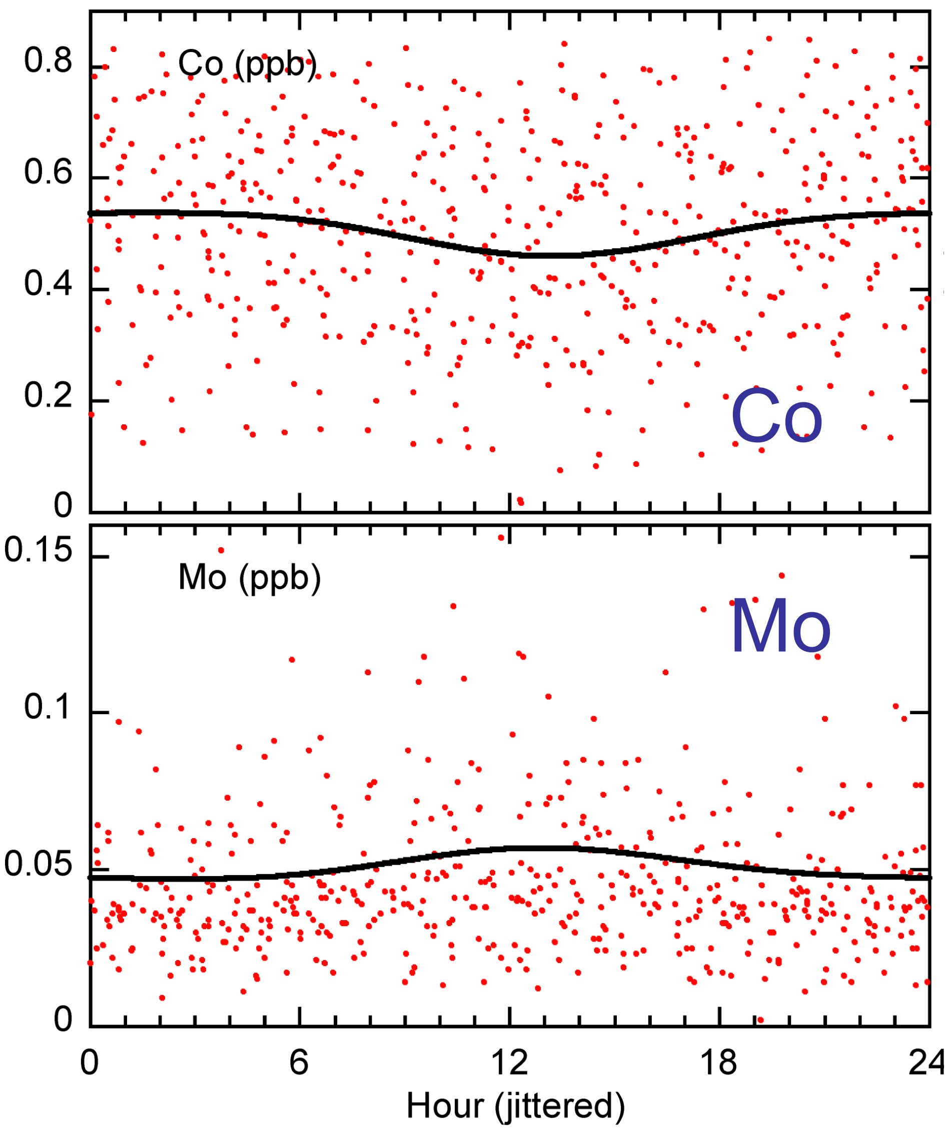
# Almost no diurnal cycle in streamflow (very humid site, ET is only ~20% of water balance).





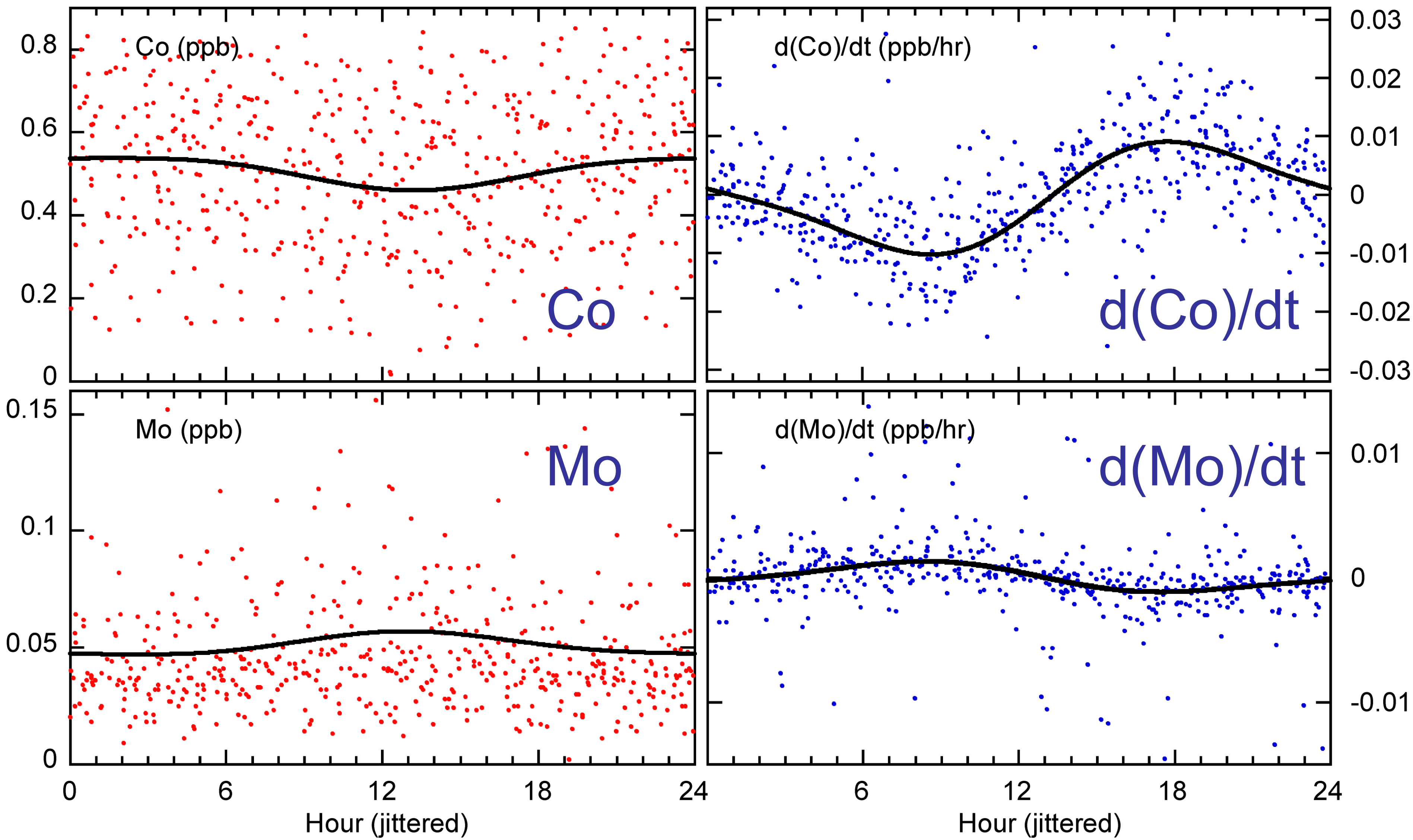

# How do we characterize the amplitude and phase of a (time-varying) 24-hour cycle, *sampled at 7-hour intervals?*

# Concentrations vs. hour show no clear pattern...

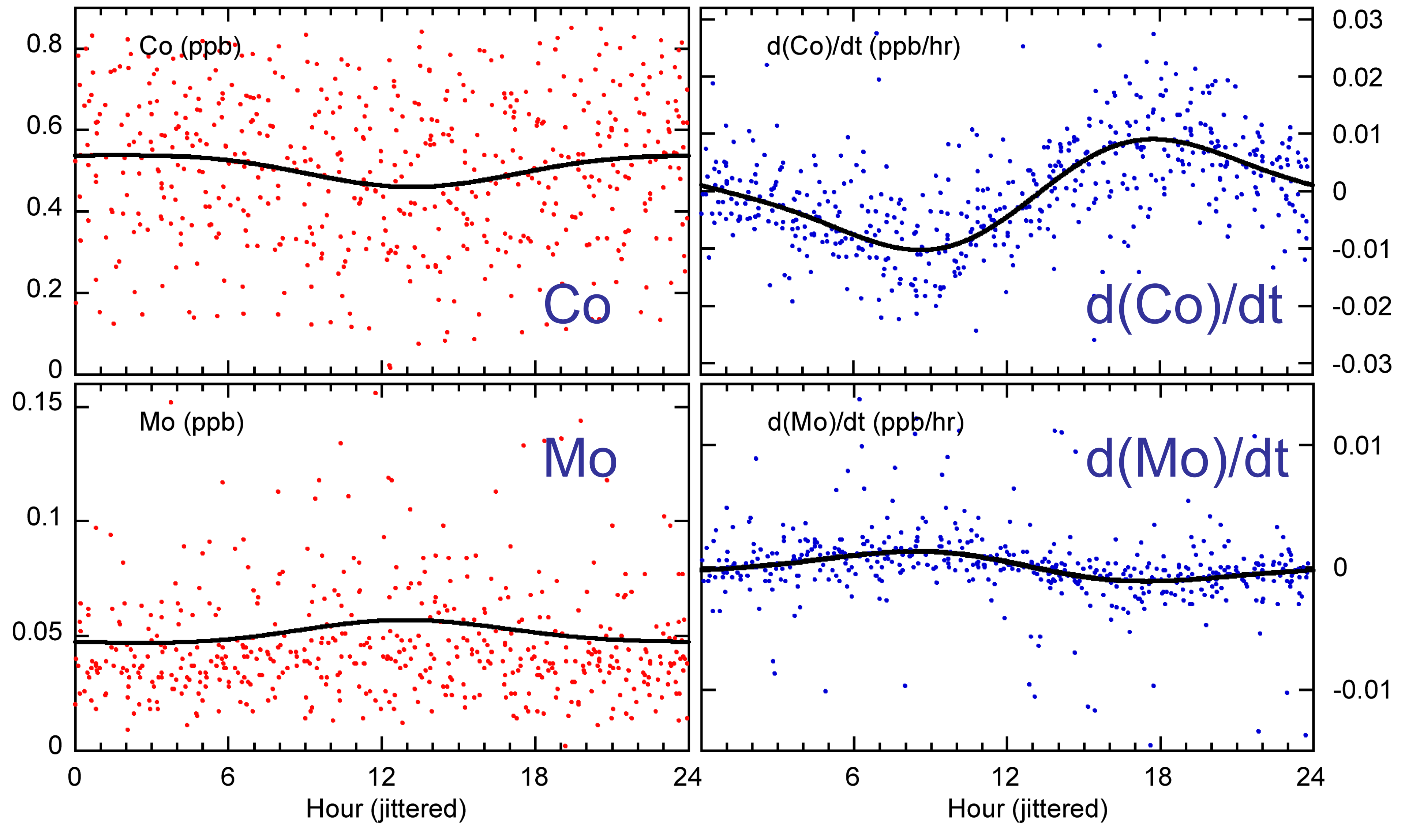


Concentrations vs. hour show no clear pattern...

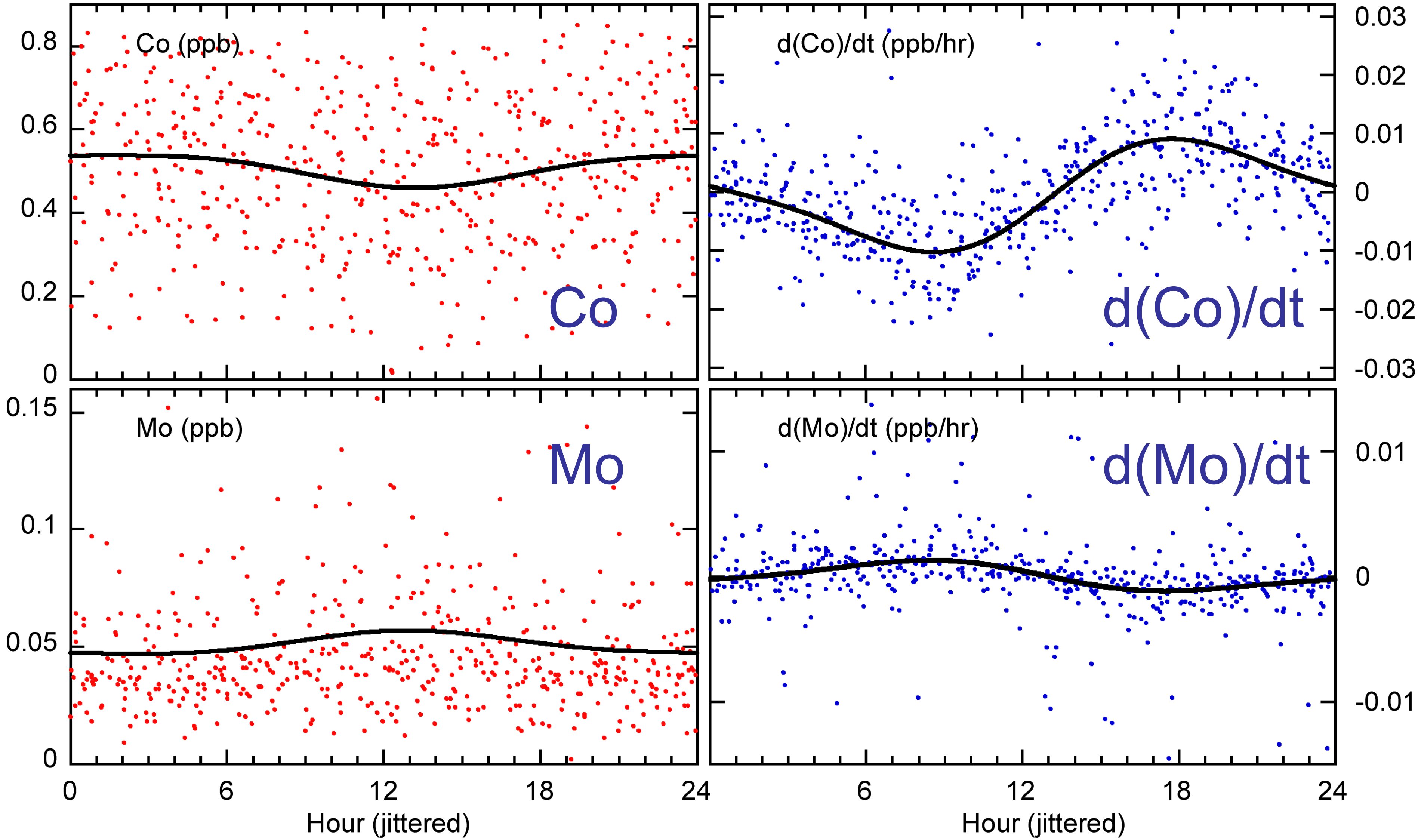
but *derivatives* vs. hour show *clear cycle*



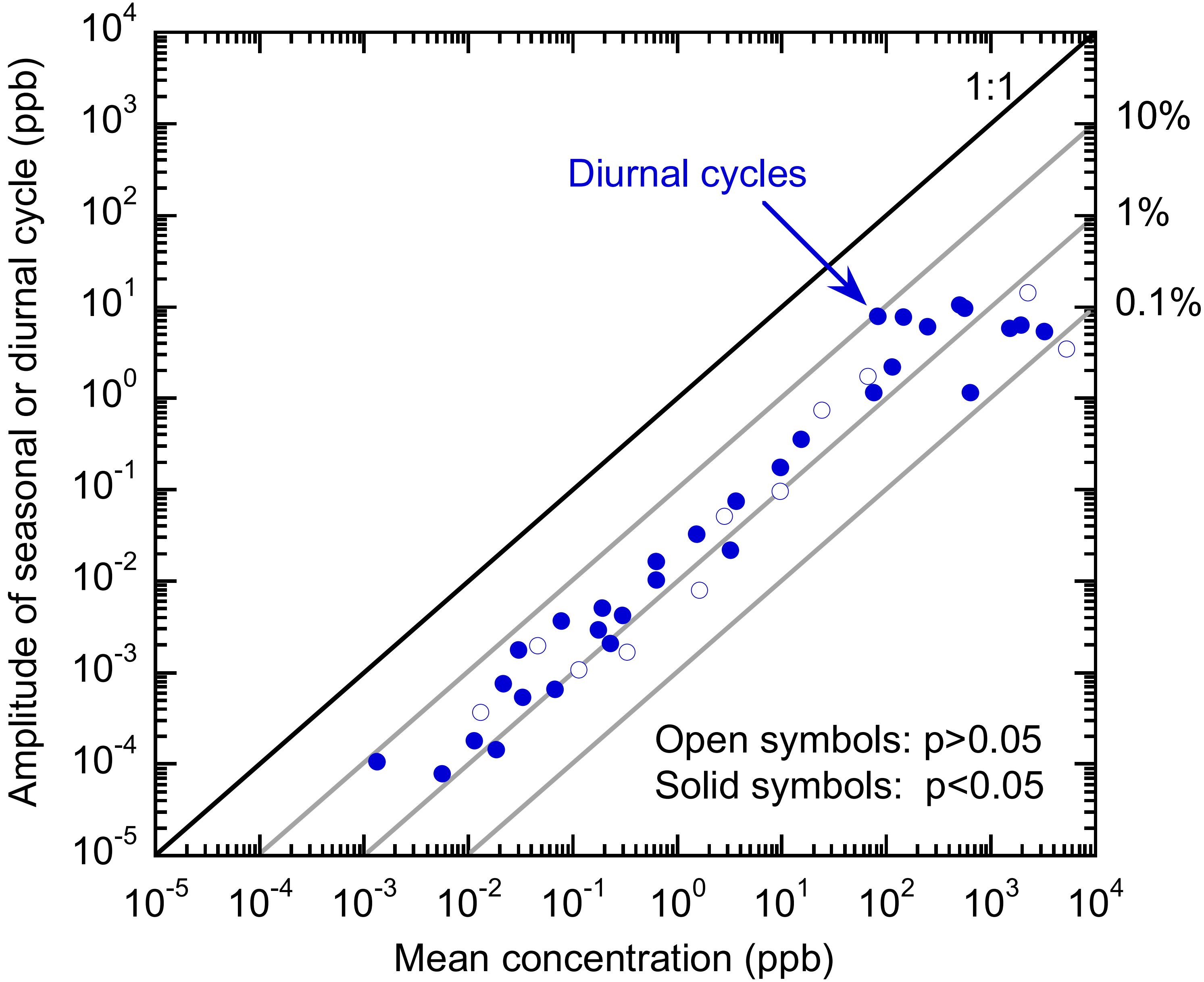
# Fit the amplitude and phase of 24-hr and 12-hr cycles (1st and 2nd harmonics) of *derivatives*, then *transform* result back into concentration space.



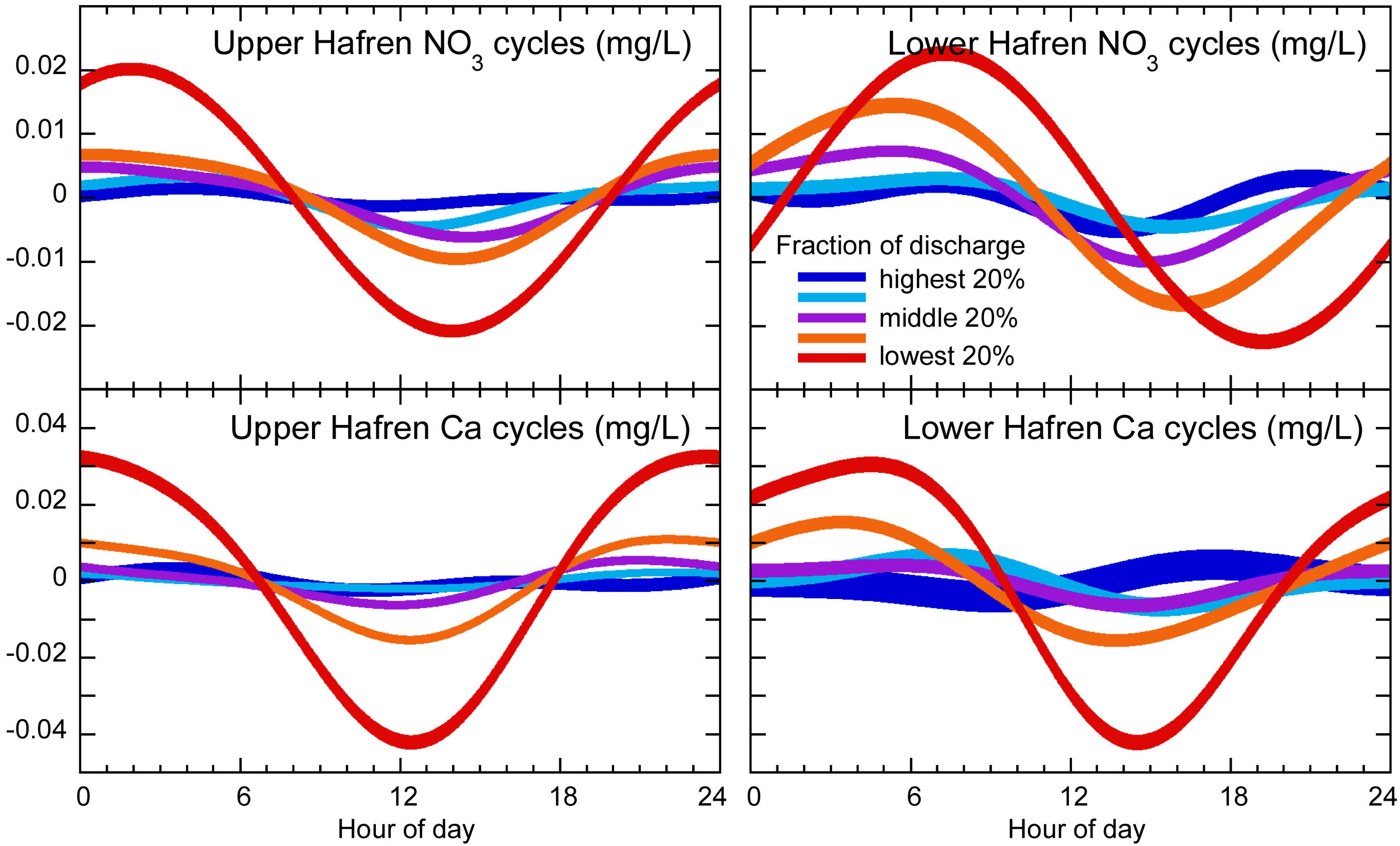
# Robust fit obtained by *Iteratively Reweighted Least Squares* (follows the bulk of the data and minimizes the influence of outliers).



# Diurnal cycles are ~ 0.4% - 4% of mean



# Diurnal cycles vary with flow, and migrate downstream

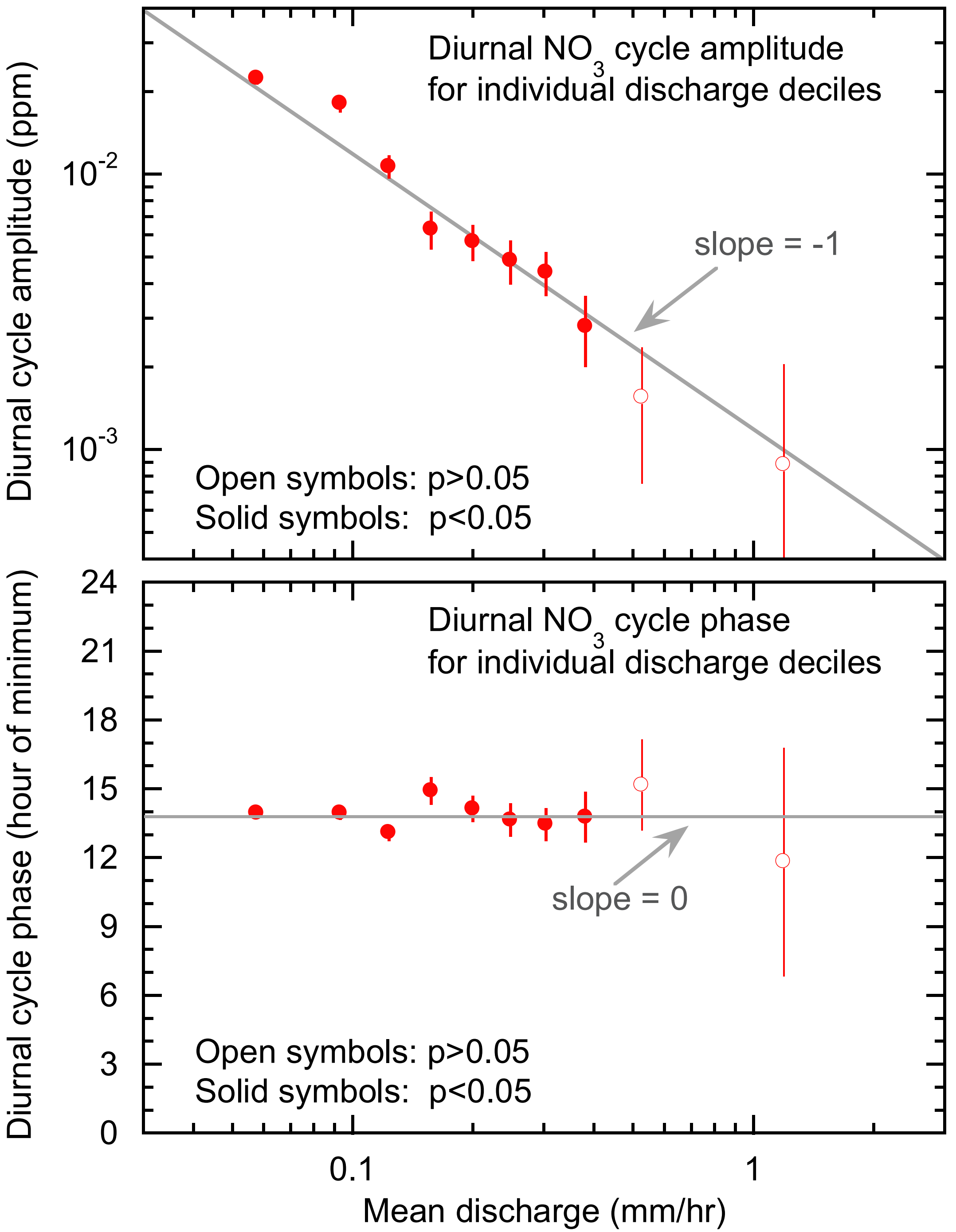


# Diurnal $NO_3$ cycles by <u>discharge deciles</u>

(lowest 10%, next 10%, etc.)

- Amplitude ~ inversely proportional to discharge

- Phase ~ constant

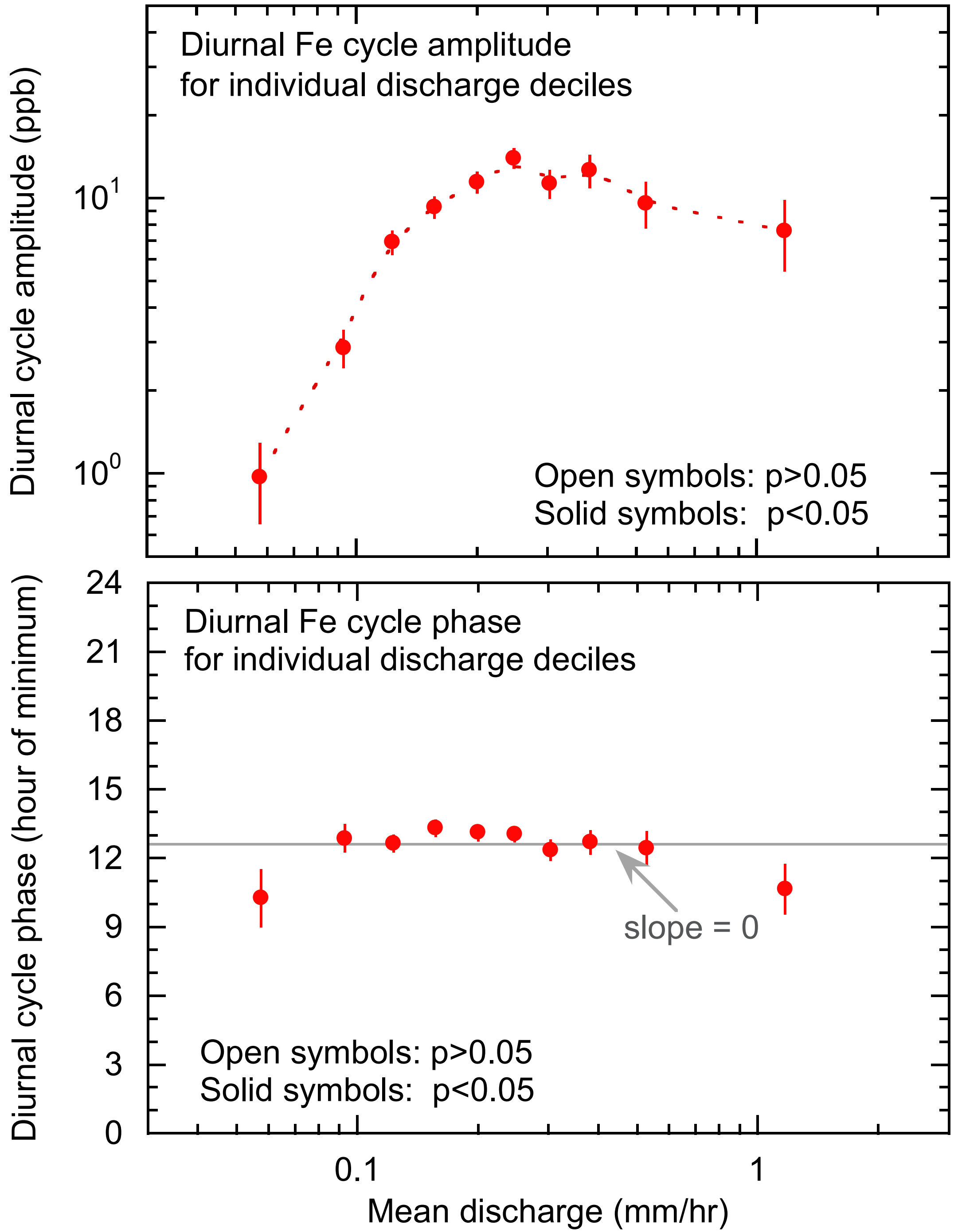


# Diurnal Fe cycles by discharge deciles

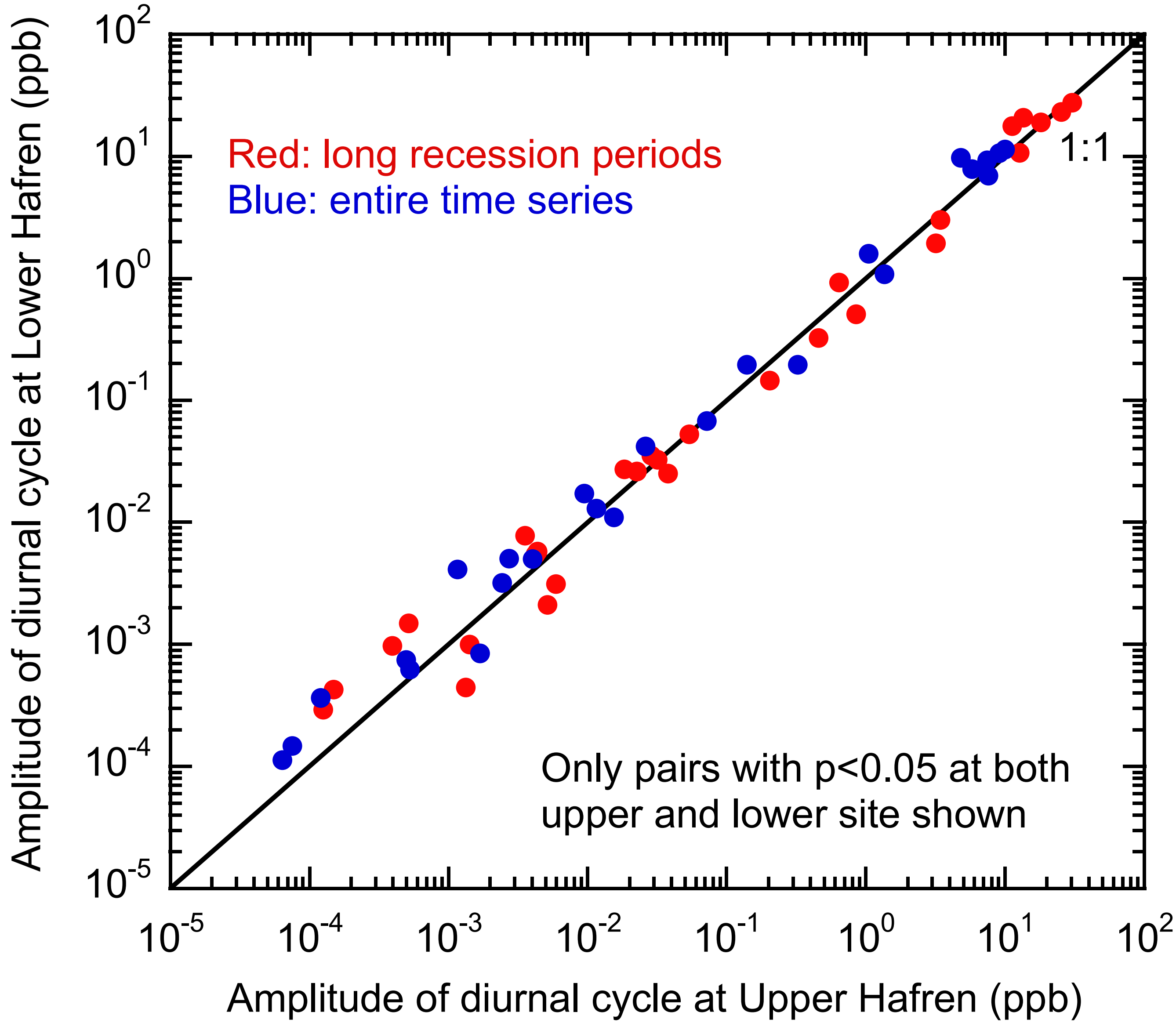
(lowest 10%, next 10%, etc.)

- Amplitude increases, then declines, with discharge

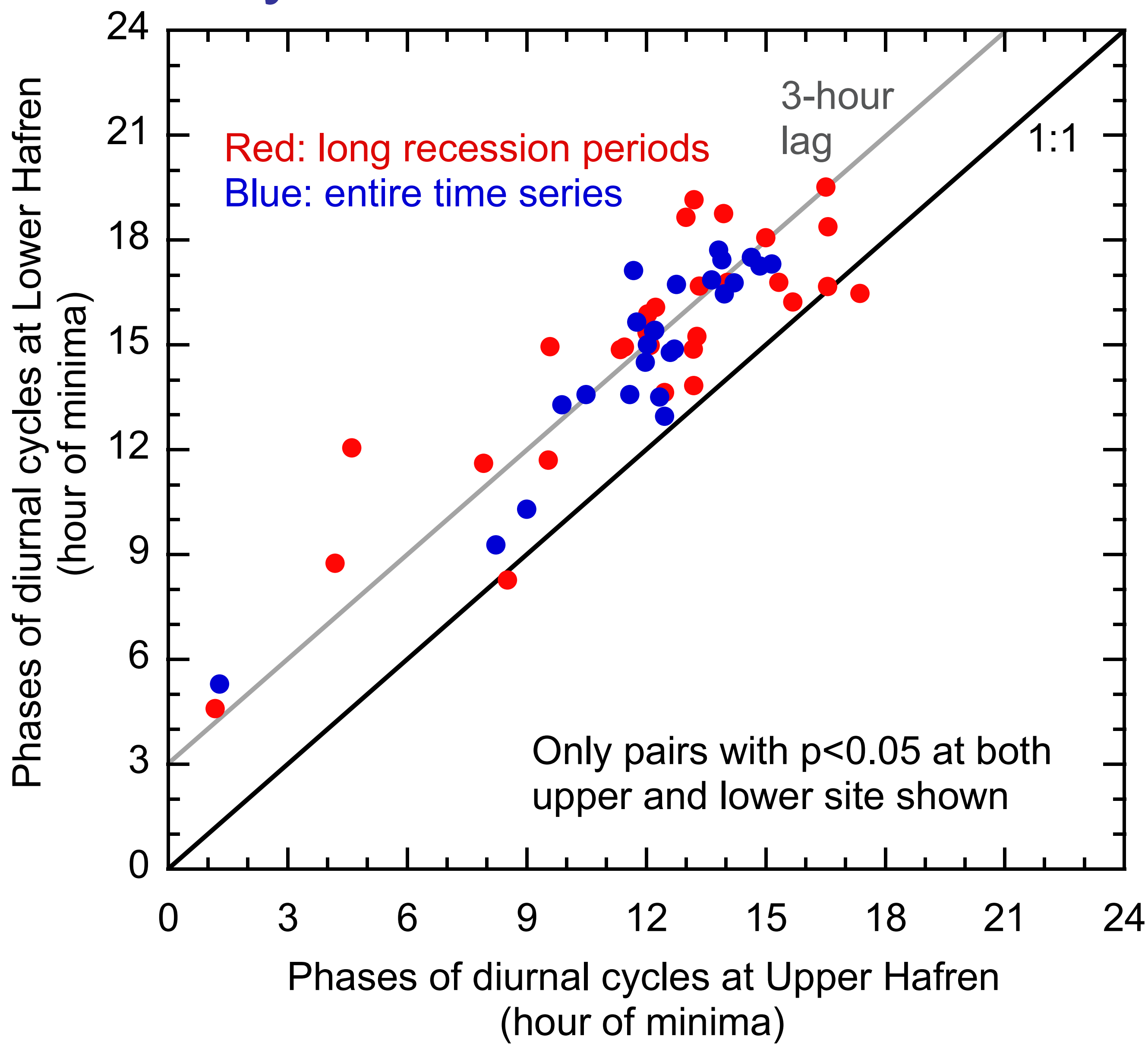
- Phase ~ constant



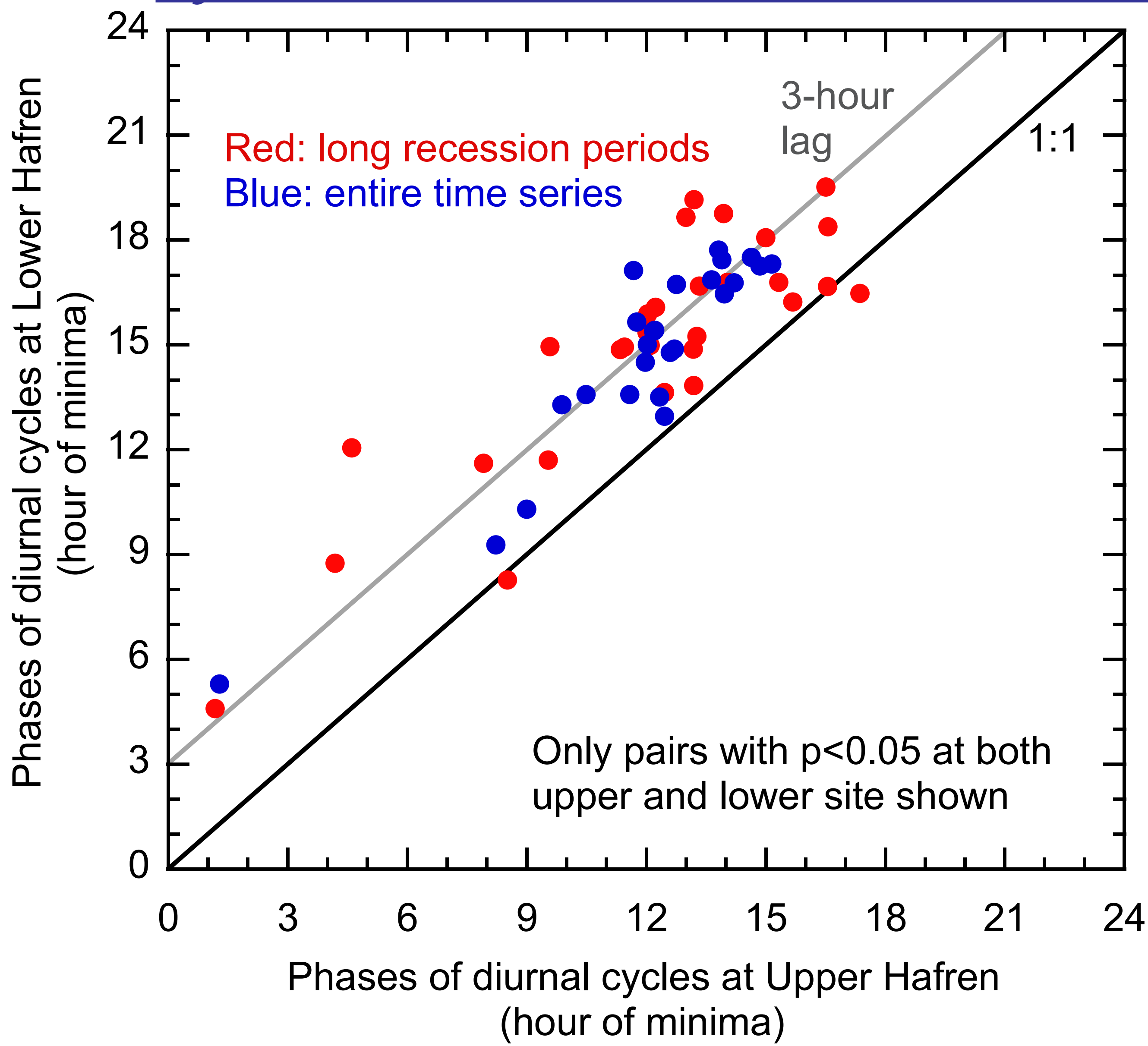
# Amplitudes of diurnal cycles: no systematic difference between upper and lower sites



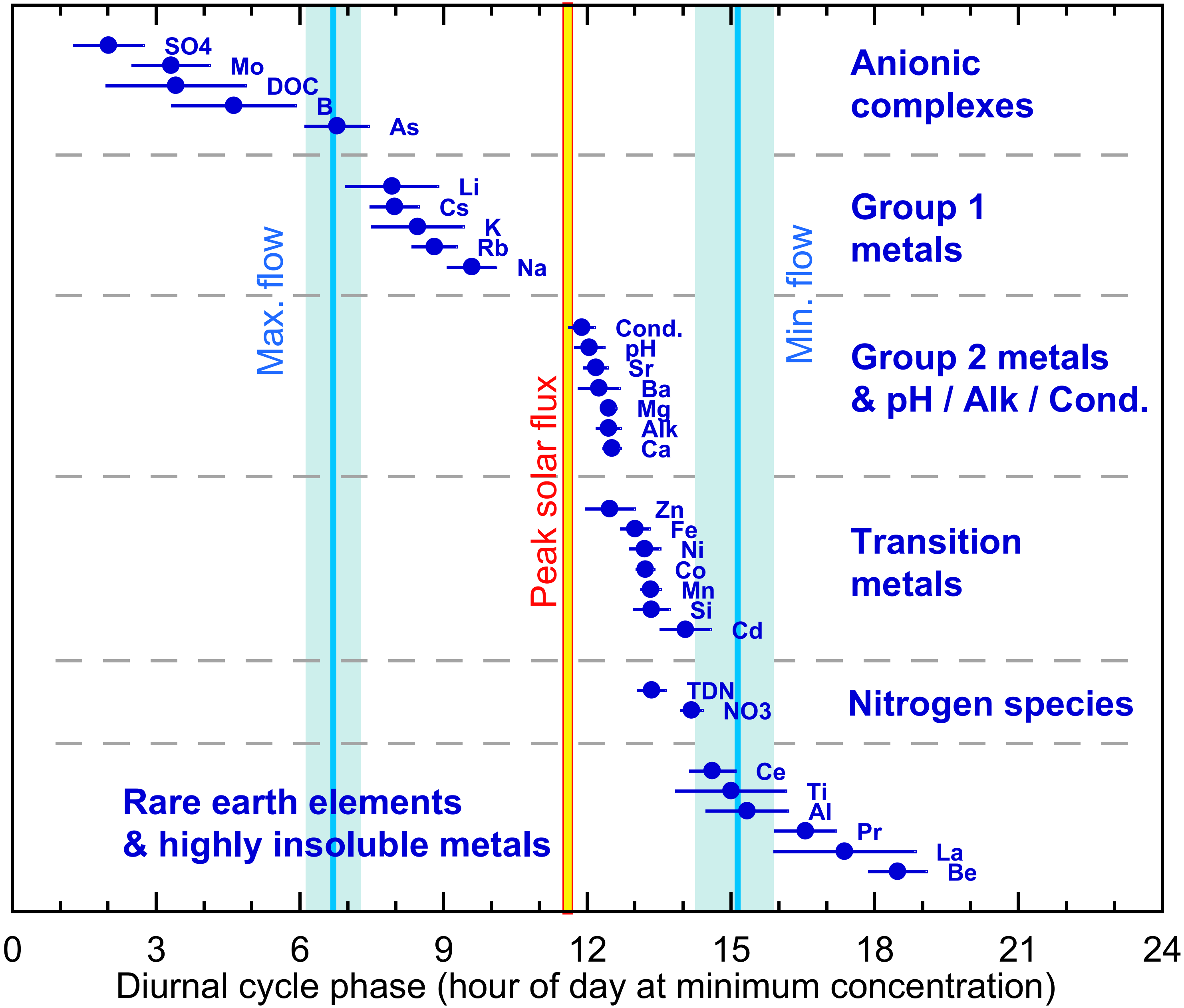
# Phases of diurnal cycles: lower site lags upper site by ~ 3 hours



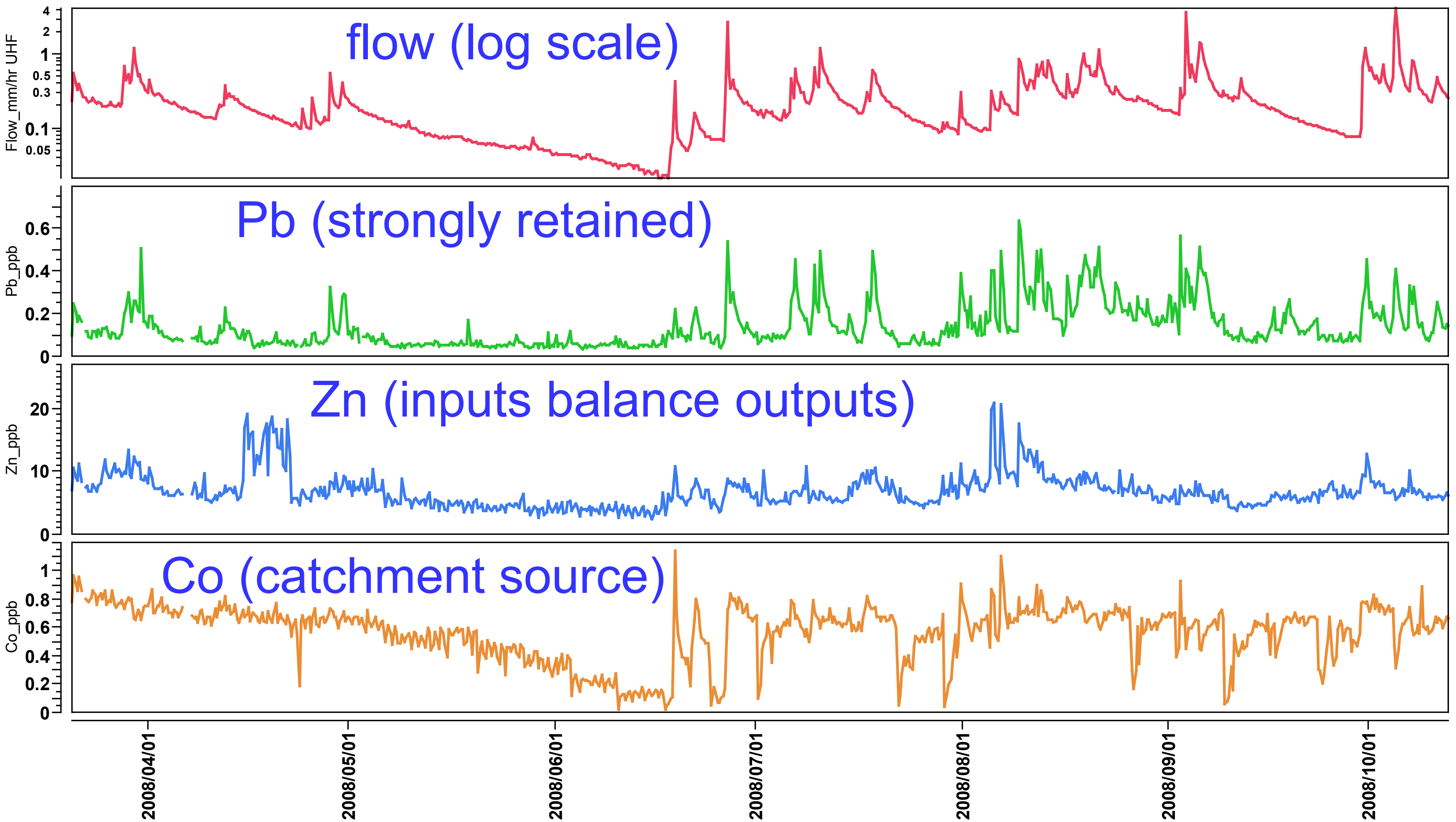
# This equals the travel time between the two sites => *cycles are advected downstream*.



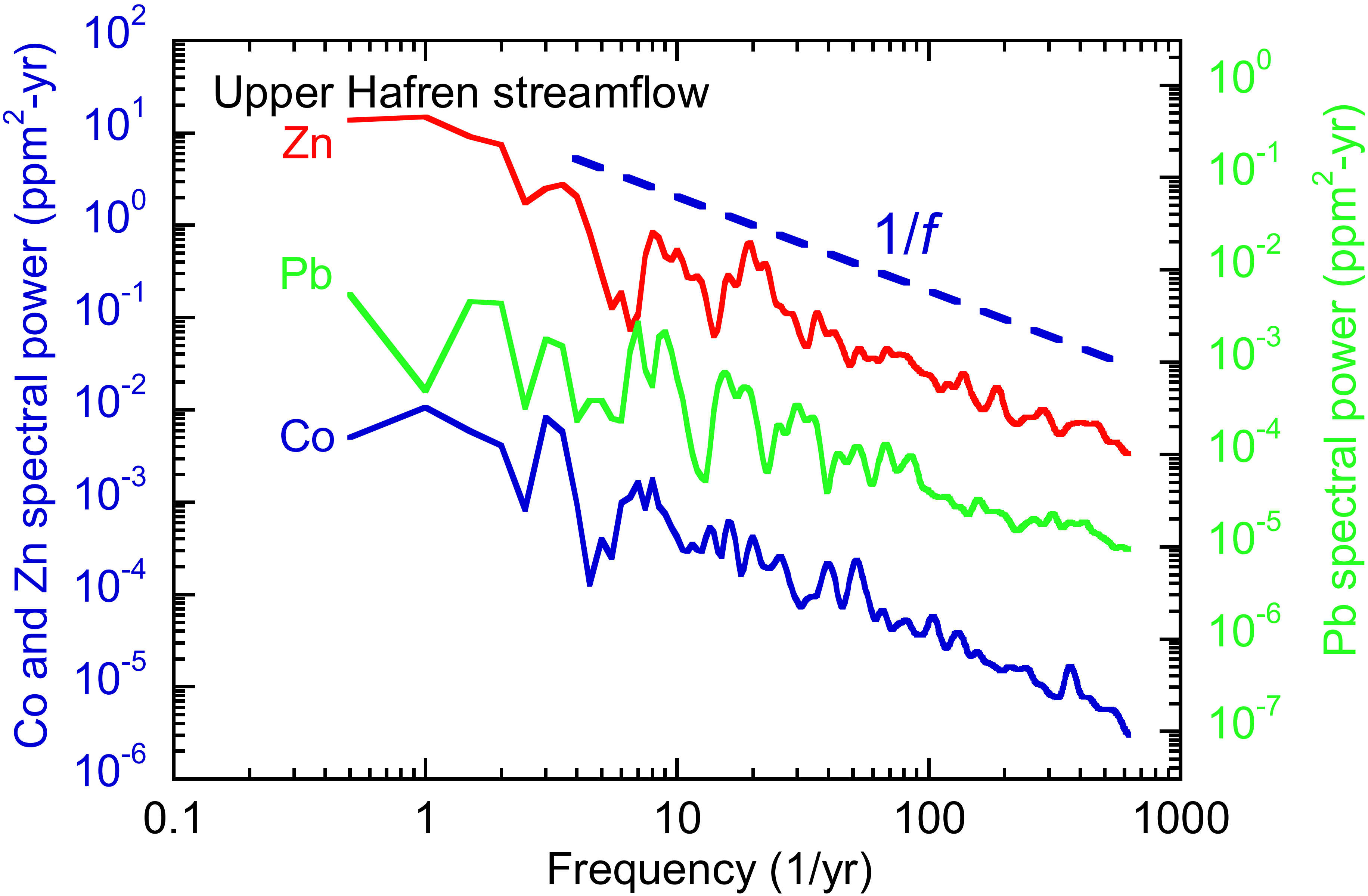
# Phases of daily cycles: landscape chromatography?

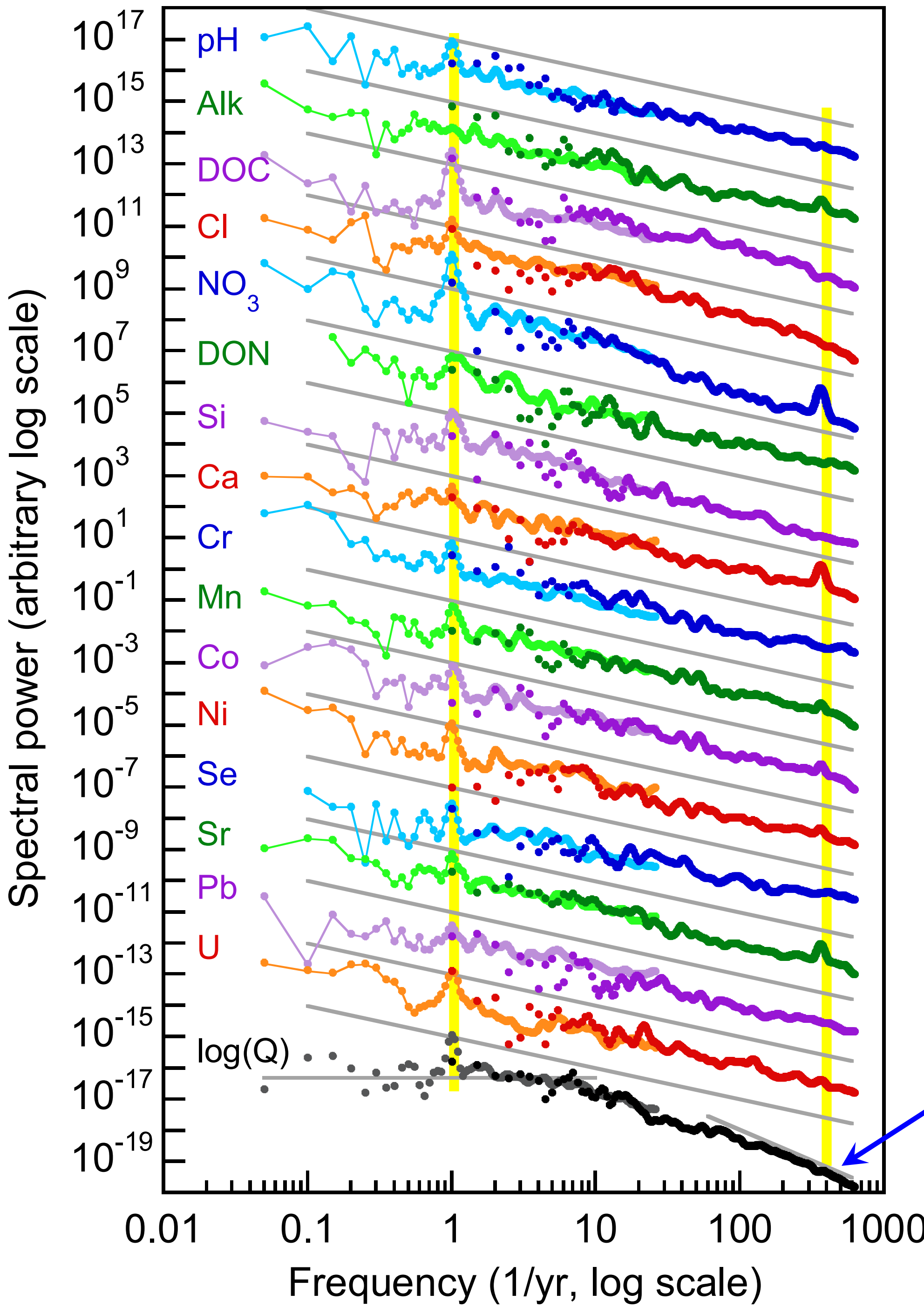


# Time series for three metals



# Spectra for three metals (all approximately 1/*f*)






Weekly and 7-hour spectra combined, for selected analytes:

Fractal scaling from hours to decades

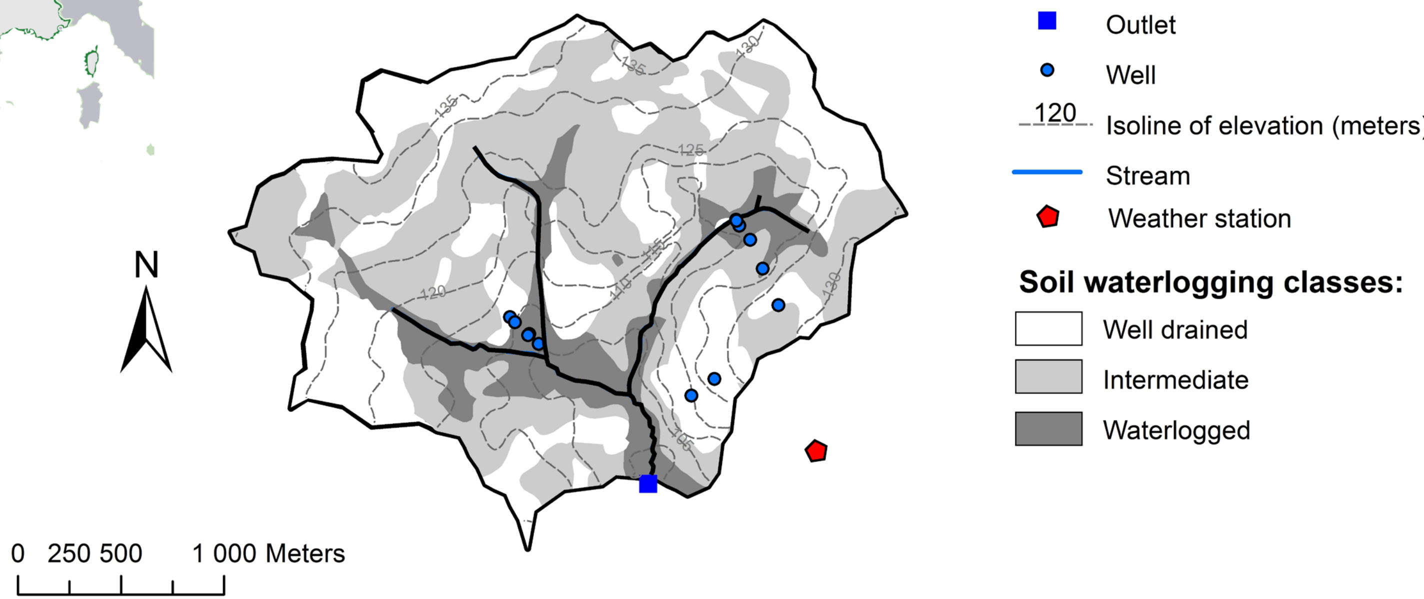
(Gray lines are ideal 1/*f* spectra)

**Vertical lines show annual and daily cycles**

Stream discharge does <u>*not*</u> follow 1/*f* scaling

**Kirchner and Neal, *PNAS* (2013)**

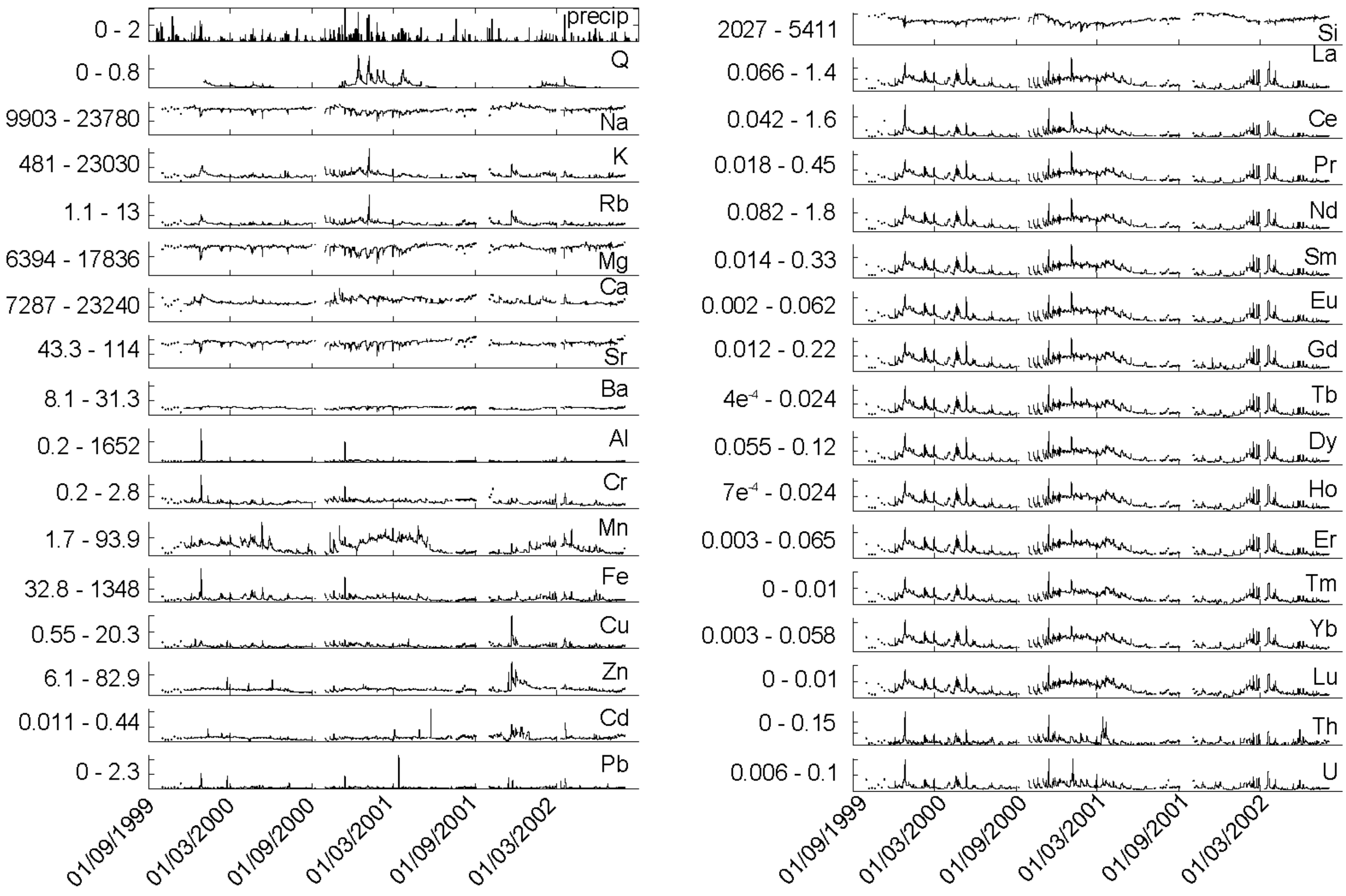

# Kervidy-Naizin catchment, Brittany, France
(Alice Aubert et al., ES&T, 2014)




## Contrasts between catchments:

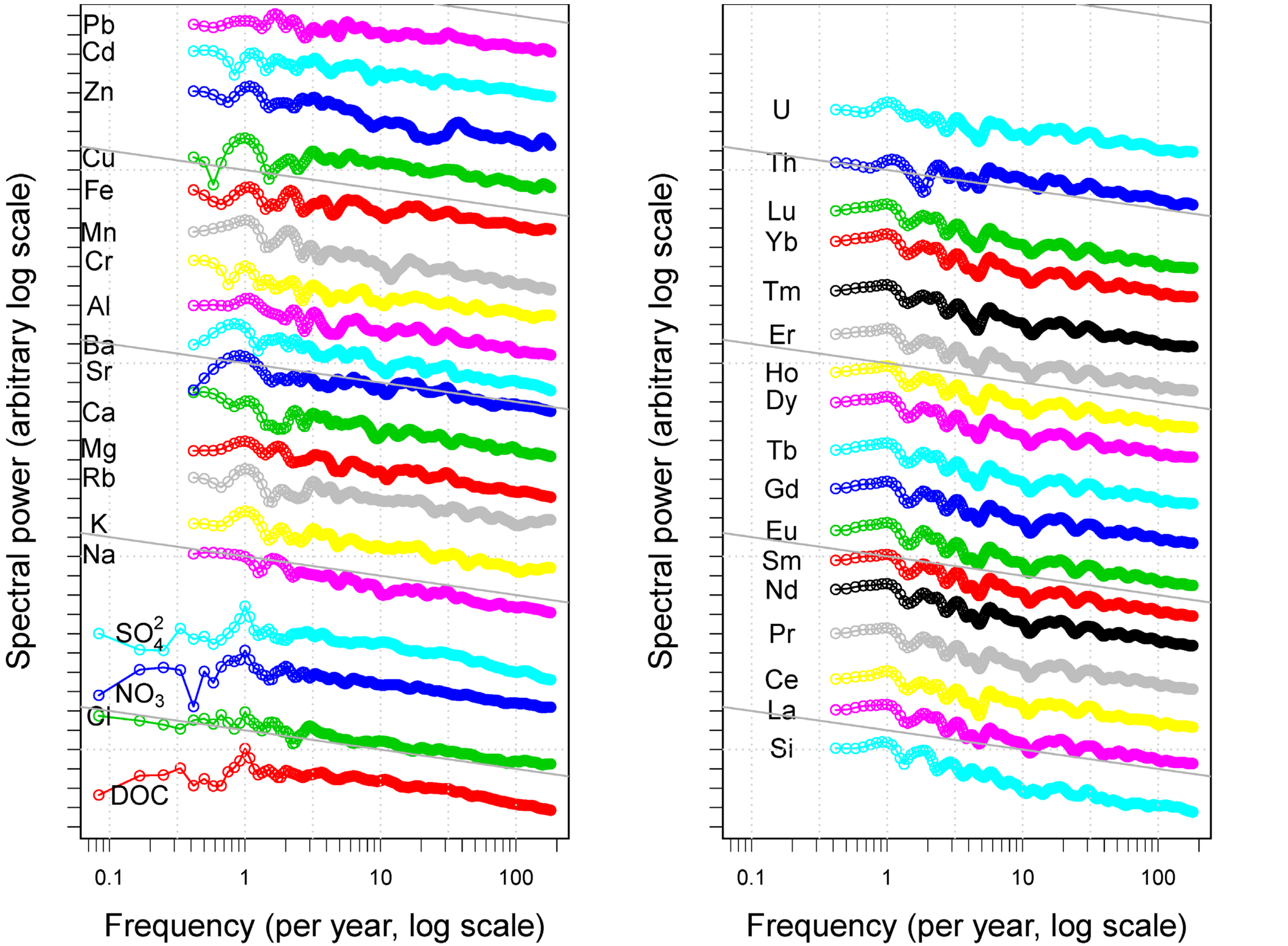
| | Plynlimon, Wales | Kervidy-Naizin, France |
|---|---|---|
| Land use: | Moorland & forest<br>~1 mg/L $NO_3$ | Intensive agriculture<br>~75 mg/L $NO_3$ |
| Precipitation: | ~2500 mm/yr | ~800 mm/yr |
| Seasonality: | Weak (ET~20%) | Strong (ET~60%) |
| Topography: | Steep (slopes~20%) | Gentle (slopes~5%) |

# Kervidy-Naizin catchment, Brittany, France: 3 years of daily chemical sampling



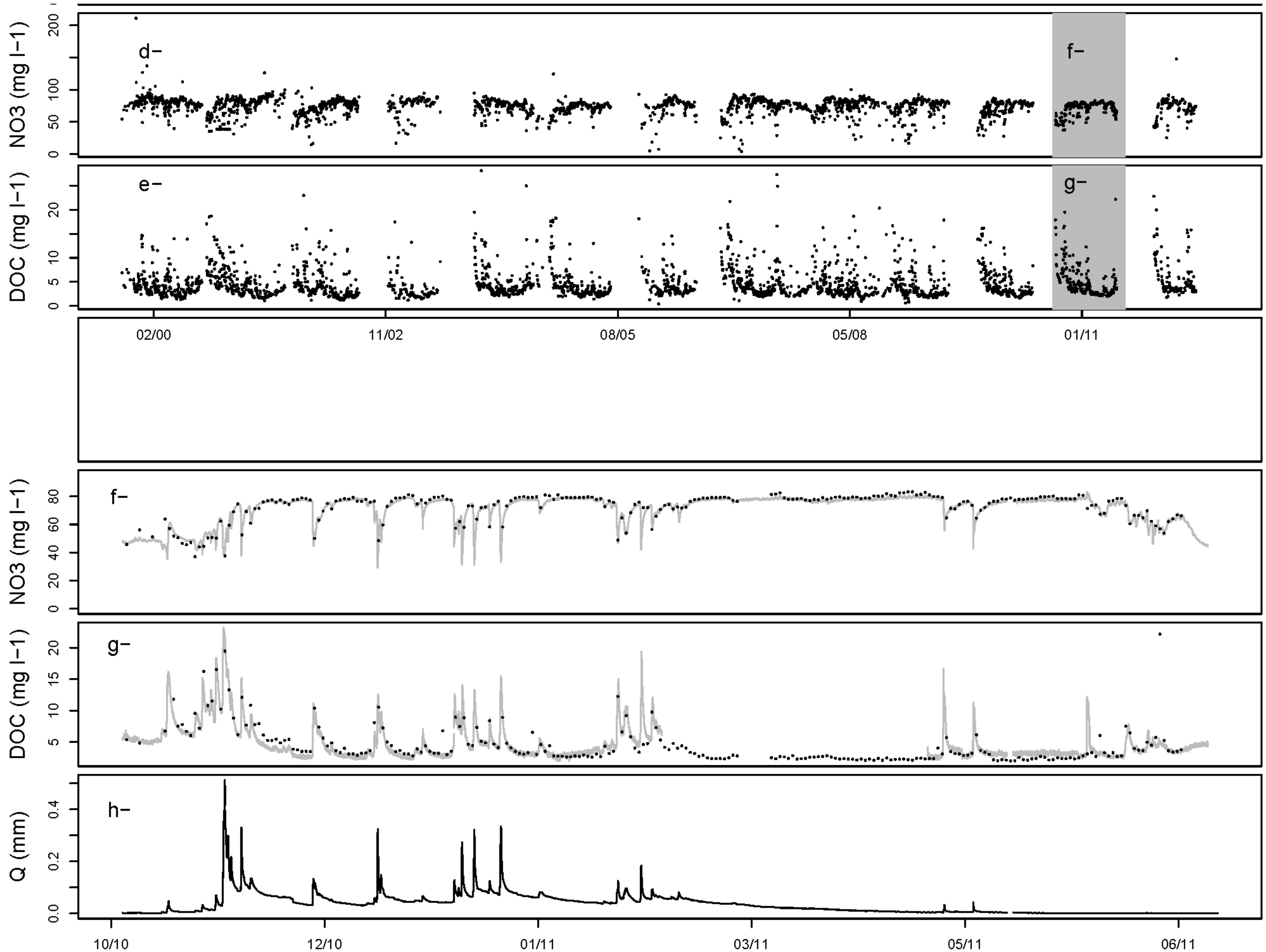

Aubert et al., ES&T, 2014.

# Kervidy-Naizin catchment, Brittany, France: approximate 1/f scaling across the periodic table (3 years of daily data)



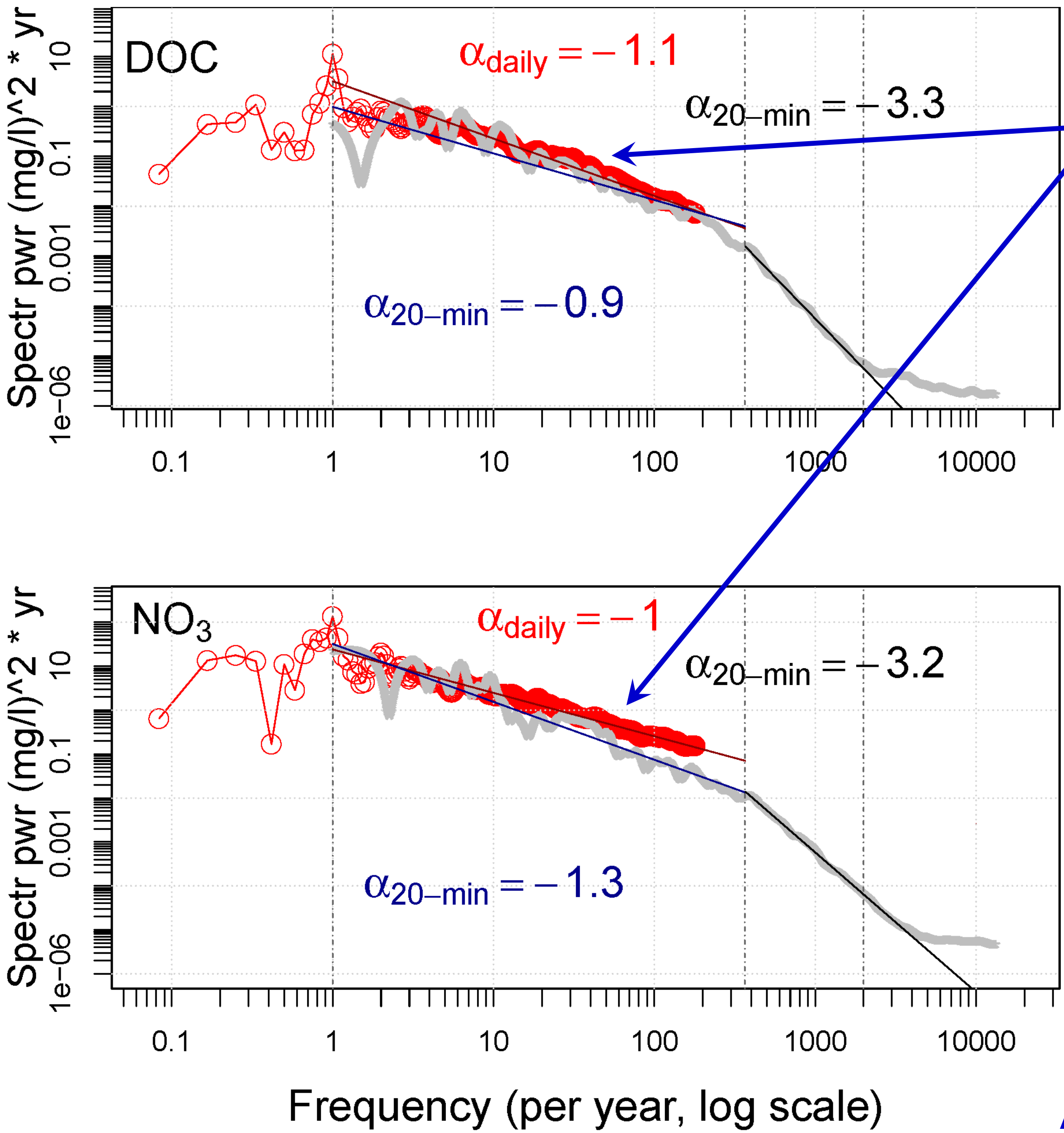

Aubert et al., ES&T, 2014.

# Kervidy-Naizin catchment, Brittany, France: 12 years of daily data and 8 months of sonde data for NO3 and DOC




Aubert et al., ES&T, 2014

# Kervidy-Naizin catchment, Brittany, France: spectra of NO3 and DOC, from 12 years to 40 minutes




1 decade to 1 day:
~1/*f* scaling

1 day to 3 hours:
~$1/f^3$ scaling
(in-stream mixing??)

higher frequencies:
~$1/f^{0.5}$ scaling
(instrumental
noise floor!)

Aubert et al., 2014.

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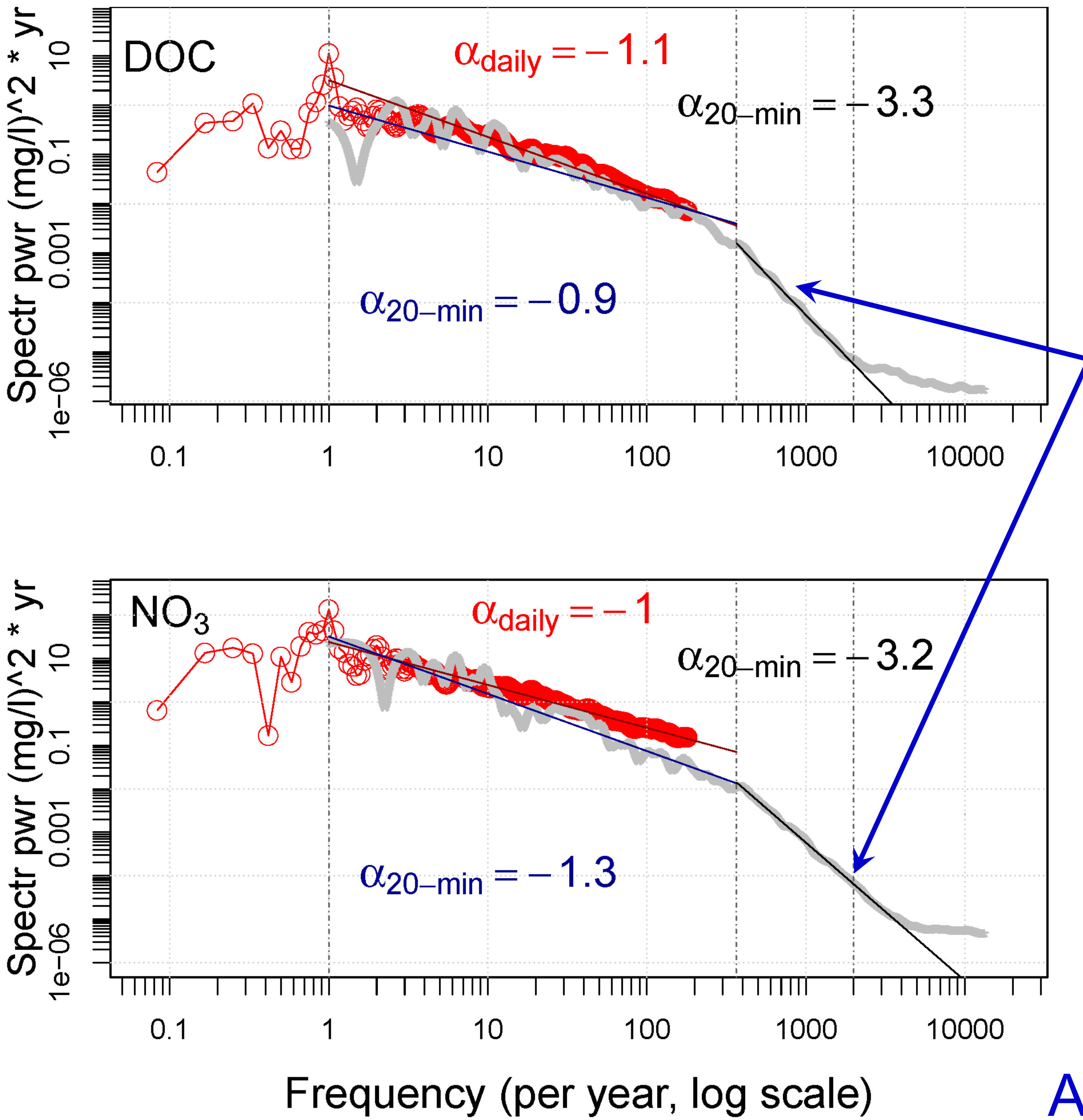


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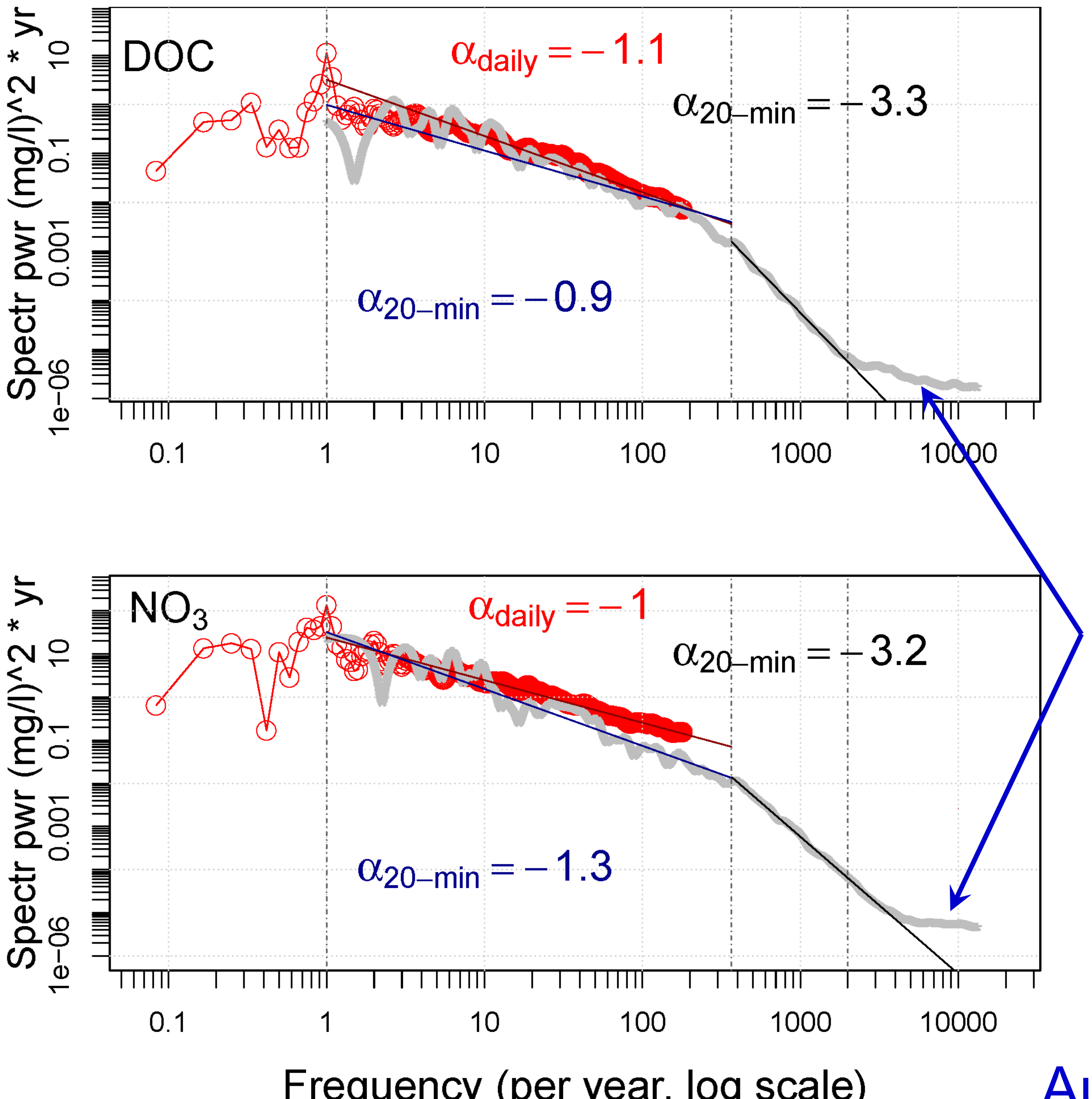


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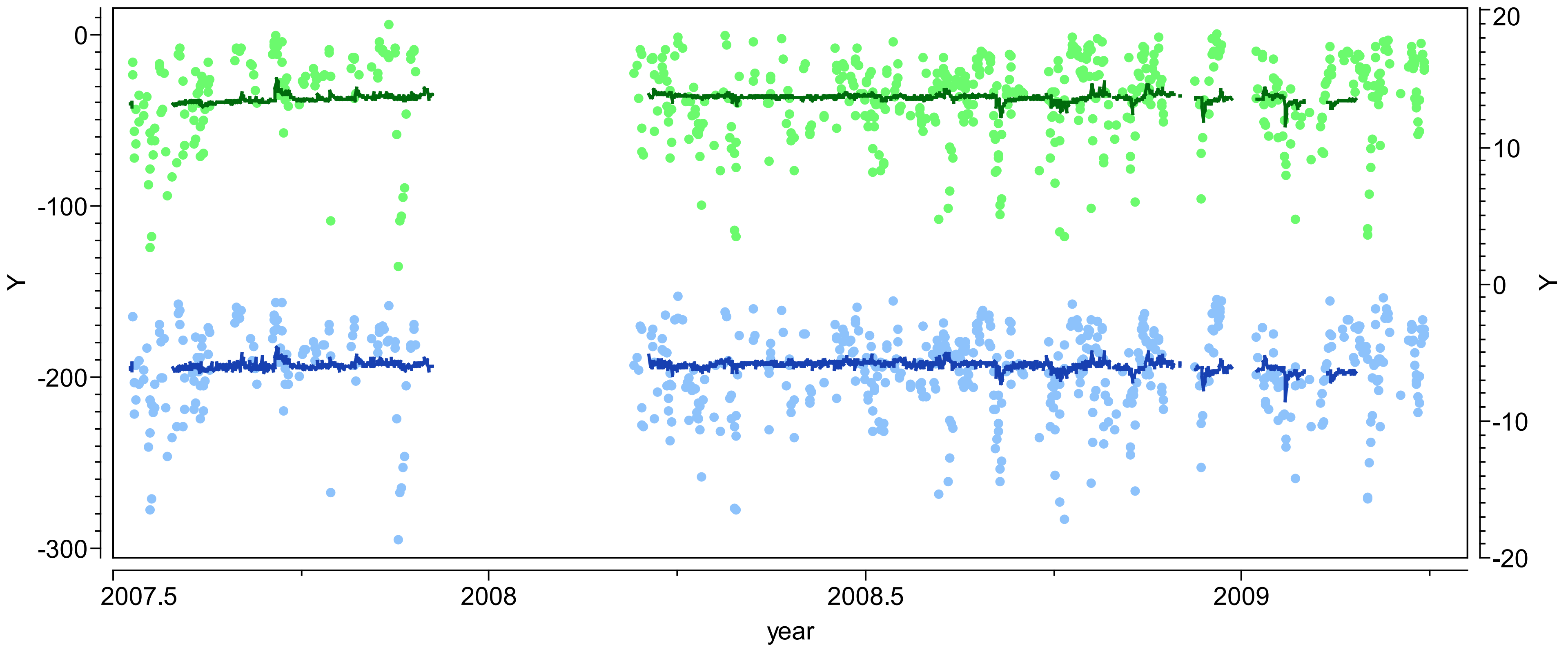
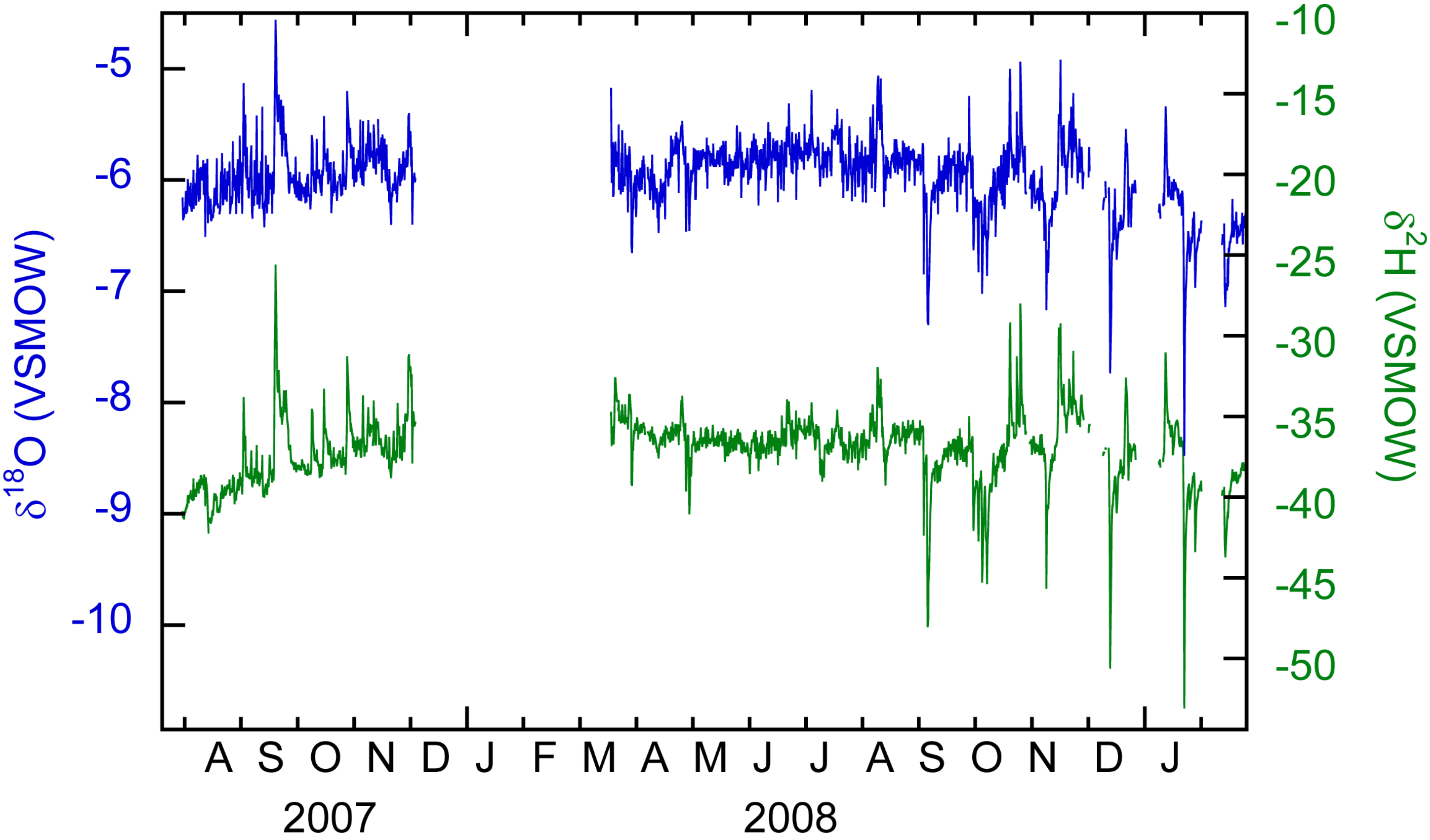
higher frequencies:
~1/$f^{0.5}$ scaling
(instrumental
noise floor!)

Aubert et al., 2014.

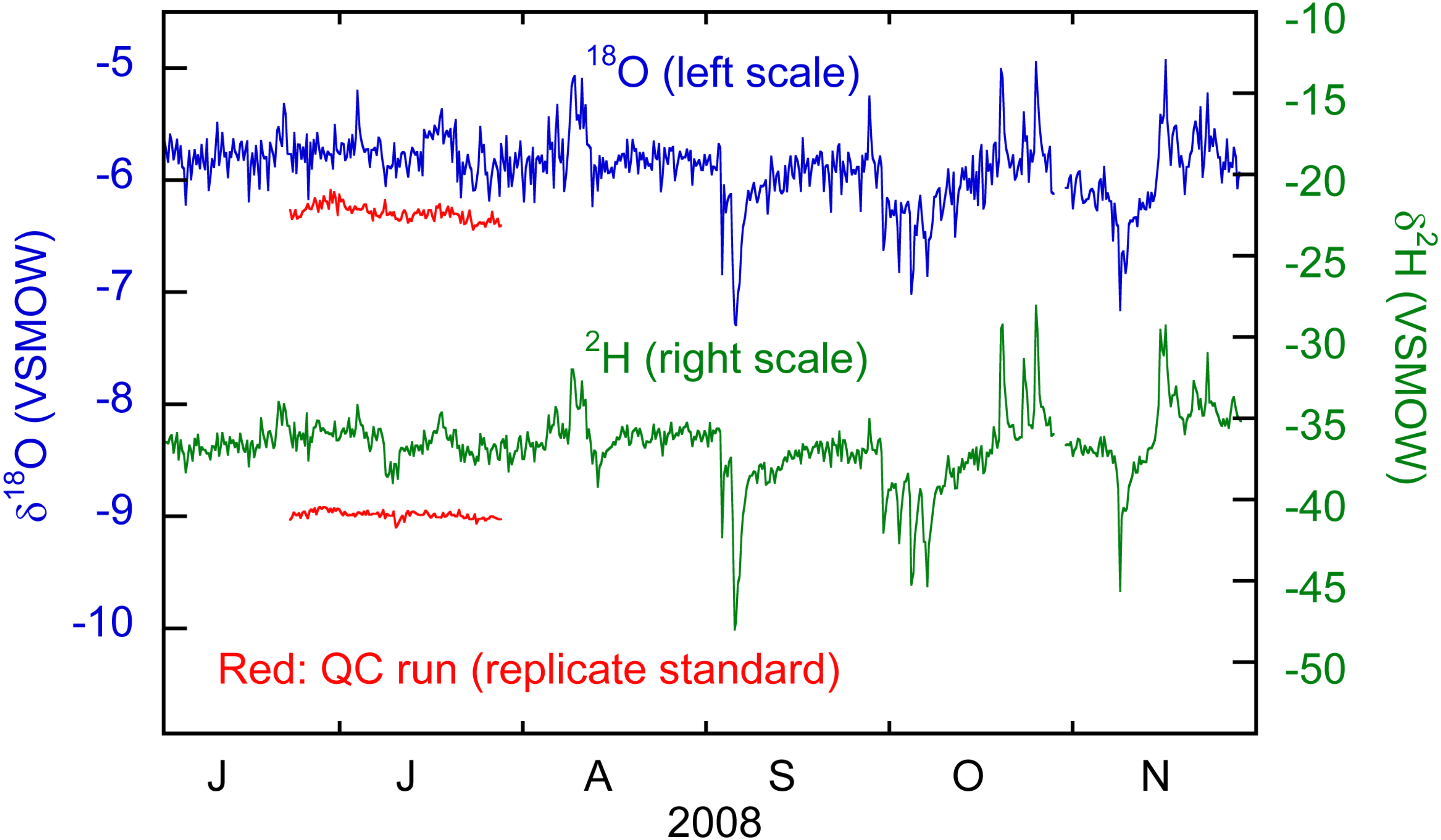
7-hourly $^{18}O$ and $^{2}H$ are both (very) strongly damped in streamwater, compared to their variability in precipitation. Implication: recent rainfall is a minor component of streamflow.



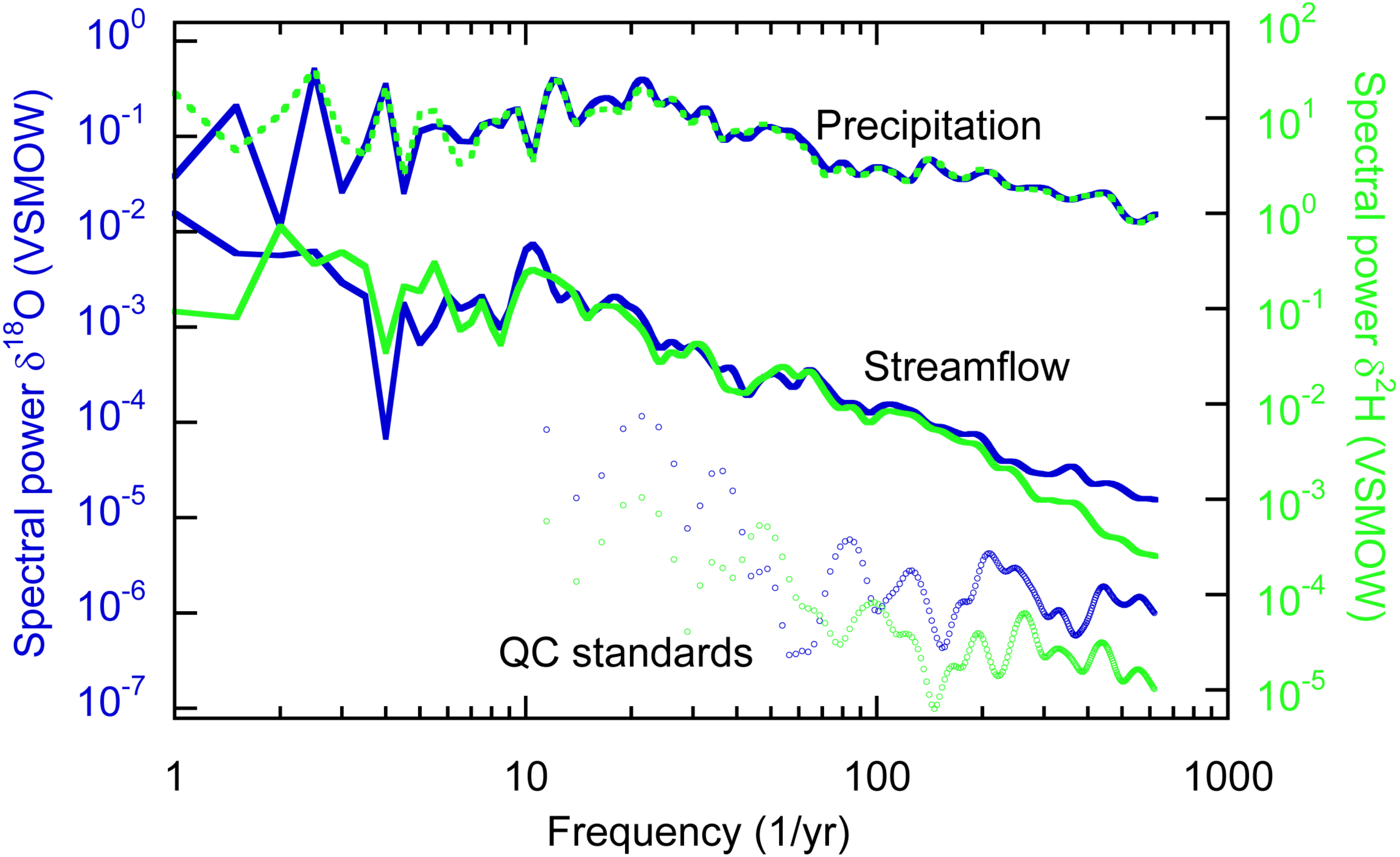
# A closer look reveals... richly detailed dynamics in streamwater isotopes



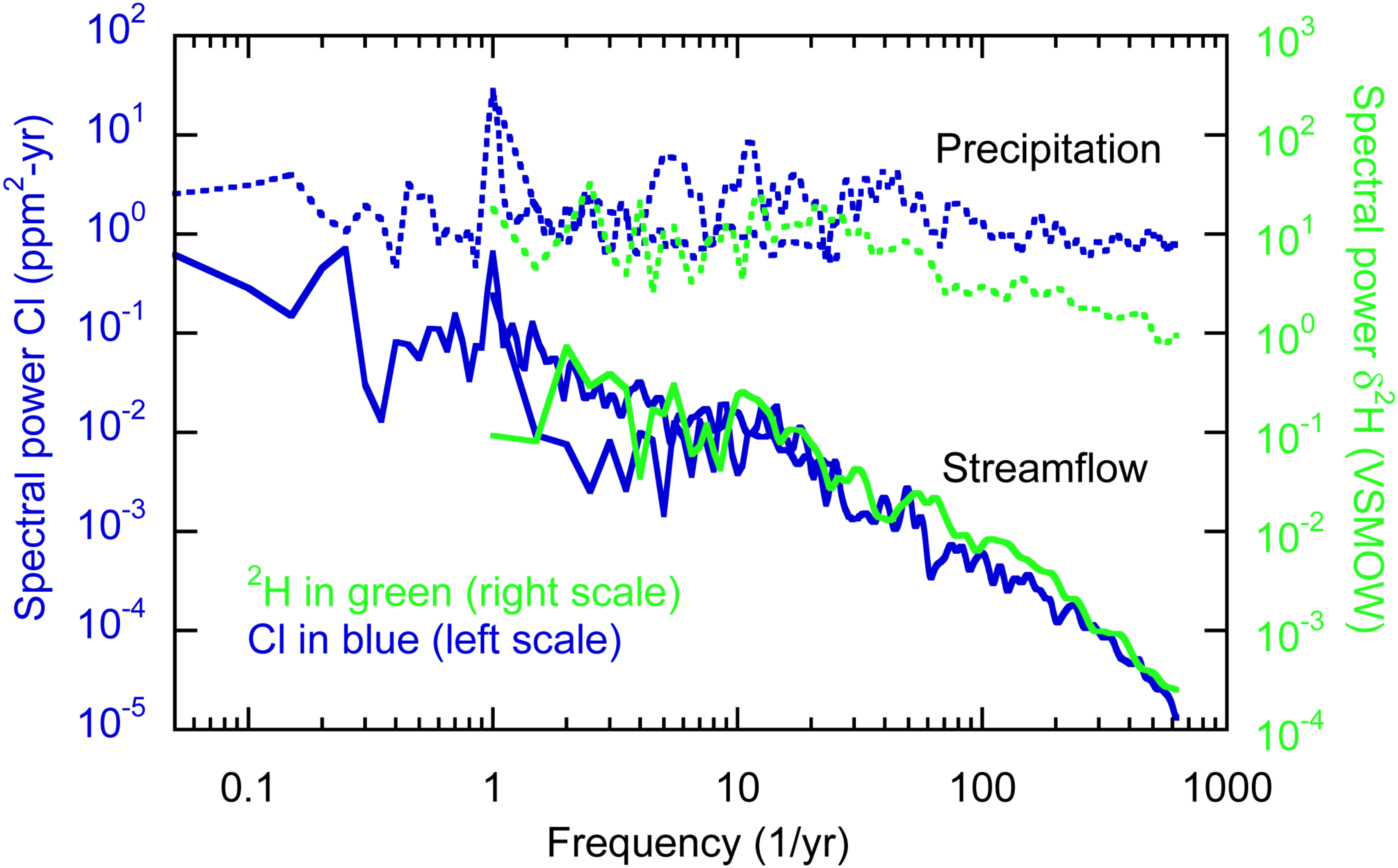
This is *not analytical noise*. Analytical noise is only ~1/3 of sample-to-sample variability (even at this sampling frequency), for both $^2H$ and $^{18}O$.



# Measurement noise is too low to affect measured spectra (... but you always need to check!)

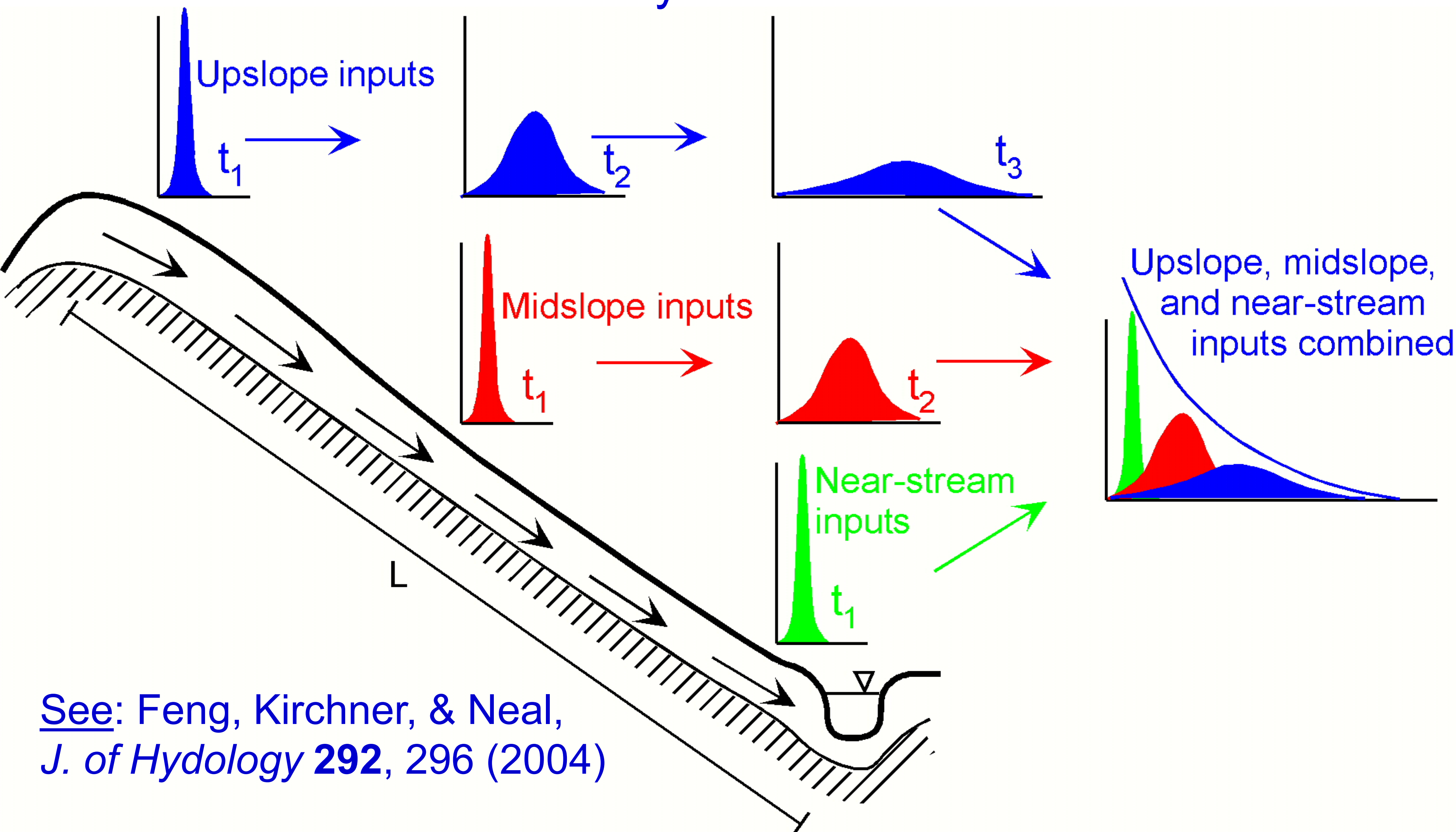


# Isotope power spectra (here, $^2H$) are broadly consistent with damping in Cl spectrum (for which we have lots more data...)



# Working Hypotheses:

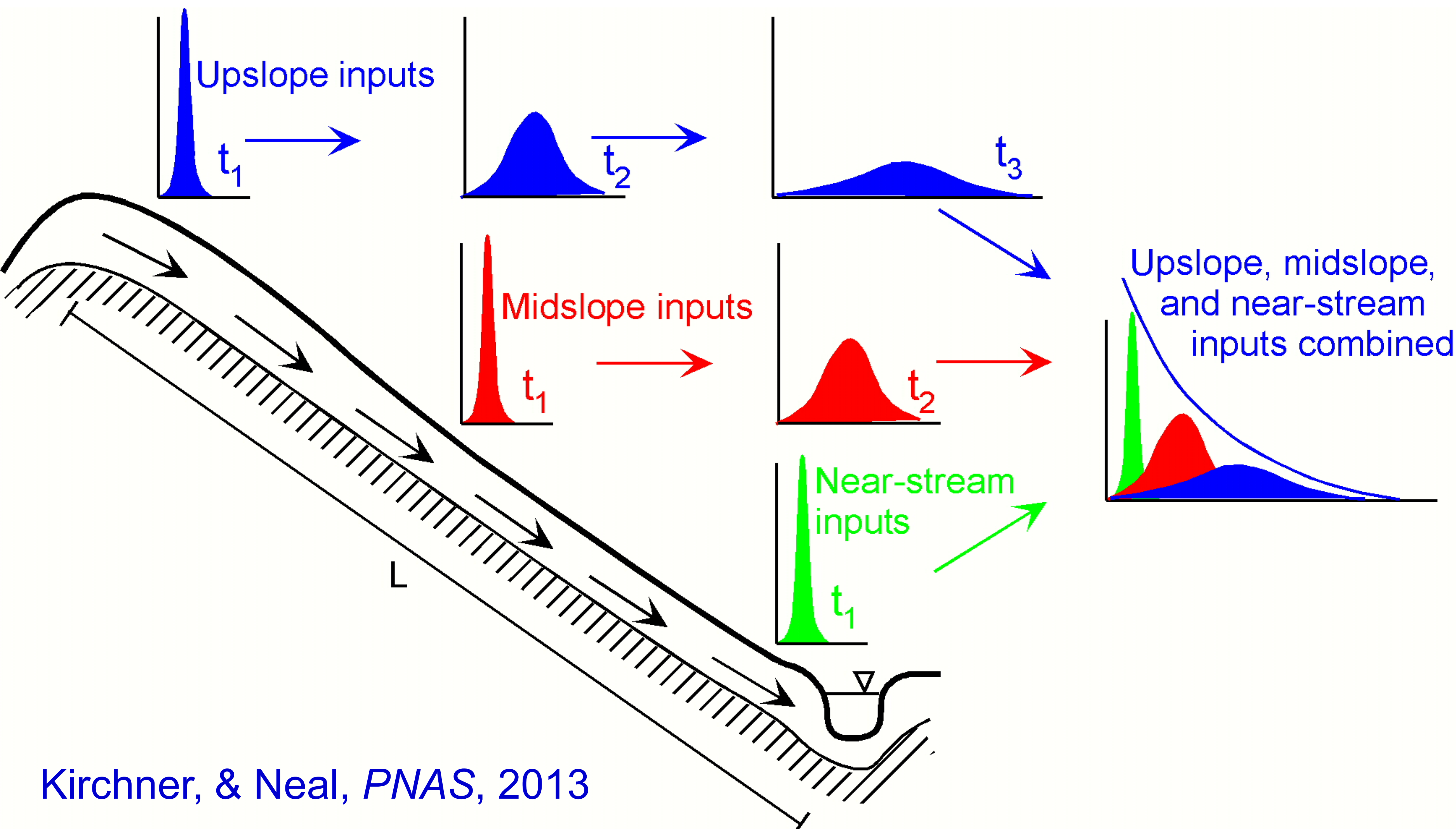
Advection and (macro)dispersion of spatially distributed rainfall inputs, potentially including chemical retardation and/or irreversible kinetically limited immobilization




See: Feng, Kirchner, & Neal, *J. of Hydology* **292**, 296 (2004)

# Working Hypotheses:

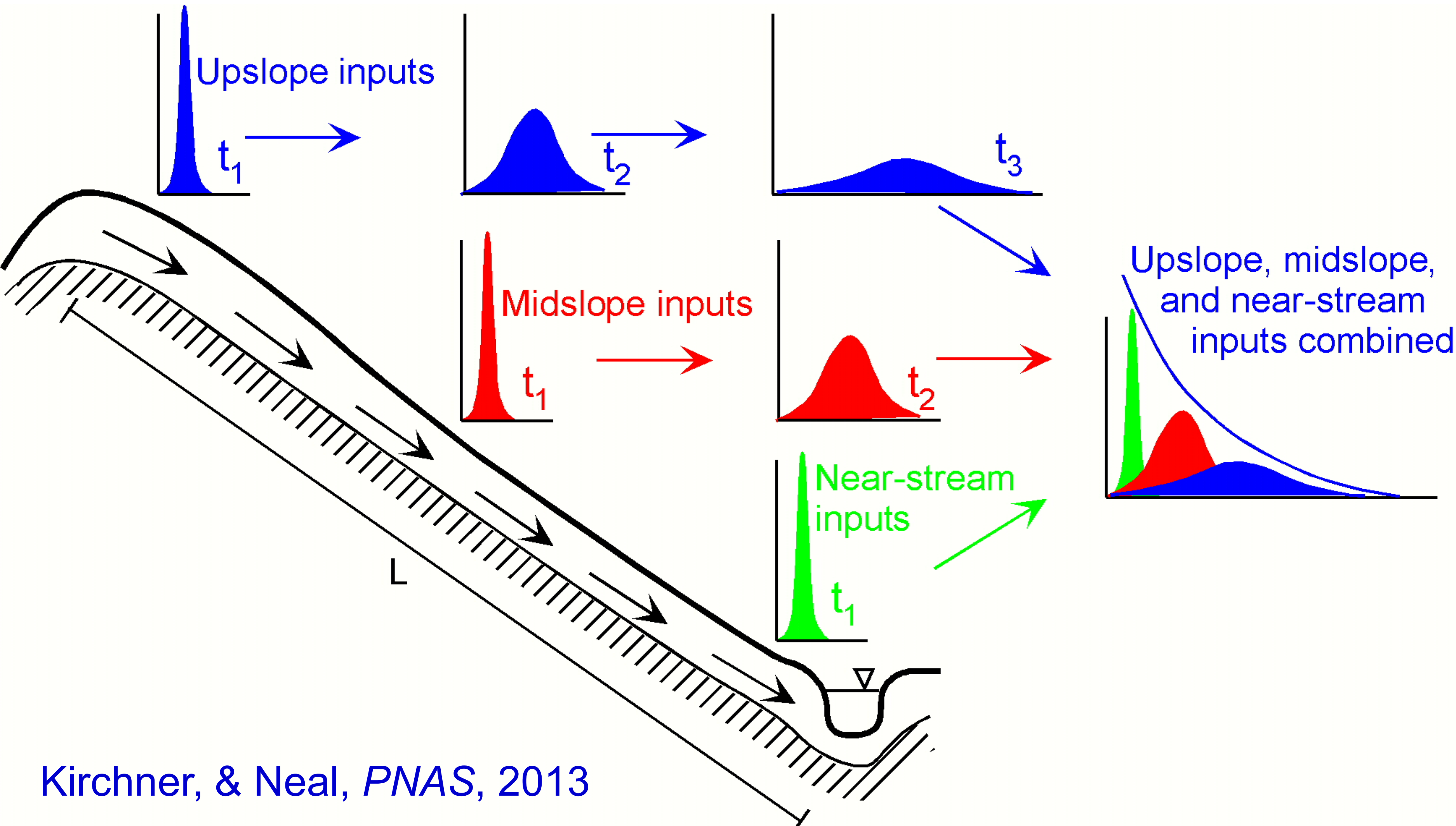
Spatially correlated white-noise reaction rates
(with or without retardation)




Kirchner, & Neal, *PNAS*, 2013

# Working Hypotheses:

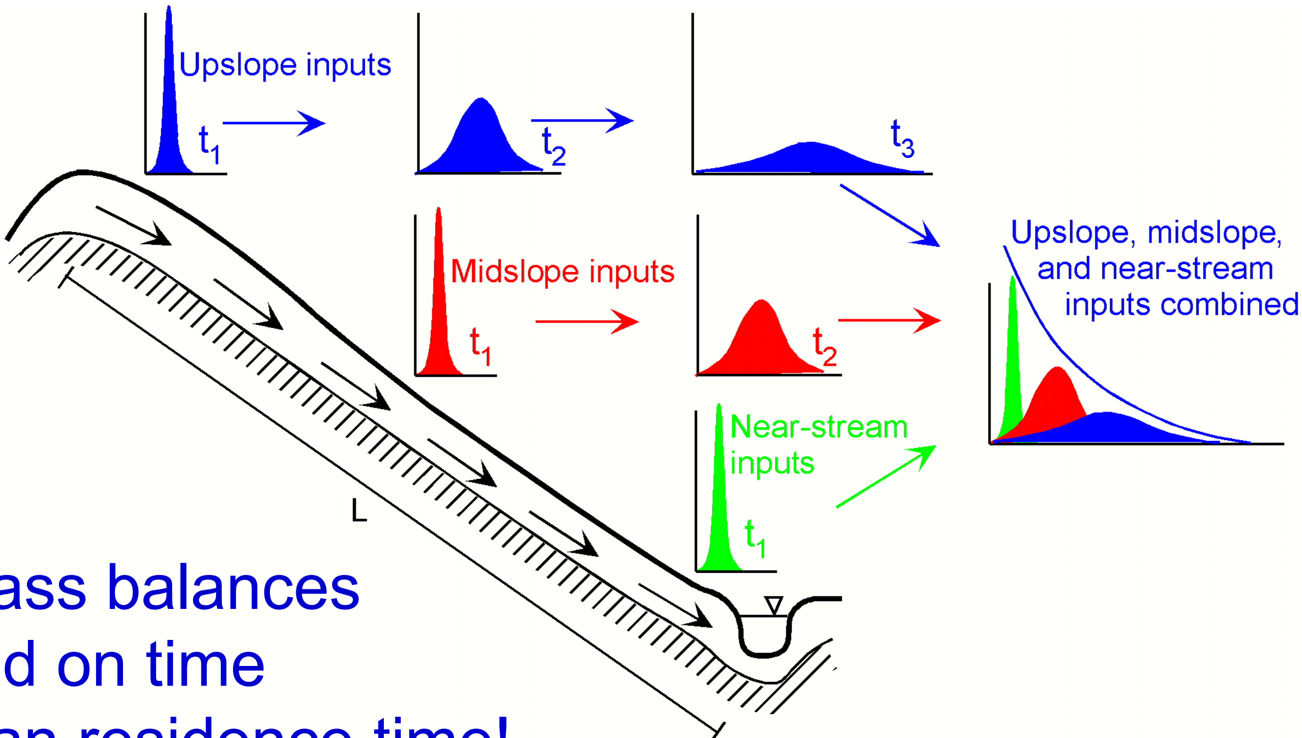
"Anomalous" dispersion of spatially uncorrelated reaction rates



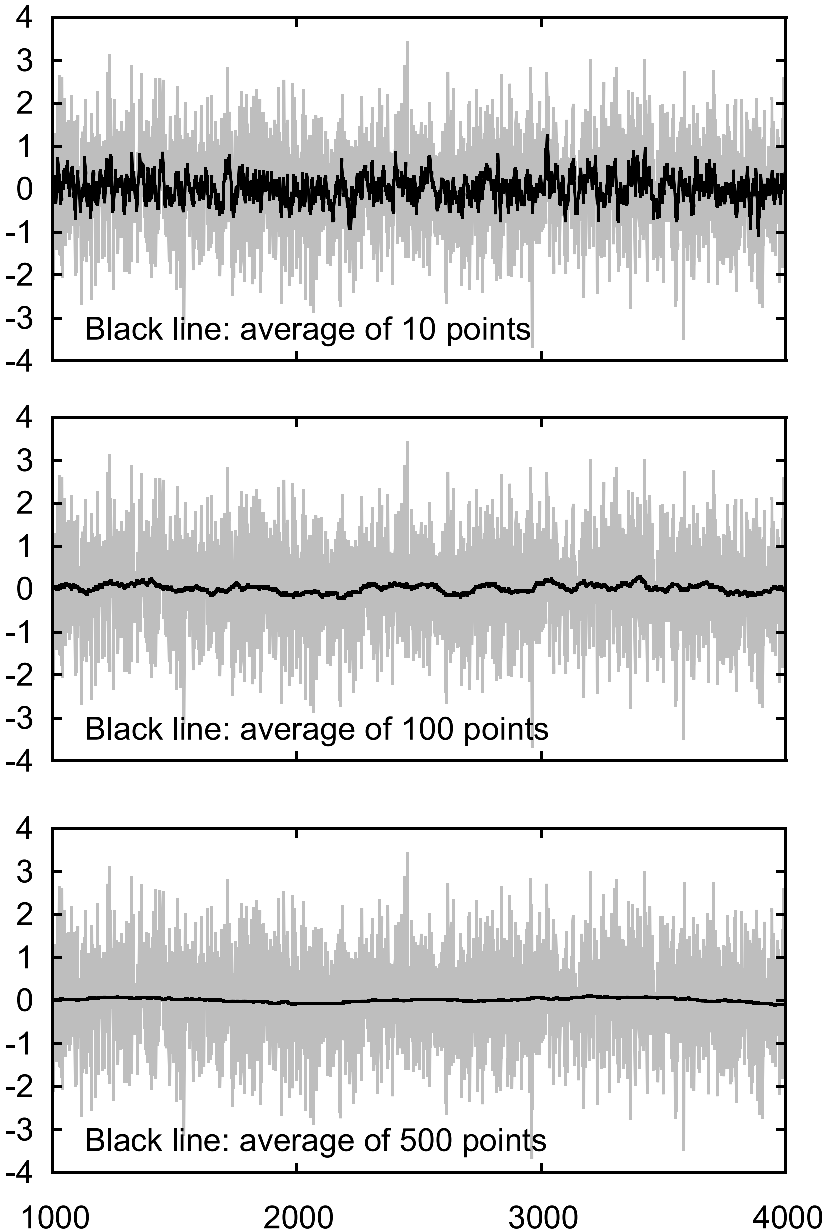

Kirchner, & Neal, *PNAS*, 2013

Implication: High-frequency (short-time) signals from most of the catchment *will not reach the stream*, but instead will be lost to dispersion/interference.

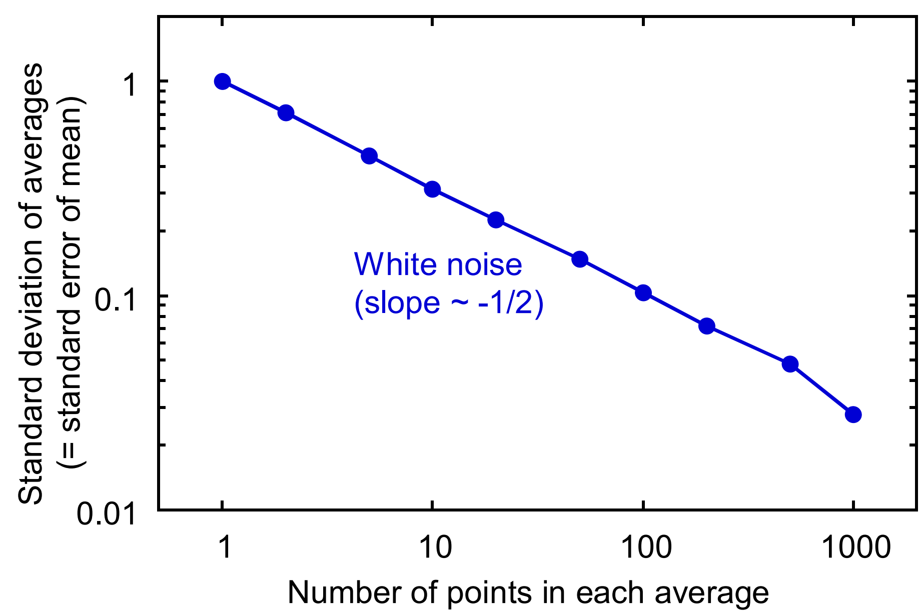
Thus streams are not "*mirrors* of the landscape", but rather *red-tinted filters* that transmit long wavelengths and filter out short ones.

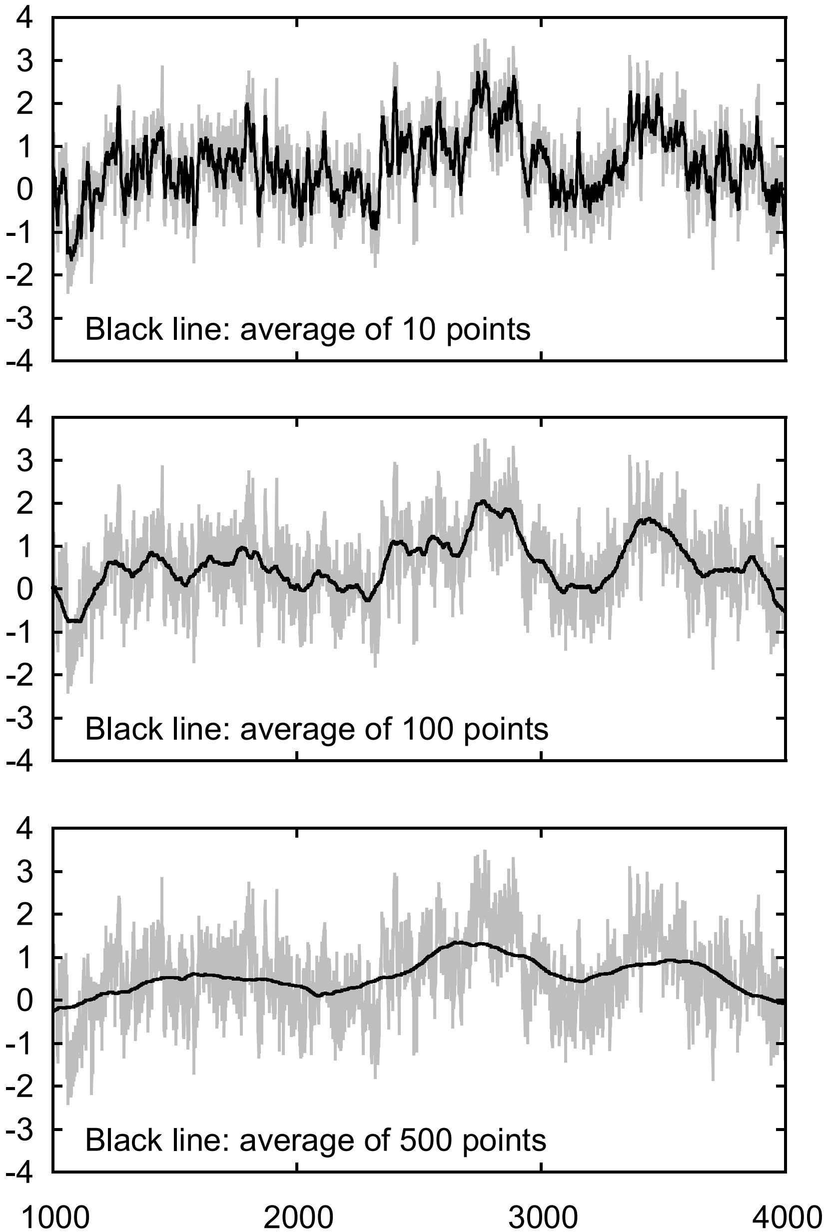



Catchment mass balances are only closed on time scales >> mean residence time!

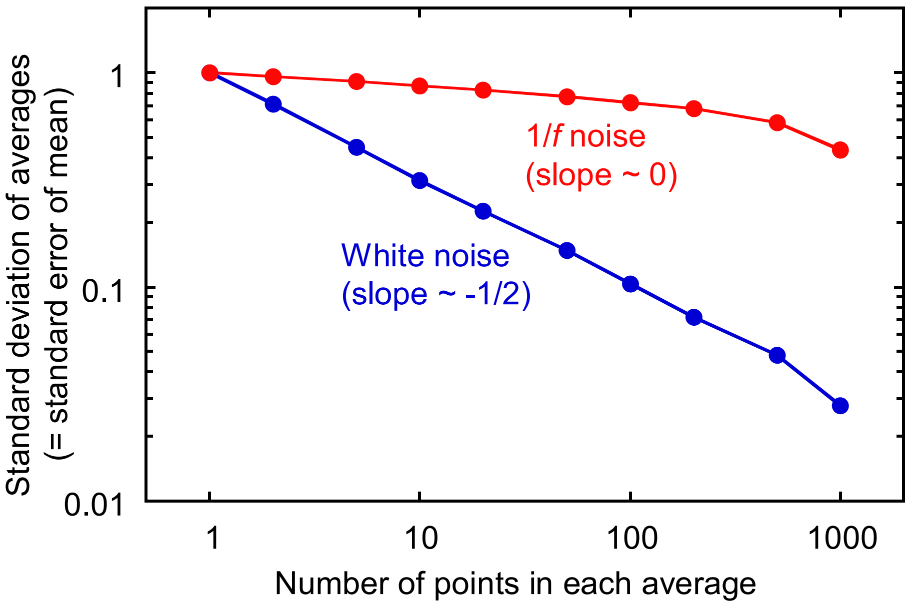


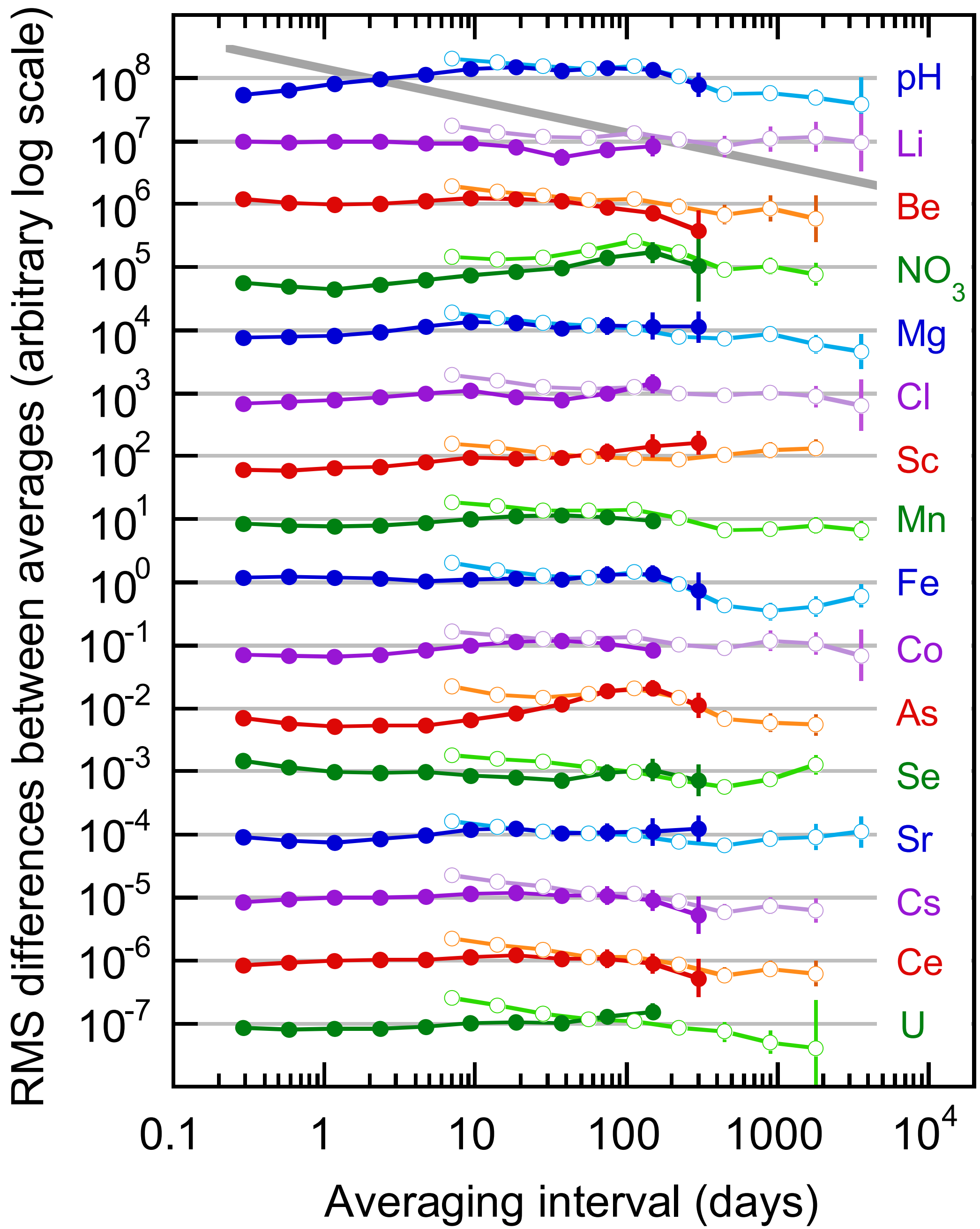

Statistics (and our expectations) are based on time series like white noise, which are *self-averaging* (meaning: averages converge to a stable mean).





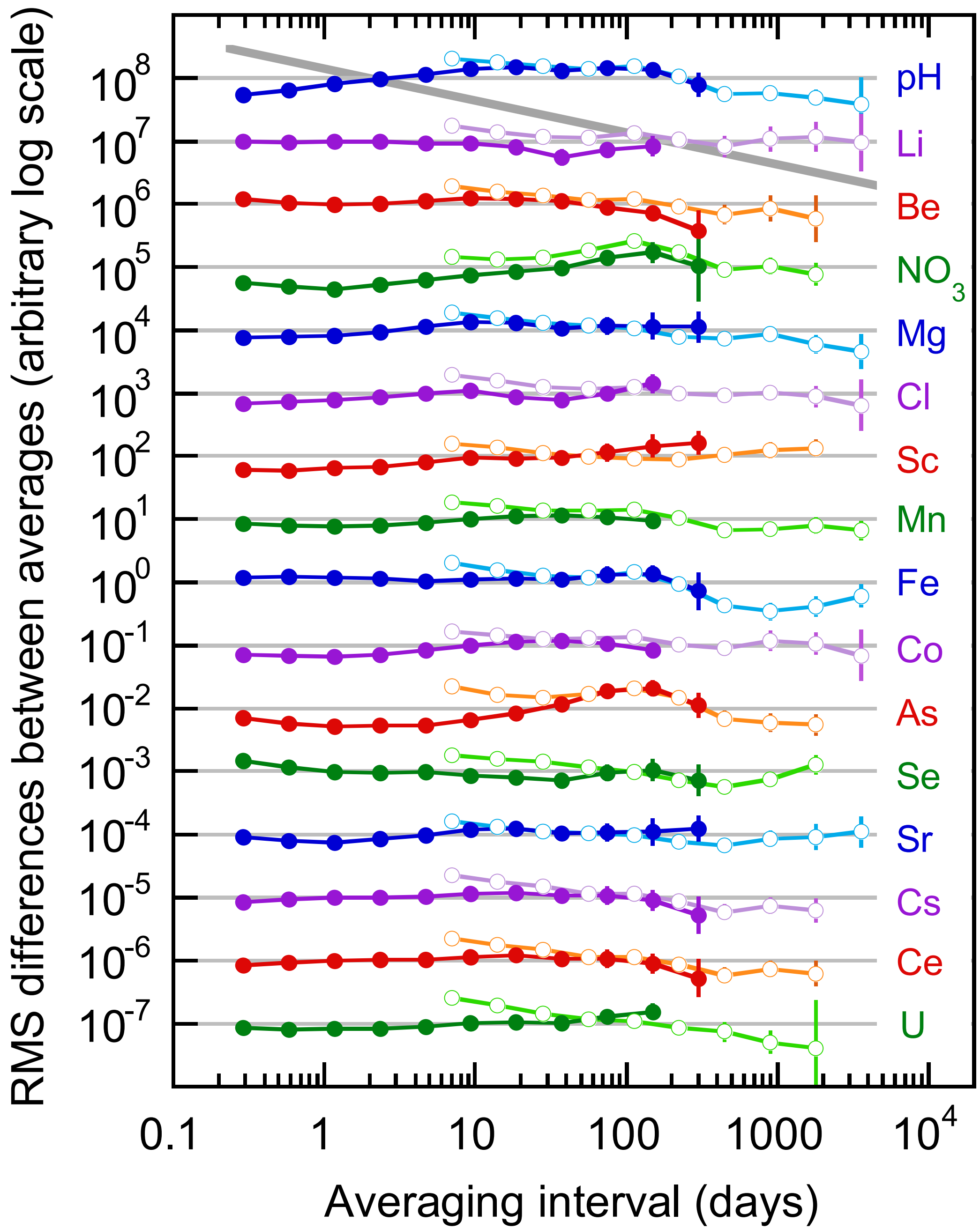

1/*f* time series are *not* self-averaging! Averages taken over longer and longer periods do *not* converge to a stable value (or do so very slowly)!



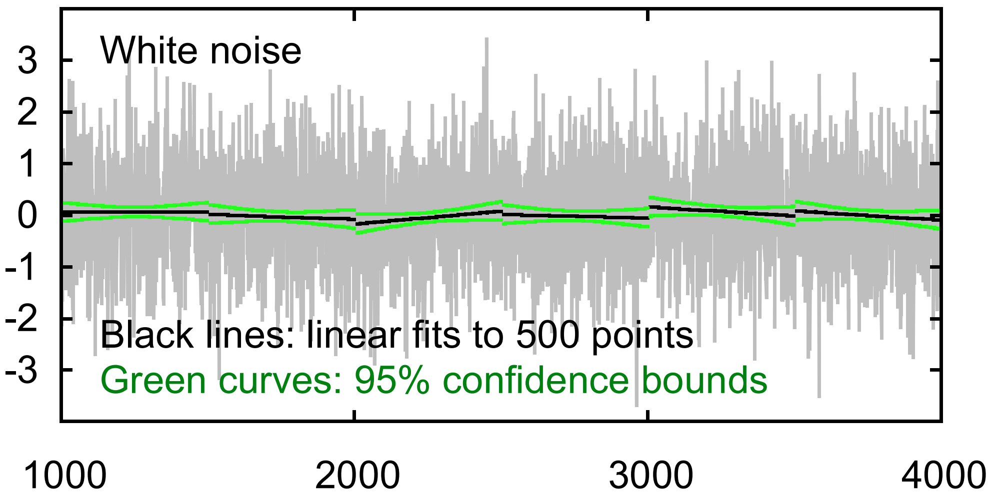



Differences between successive averages of weekly and 7-hour data (averaged over intervals from 7 hours to ~5 years):

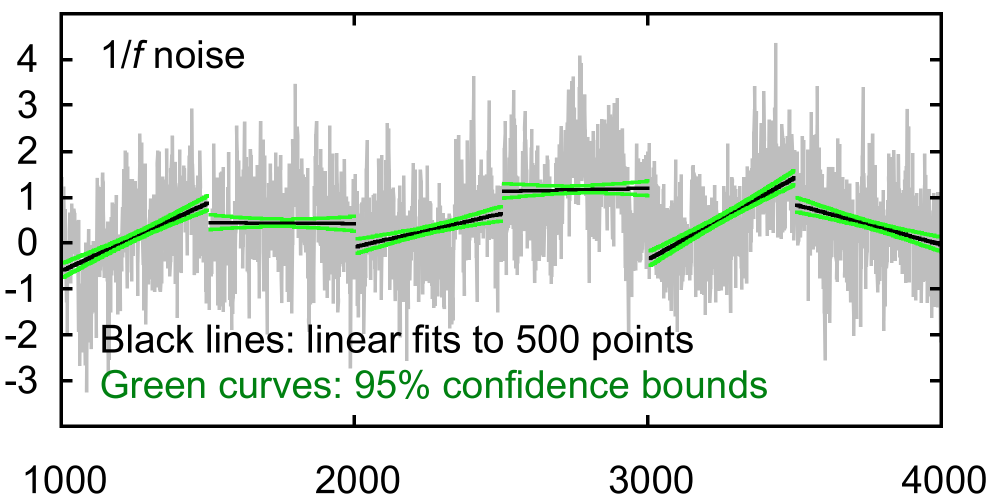
Yearly averages, a year apart, are as different as daily averages, a day apart!



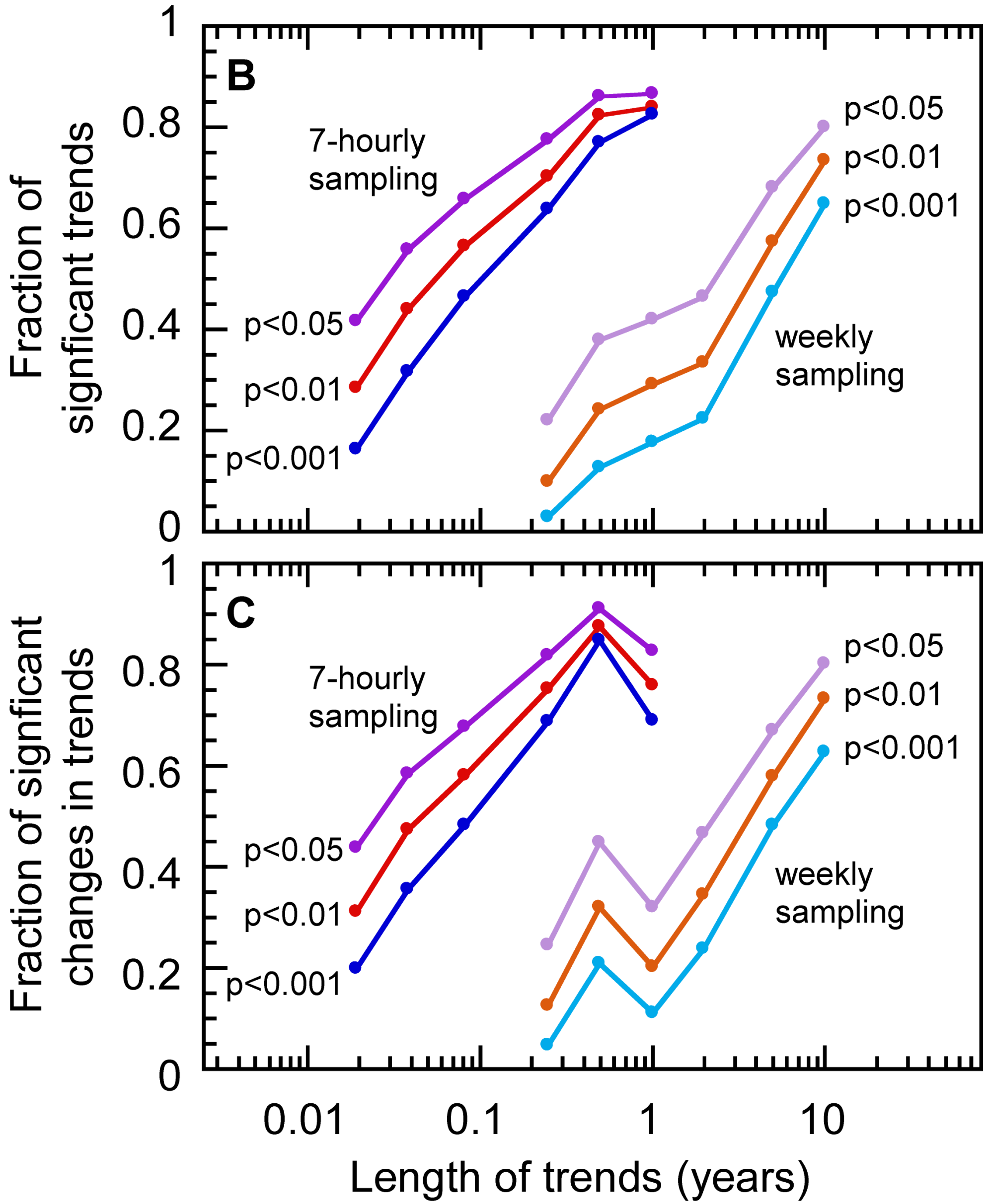

Implication: normal statistics (derived from the Central Limit Theorem) may give ***'significant' but inconsistent long-term trends.***




White noise: trend lines for individual time intervals are usually consistent with those for adjacent time intervals, within statistical confidence bounds (green curves).




1/*f* noise: trend lines for individual time intervals are <u>*poor predictors*</u> of trends in other time intervals (they lie far outside each others' confidence bounds). Fitting trends to longer time intervals <u>*makes this problem worse*</u>.

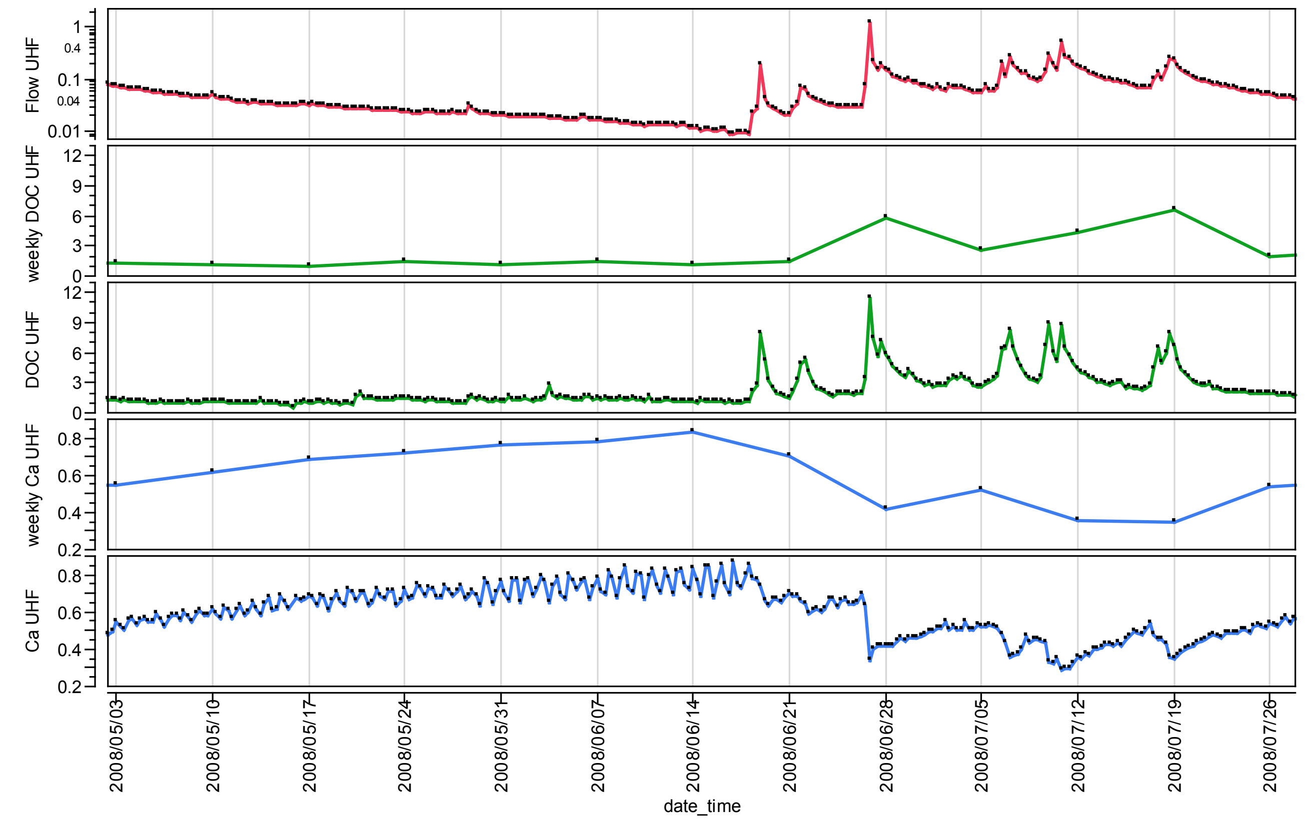



Over 50% of all trends longer than ~2 months (7-hr sampling) or ~5 years (weekly sampling) are statistically *'significant'* ... at $p<0.001$!

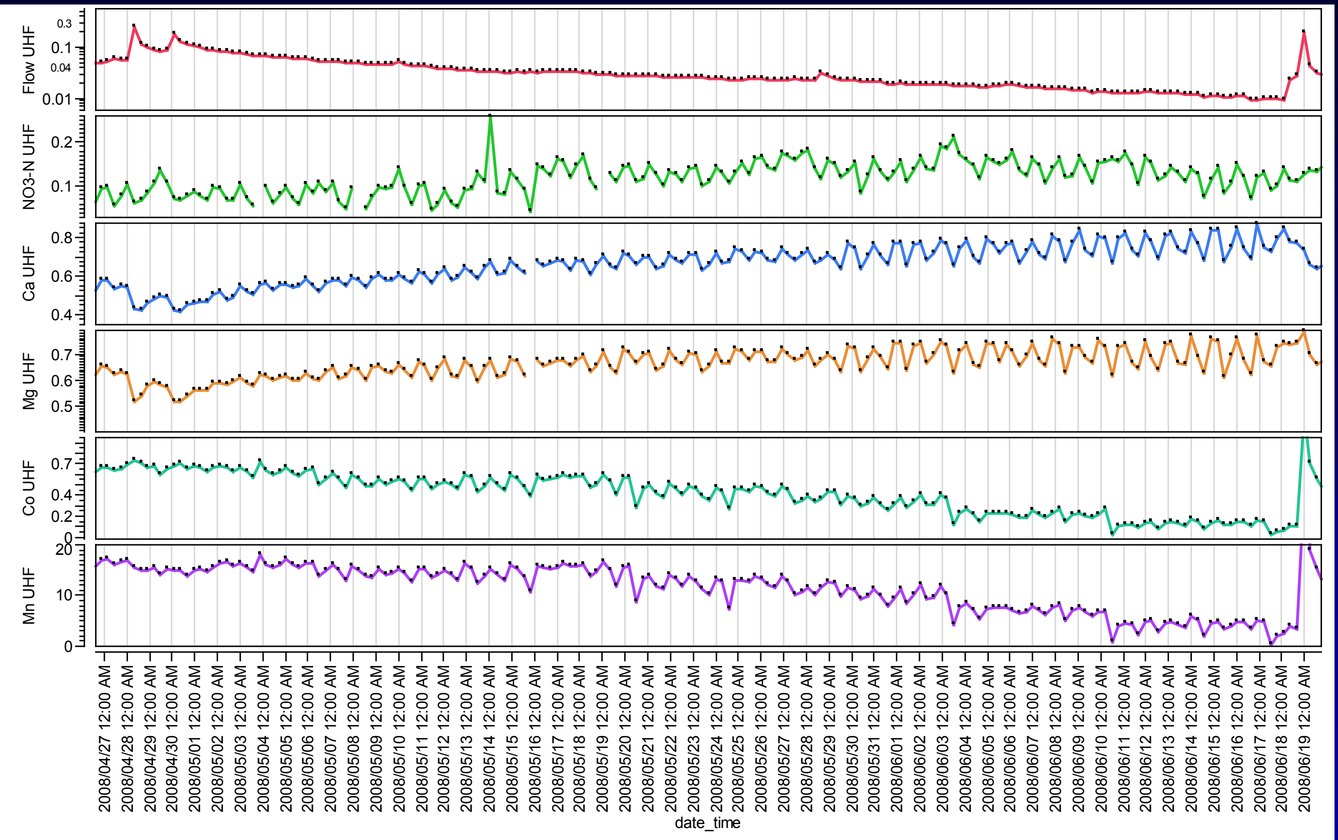
... but they are <u>poor predictors of future trends</u>

(>50% chance that the next interval's trend is significantly <u>different</u> ... also at $p<0.001$!

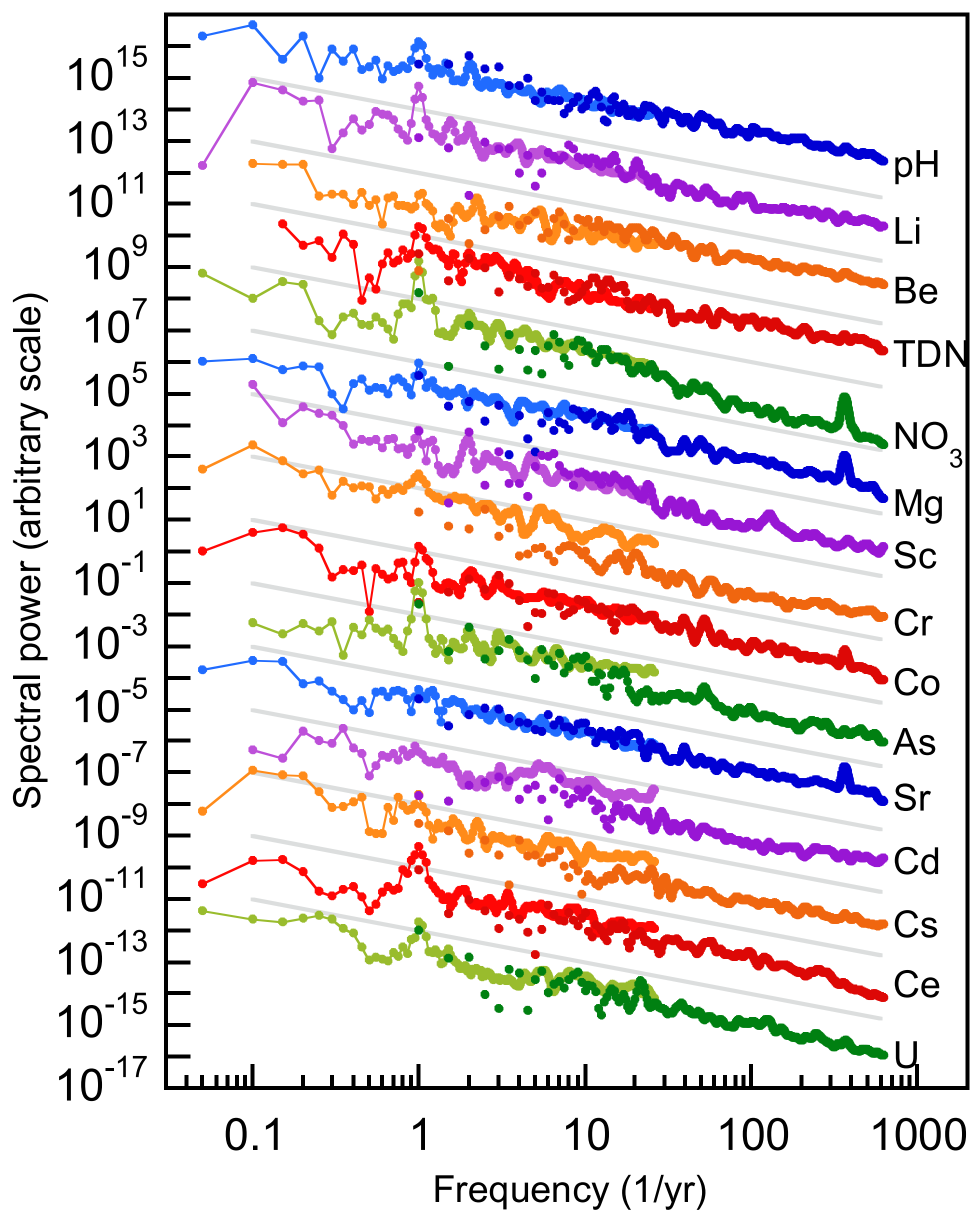
# High-frequency sampling reveals close connections with streamflow dynamics



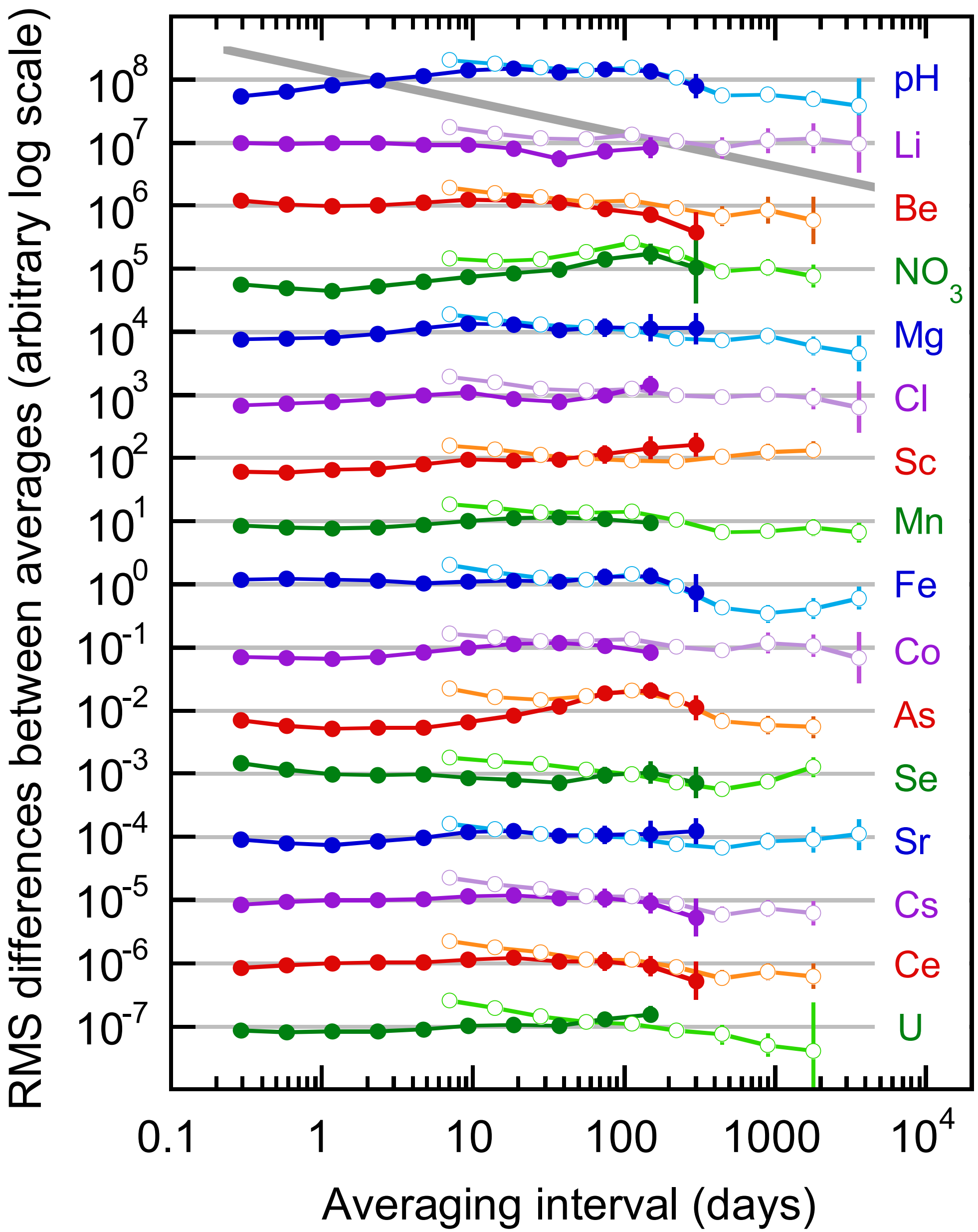

# Diurnal cycles in many elements



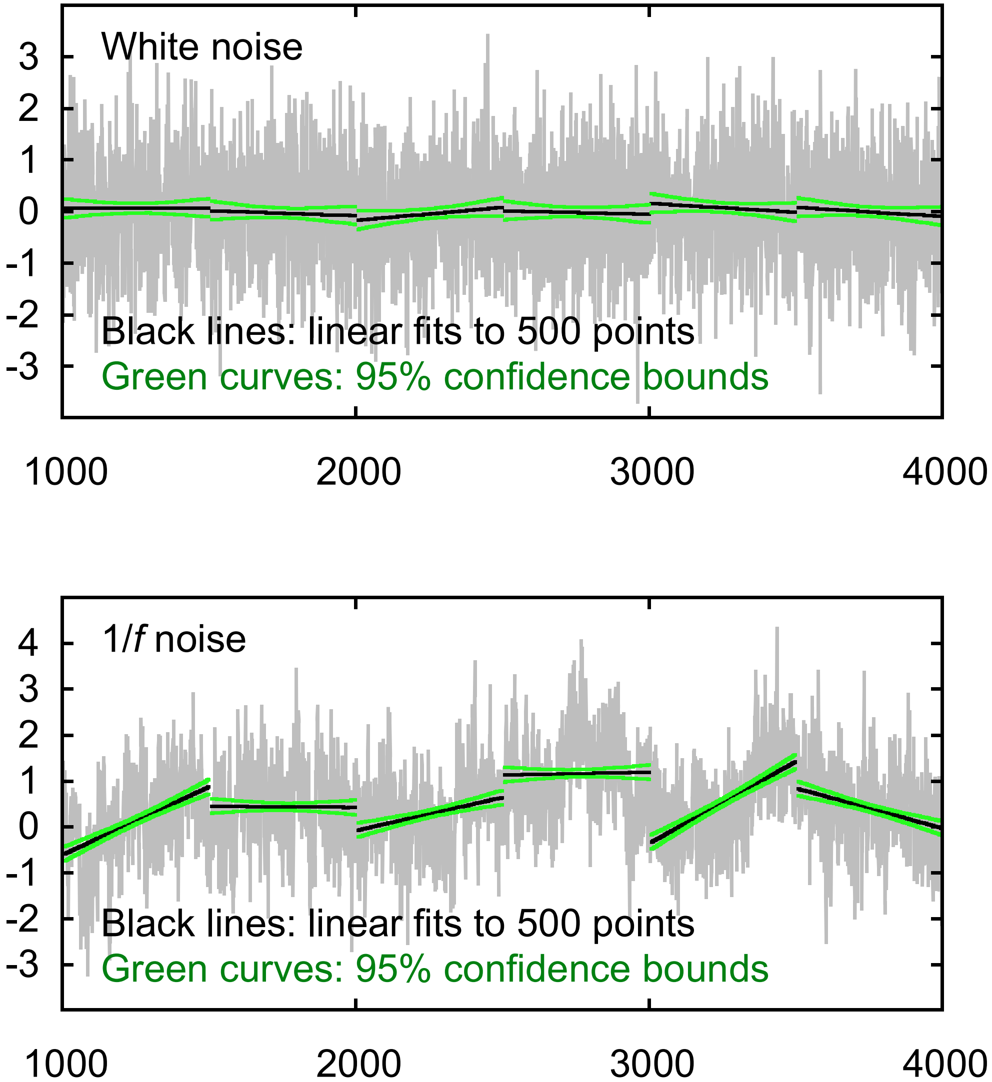

# Universal 1/*f* spectral scaling in water quality




# Lack of self-averaging: a challenge for change/trend detection!




# Convincing, but inconsistent, trends on all time scales

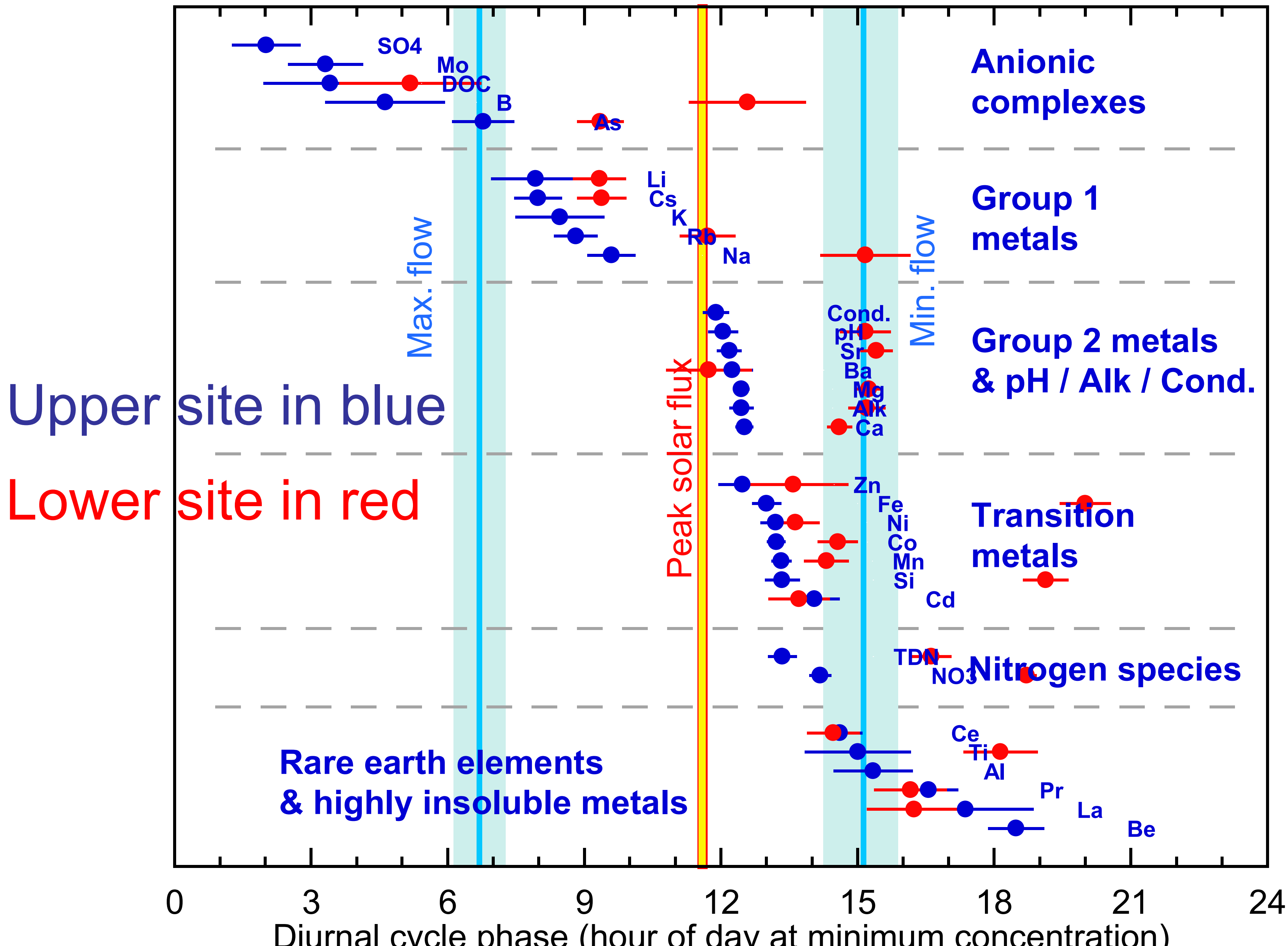



Complete data set *is publicly available* as a community resource for research and education

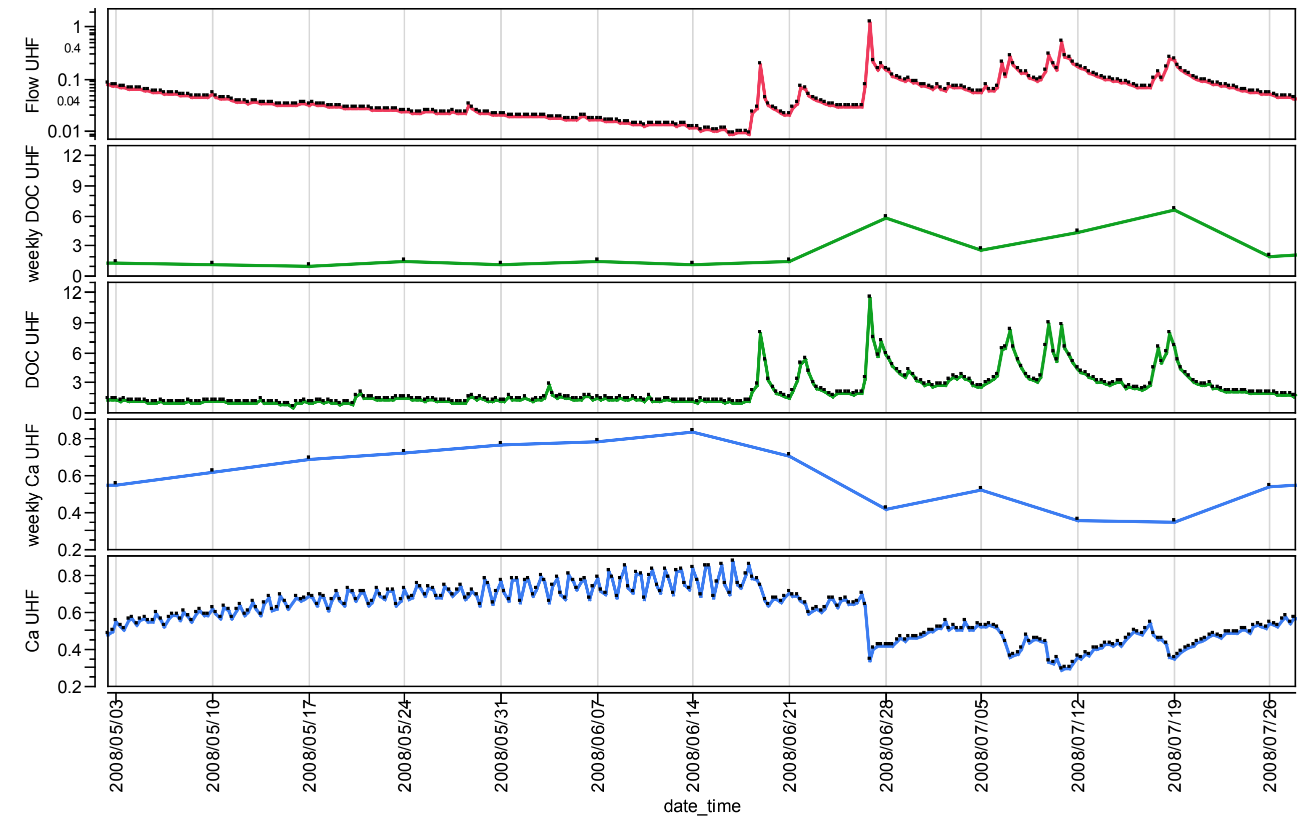
Neal et al., 2013, *Hydrological Processes*
Kirchner and Neal, 2013, *PNAS*

With thanks to:
Colin Neal
Margaret Neal
Mark Robinson
Ken Blyth
Phil Rowland
Darren Sleep
Brian Reynolds
– and –
The Plynlimon
field staff

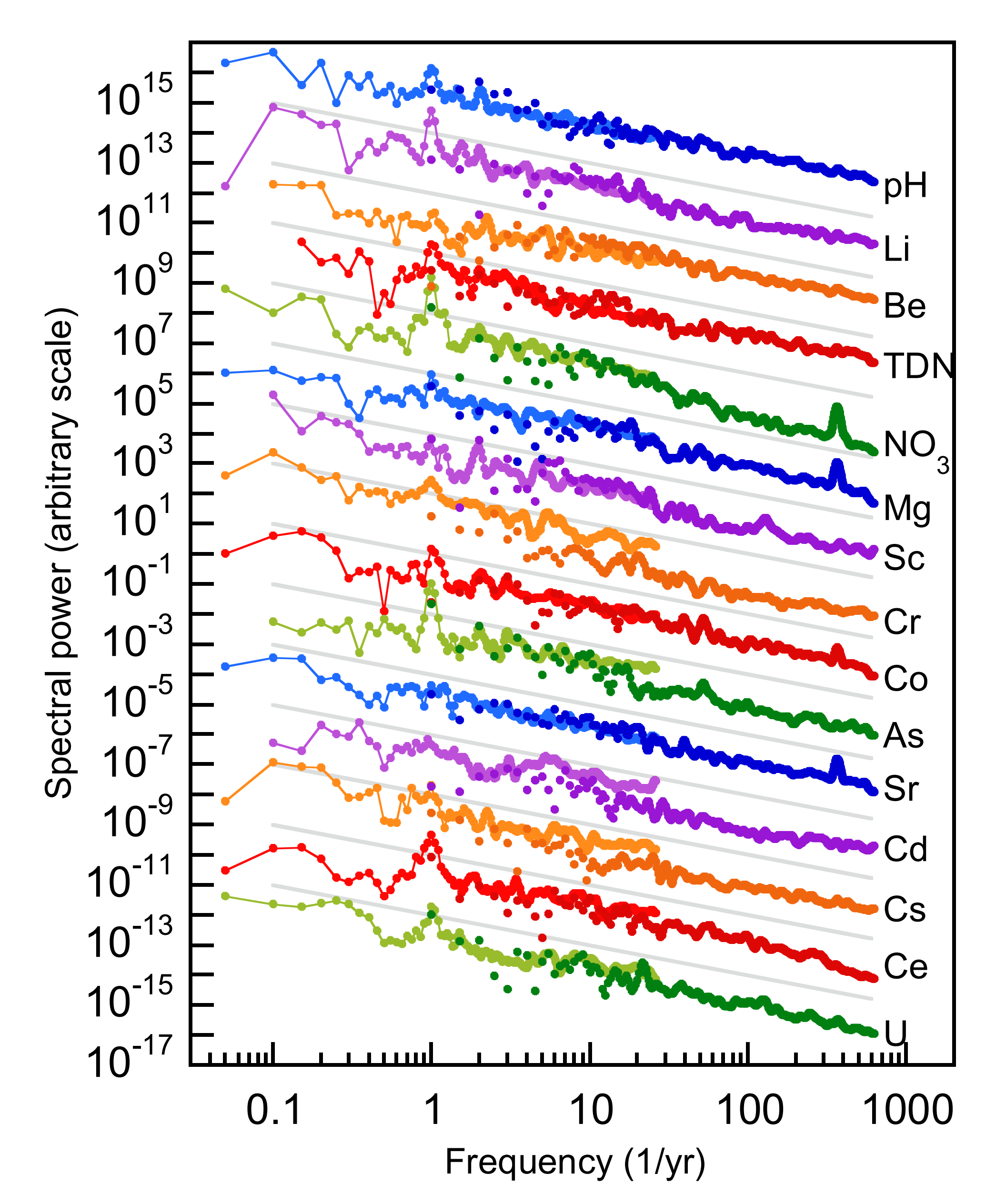
# Phases of daily cycles: landscape chromatography?



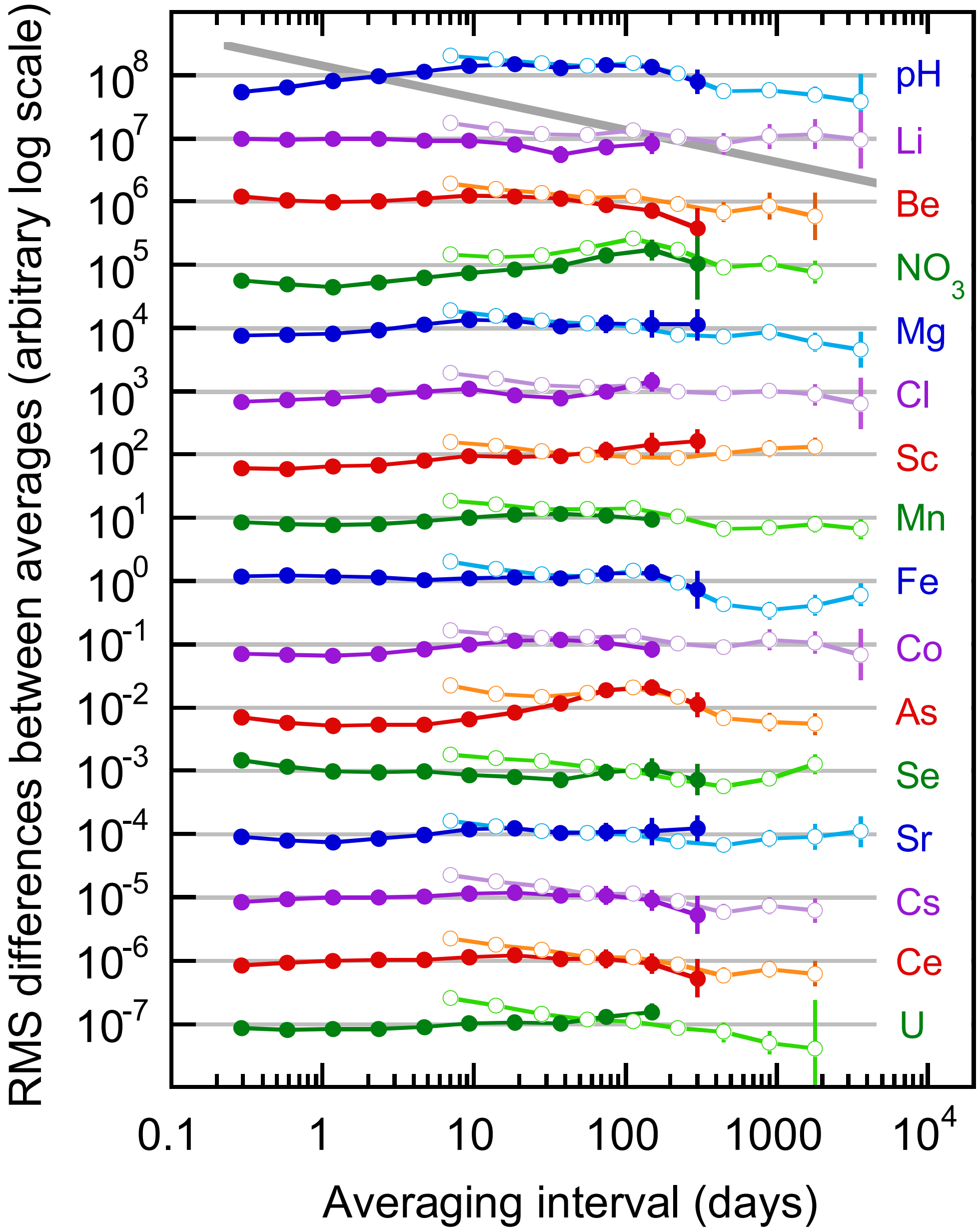
# High-frequency sampling reveals close connections with streamflow dynamics




# Universal 1/*f* spectral scaling in water quality




# Lack of self-averaging: a challenge for change/trend detection!




# Convincing, but inconsistent, trends on all time scales