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Supplement of

The potamochemical symphony: new progress in the high-frequency acquisition of stream chemical data

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Associated content

Design of the River Lab

Tangential filtration characteristics

The primary circuit flows through a porous pipe, from which flows 1 liter per hour of water to feed a secondary circuit (filtered water circuit). Every 5 minutes, an ultrasound motor and a back flushing of compressed air clean the filtration system. The porous pipe is composed of stainless steel. It is changed every 6 months. The 0.2 µm cellulose acetate filter is changed each two weeks to prevent clogging and cross contamination. After the filtration, the material in contact with the sample solution is made of PEEK (poly-ether–ether–ketones).

Ion Chromatographs characteristics

Both ICS2100 chromatographs work under an isocratic eluent regime. The running time is 39 minutes and the injection time is 2 minutes. The sample is injected with a 25-µL PEEK catheter. A deionised water tank purified by a Millipore® system purveys pure water for elution preparation. The software developed by Dionex, Chromeleon 7® controls the whole system. For more details and information, please see the company website: http://www.dionex.com.

1) Cation measurement

The column and the detection cell of the cation chromatograph is thermostated at 40.0 ± 0.1 °C. The system is provided with a guard column (2x50mm). The chromatograph is equipped with IonPac® Cation Trap Columns (CR-CTC). The precolumn is a CG16 and the column is a CS16 in 2 mm. The system is equipped with a suppressor system CSRS

500 (2 mm) set to 32 mA. The eluent is generated from a concentrated cartridge of EGCIII, MSA. The eluent concentration is 30.00 mM. The flow rate is 0.36 ml/min. The eluent cartridge autonomy is around 3 months.

2) Anion measurement

The anion chromatograph is thermostated at 30.0 ± 0.1 °C for the column and at 35.0 ± 0.1 °C for the detection cell. The system is provided with a guard column (2x50mm). The chromatograph is equipped with IonPac® Anion Trap Columns (CR-ATC). The precolumn is an AG18 and the column is an AS18 in 2mm. The system is equipped with a suppressor system ASRS 300 (2 mm) set to 15 mA. The eluent is generated from a concentrated cartridge of EGCIII, KOH. The eluent concentration is 23.00 mM. The flow rate is 0.25 ml/min. The eluent cartridge autonomy is around 9 months.

3) Blank Control

Pure distilled water is regularly (every two weeks) introduced and measured to check the contamination. The blank level is always satisfactory for all elements except for two cationic species (Calcium and Magnesium). When the check blank is unsatisfactory, concentration measurements of the species are not considered between to checks.

Performances of the River Lab

Reproducibility test conditions

The conventional method for river sampling is described hereafter. For each sample, water collected was immediately filtered using using a Teflon® filtration unit with 0.2-µm porosity cellulose acetate filters. Samples were consigned in two acid-washed polypropylene bottles. One bottle was acidified to pH 2 with ultra purified HNO_3 for cation analysis. The second one was kept non-acidified for anion analysis. Solute concentration of major elements, i.e. Na, K, Mg, Ca, Cl, NO_3 and SO_4 were measured by ionic chromatography (IC). We used Dionex® 120 for anionic species and ICS 5000 Thermo Fisher® for cationic species at IPGP, Paris. Each sample has been measured 3 times with a relative external reproducibility better than 1% (2 σ).

Additional discussion about the tests performed in the RL

Sampling frequency

The resampling approach presented in the part 5.2 of the main text is generalized and expanded to other elements for both the summer and rain events. In Figures 5 and 6, we arbitrarily chose the hour of sampling (10 a.m. and 2 p.m., respectively). In Figure SI 3, the sub-sampling is performed at each of the possible sampling hours: 24 for the daily sampling frequency (one time a day) and at each of the 7 for the 7-hourly sampling frequency. For each of these sampling frequencies we computed the PDF of every element concentration and presented the average and the standard deviation (Fig. SI 3). Figure SI 3 shows that the concentration PDFs are strongly sensitive to the sampling frequency. The standard deviation, reflecting variability of the concentration, systematically decreases with the sampling frequency indicating narrower distributions at low frequencies for all species. This consequence of sampling frequency on signal variability is more important during the summer event compared to the rain event, where the amplitude of concentration changes are much higher (30-40%) compared to the summer event (8%). The skweness is presented in the figure SI 5 for the rain event and in the figure SI 6 for the summer event. The skewness is clearly the most affected parameter when the sampling frequency is decreased. Depending on the element, the skewness varies as a function of sampling frequency indicating complete changes in the asymmetry of the PDFs. This statistical analysis quantitatively demonstrates that only high frequency measurements are able to capture the day-night chemical cycles of the Orgeval River. Given the amplitude and duration of typical rain events in the catchment, the alteration of the signal by lowering the sampling frequency is less critical but still significant during these periods.

Analytical precision.

The approach presented in the part 5.3 of the main text is expanded to other elements for both the summer and rain events, as shown in the figure SI 4, indicating that concentration PDFs are strongly sensitive to the analytical precision for all species. For both selected events (rain and summer), changes in the three statistical parameters are more significant for the 4% precision signal than for the 2% precision signal. The average is not sensitive to analytical precision, as expected as the added noise has a zero-mean. The standard deviation systematically increases as the precision is compromised, leading to a much larger variability at low precision. The skewness values are presented in the figure SI 7 for the rain event and in the figure SI 8 for the summer event. Skewness decreases for all elements considered both for the rain and drought event. Given that the concentration PDF calculated from the RL original signal is asymmetrical with a positive skweness, this observation indicates that the PDFs become more symmetrical at degraded analytical precision. Based on the resampling test, the observed effects are more drastic for the summer event than for the rain event, indicating that the high precision record is particularly necessary in order to capture subtle day-night variations.

Figure Captions

Figure SI 1. Sketch of the River Lab. Bold large dark blue arrows indicate the primary circuit of unfiltered water. Thin dark blue arrows indicate filtered water supplied to IC instruments (see part 3 and Fig. 1). Thin light blue arrows indicate pure water supplied to IC instruments for eluent generation. Each grey box represents a controlled parameter.

Figure SI 2. Water conductivity, pH and temperature measurements during the experiment aiming at testing the precision of the whole RL system including the primary circuit, filtration systems and IC instruments (see part 4.2 and Fig. 2). A closed system is established on the primary circuit of the RL by connecting the inlet and the outlet through a 300-L tank of river water. The experiment is then run for a period of 24 hours. This particular test was performed on the 17th of April 2016.

Figure SI 3. Values of the average and standard deviation obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL. The average and standard deviation are calculated from data collected over two periods: 'rain event' (left panels) and 'summer event' (right panels). Each statistical parameter is calculated for three sampling frequencies: every 40 minutes (RL original signal) and artificially sub-sampled every 7 hours and every day. The average and standard deviation values obtained from the RL original signal are considered as the reference against which all values are compared. The figure thus shows the relative deviation of the average and standard deviation values of the sub-sampled signals compared to the RL original signal-derived value, in %. For the daily and 7-hourly frequency signals, the value reported for each statistical parameter is the average over the 24 and 7 possible sub-sampling schemes (one every hour), respectively; and the error bar corresponds to the standard deviation of these statistical parameters over these 24 and 7 possible sub-sampling schemes respectively. The standard deviation (Std D.) is not available for the daily subsampling because of the too small number of points (5).

Figure SI 4. Values of the average and standard deviation obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL. The average and standard deviation are calculated from data collected over two periods: 'rain event' (left panels) and 'summer event' (right panels). Each statistical parameter is calculated for three different signals: the original RL signal (characterized by an analytical precision over one week, given in Tab. 1) and two artificially degraded signals using a normally distributed noise with standard deviation of 2% and 4%, to reflect the effect of analytical uncertainty. For each event and each level of precision, the concentrations PDFs were computed 10,000 times. The average and standard deviation values obtained from the RL original signal were considered as a reference value against which all numerical values are compared. We thus present the relative deviation of the value of the average and standard deviation for the artificially degraded signals compared to the RL original signal-derived value, in %. The value and error bar reported for each

statistical parameter is the average and standard deviation over the 10,000 calculations, respectively.

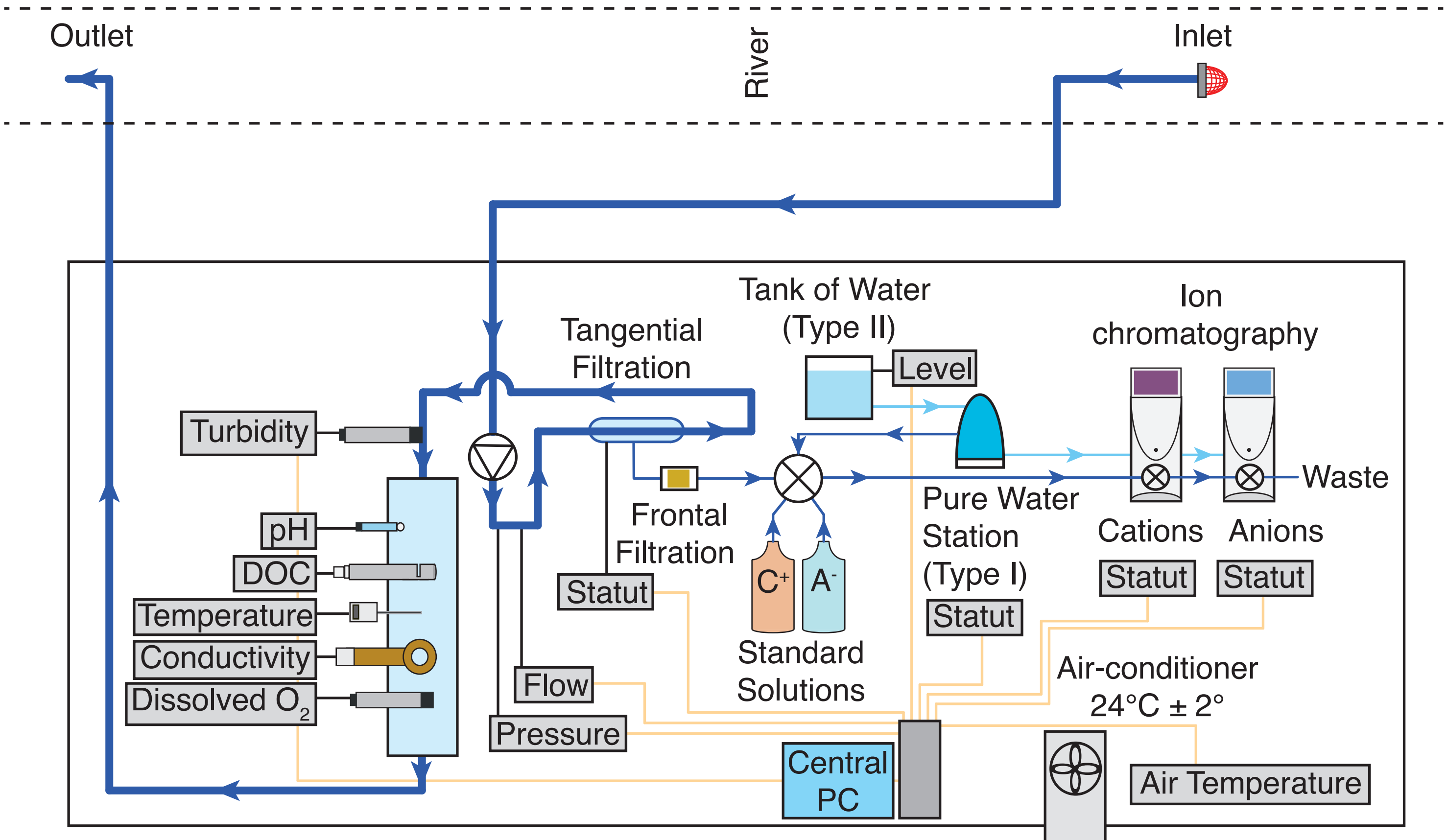
Figure SI 5. Values of the skewness obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL over the 'rain event'. The skewness is calculated for three sampling frequencies: every 40 minutes (RL original signal) and artificially sub-sampled every 7 hours and every day. For the daily and 7-hourly frequency signals, each point indicates one of the 24 and 7 possible sub-sampling schemes respectively.

Figure SI 6. Values of the skewness obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL over the 'summer event'. The skewness is calculated for three sampling frequencies: every 40 minutes (RL original signal) and artificially sub-sampled every 7 hours and every day. For the daily and 7-hourly frequency signals, each point indicates one of the 24 and 7 possible sub-sampling schemes respectively.

Figure SI 7. Values of the skewness obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL over the 'rain event'. The skewness is calculated for three different signals: the original RL signal (characterized by an analytical precision over one week, given in Tab. 1) and two artificially degraded signals using a normally distributed noise with standard deviation of 2% and 4%, to reflect the effect of analytical uncertainty. For each level of precision, the concentration PDF was computed 10,000 times. The grey bar represents the 10.000 different calculations for each precision.

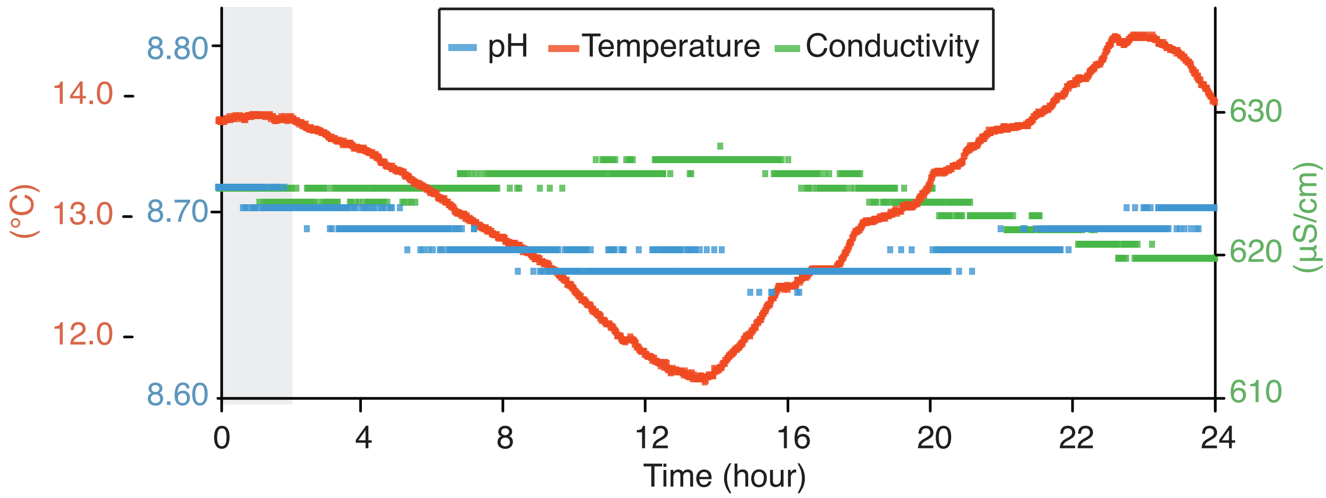
Figure SI 8. Values of the skewness obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL over the 'summer event'. The skewness is calculated for three different signals: the original RL signal (characterized by an analytical precision over one week, given in Tab. 1) and two artificially degraded signals using a normally distributed noise with standard deviation of 2% and 4%, to reflect the effect of analytical uncertainty. For each level of precision, the concentration PDF was computed 10,000 times. The grey bar represents the 10.000 different calculations for each precision.

Figure SI 1



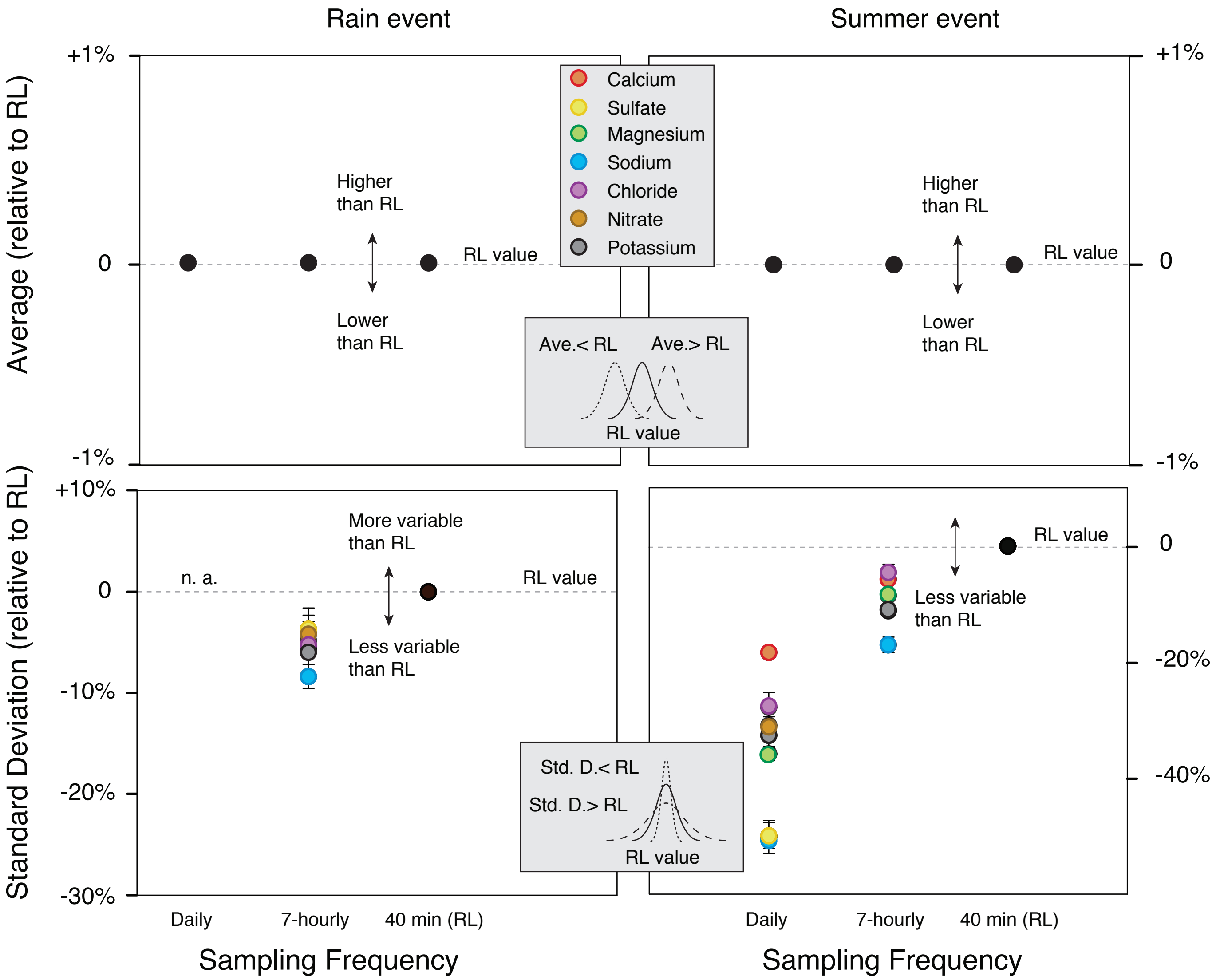
Outlet
River
Inlet
Tank of Water
(Type II)
Ion
chromatography
Tangential
Filtration
Level
Turbidity
Waste
Frontal
Filtration
Pure Water
Station
(Type I)
Cations
Anions
pH
DOC
Temperature
Conductivity
Dissolved O_2
Statut
Statut
Statut
Statut
C^+
A^-
Standard
Solutions
Flow
Pressure
Air-conditioner
24°C ± 2°
Central
PC
Air Temperature
River Lab

Figure SI 2



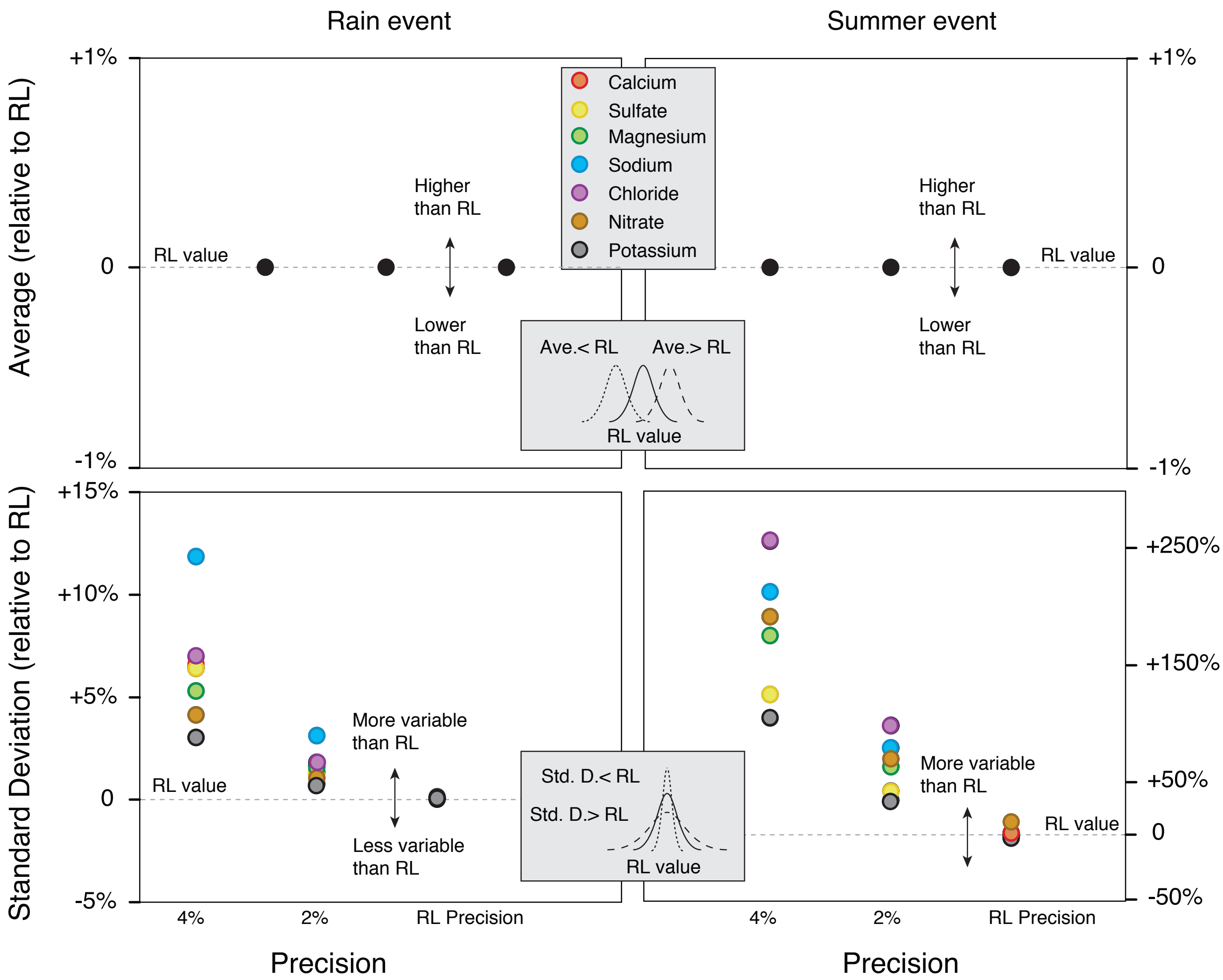
pH
Temperature
Conductivity
8.80
14.0
13.0
8.70
12.0
8.60
(°C)
630
620
610
(µS/cm)
0
4
8
12
16
20
22
24
Time (hour)

Figure SI 3



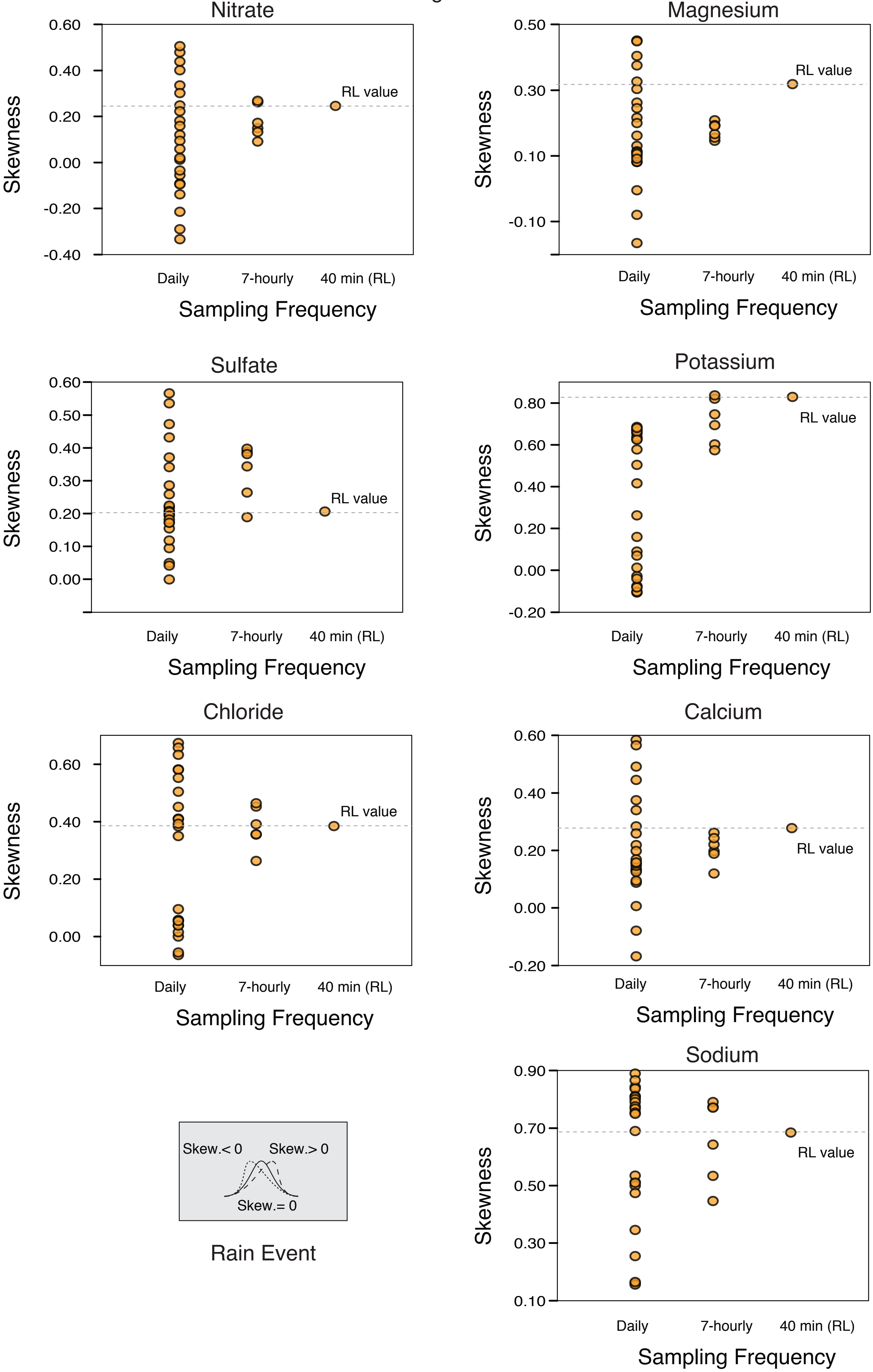
Rain event
Summer event
+1%
0
-1%
Average (relative to RL)
Higher than RL
Lower than RL
RL value
Calcium
Sulfate
Magnesium
Sodium
Chloride
Nitrate
Potassium
Ave.< RL
Ave.> RL
RL value
+10%
-10%
-20%
-30%
-40%
Standard Deviation (relative to RL)
n. a.
More variable than RL
Less variable than RL
Std. D.< RL
Std. D.> RL
Daily
7-hourly
40 min (RL)
Sampling Frequency

Figure SI 4



Rain event
Summer event
Average (relative to RL)
+1%
0
-1%
RL value
Higher than RL
Lower than RL
Calcium
Sulfate
Magnesium
Sodium
Chloride
Nitrate
Potassium
Ave.< RL
Ave.> RL
RL value
Standard Deviation (relative to RL)
+15%
+10%
+5%
0
-5%
More variable than RL
Less variable than RL
Std. D.< RL
Std. D.> RL
+250%
+150%
+50%
-50%
4%
2%
RL Precision
Precision

Figure SI 5



Nitrate
Skewness
0.60
0.40
0.20
0.00
-0.20
-0.40
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Magnesium
Skewness
0.50
0.30
0.10
-0.10
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Sulfate
Skewness
0.60
0.50
0.40
0.30
0.20
0.10
0.00
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Potassium
Skewness
0.80
0.60
0.40
0.20
0.00
-0.20
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Chloride
Skewness
0.60
0.40
0.20
0.00
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Calcium
Skewness
0.60
0.40
0.20
0.00
-0.20
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Skew.< 0
Skew.> 0
Skew.= 0
Rain Event
Sodium
Skewness
0.90
0.70
0.50
0.30
0.10
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency

Figure SI 6

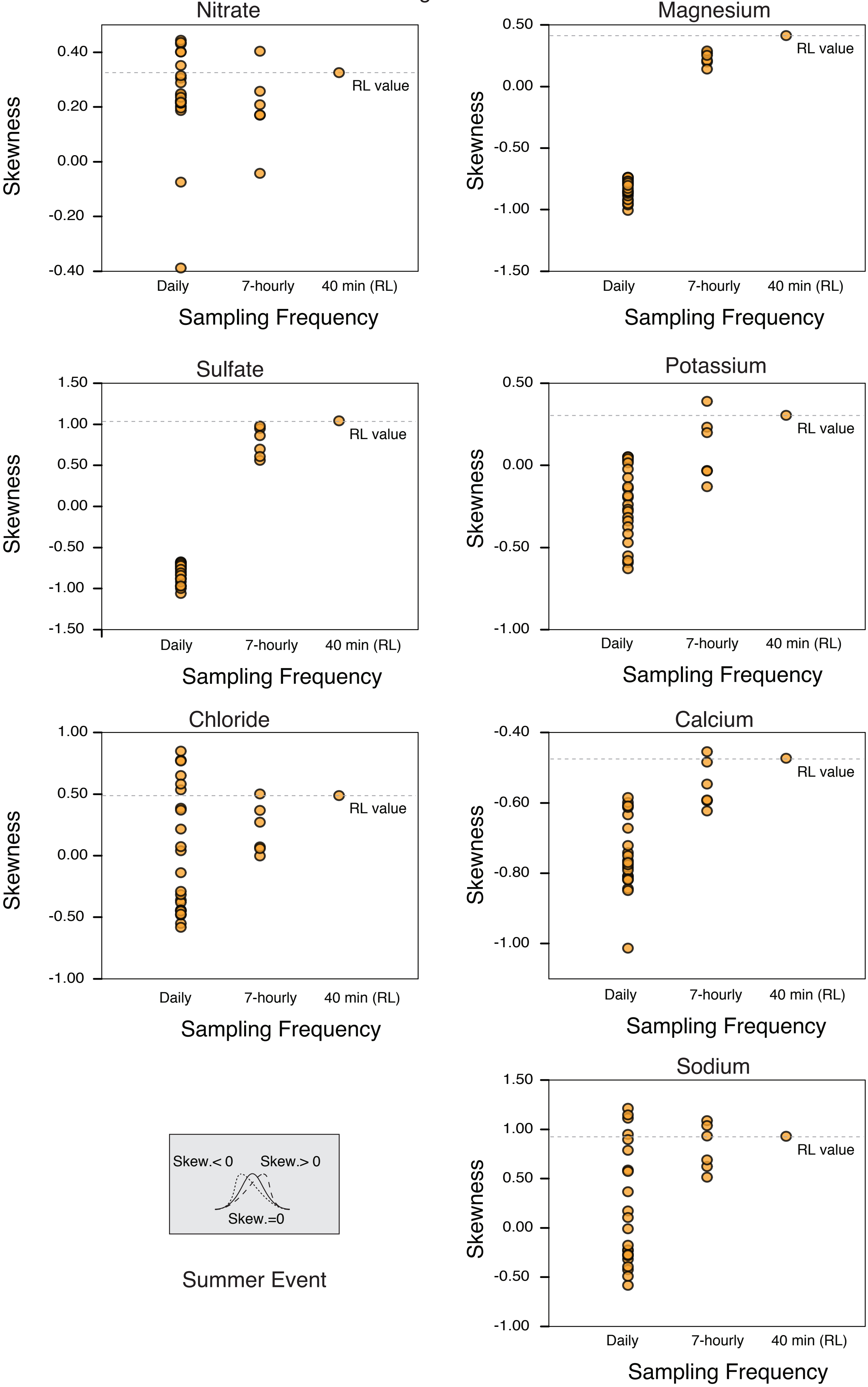

Nitrate
Skewness
0.40
0.20
0.00
-0.20
-0.40
RL value
Daily
7-hourly
40 min (RL)
Sampling Frequency
Magnesium
0.50
0.00
-0.50
-1.00
-1.50
Sulfate
1.50
1.00
0.50
0.00
-0.50
-1.00
-1.50
Potassium
Chloride
Calcium
-0.40
-0.60
-0.80
-1.00
Sodium
Skew.< 0
Skew.> 0
Skew.=0
Summer Event

Figure SI 7

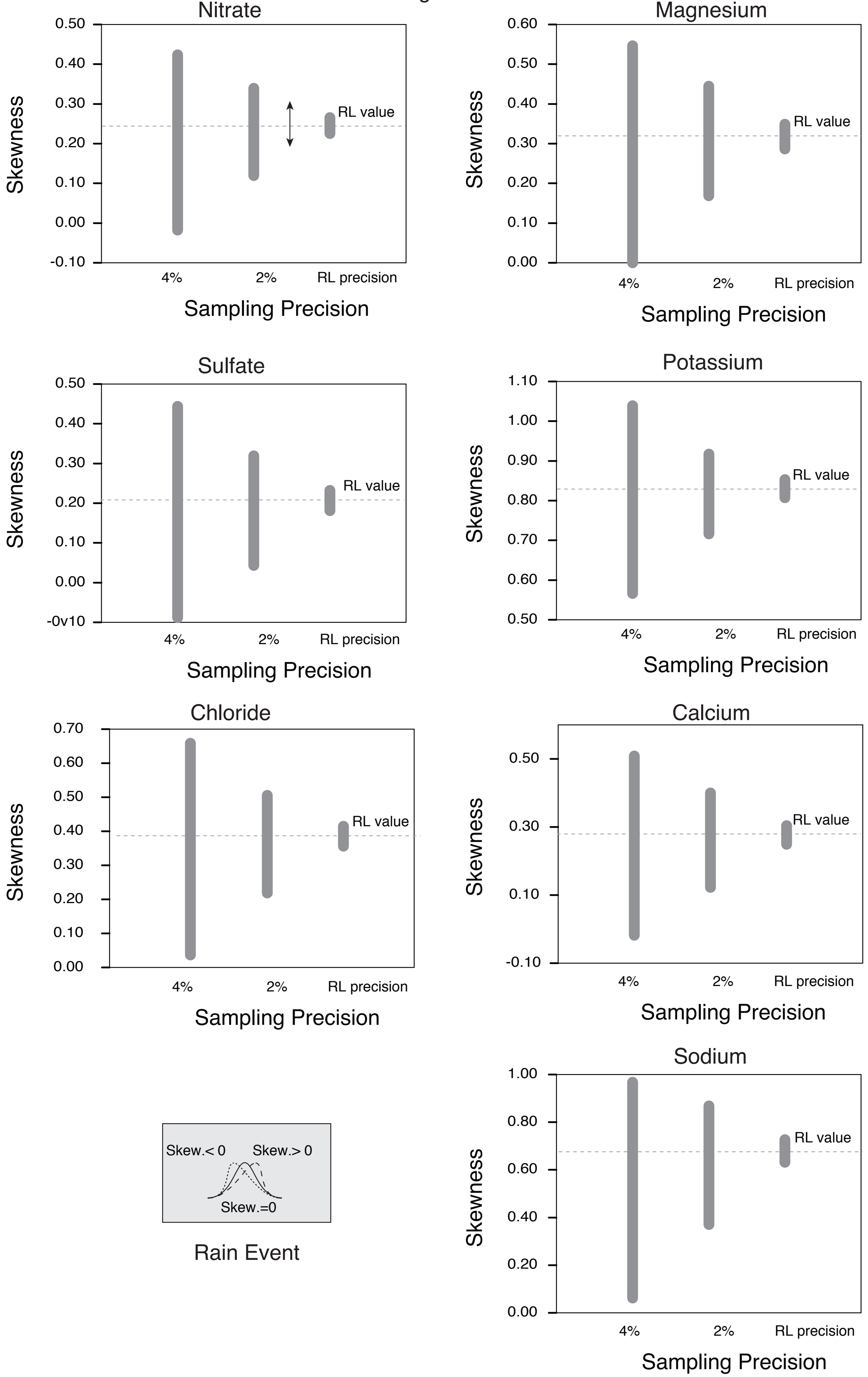
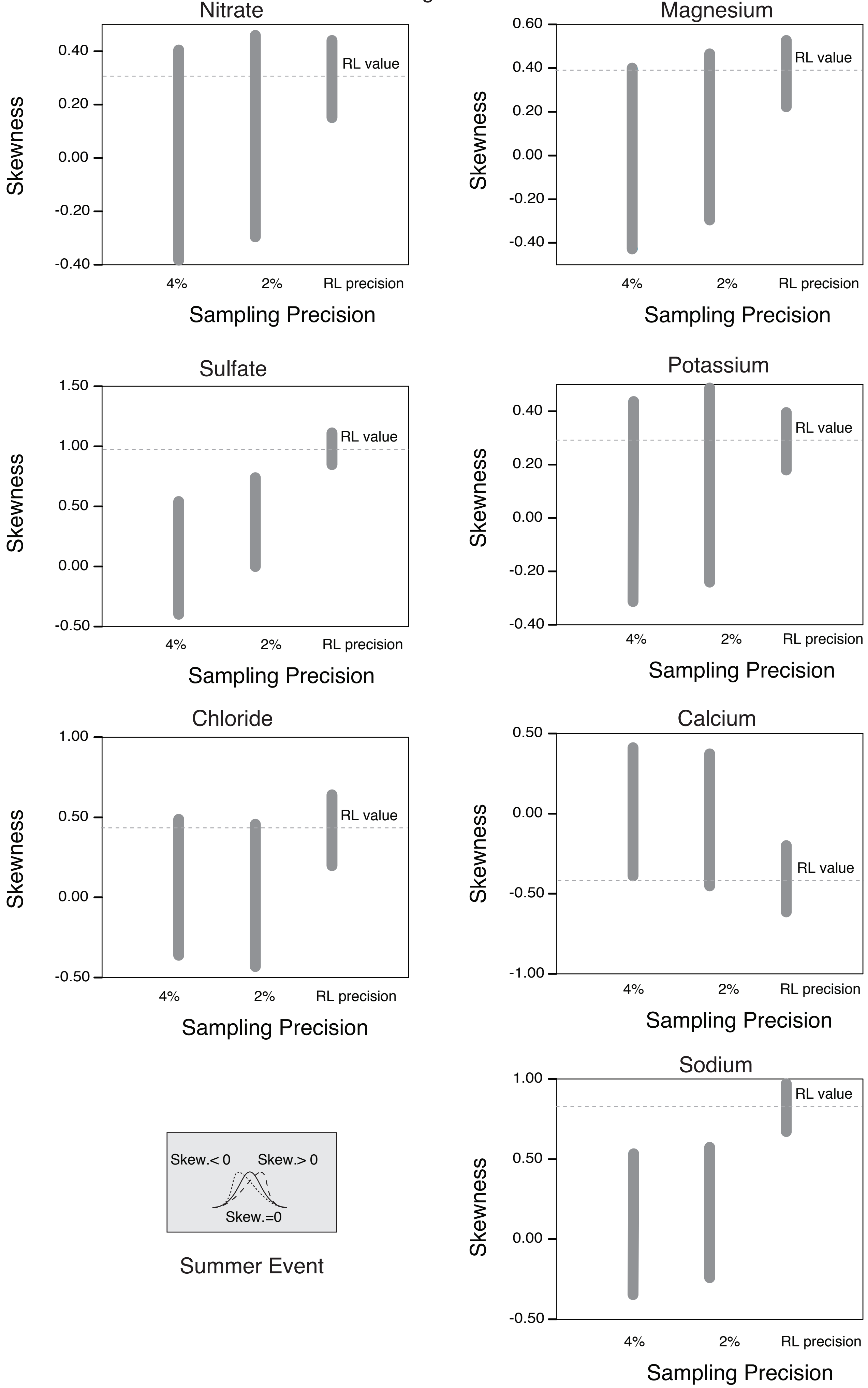

Nitrate
Skewness
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
RL value
4%
2%
RL precision
Sampling Precision
Magnesium
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Sulfate
-0v10
Potassium
1.10
1.00
0.90
0.80
0.70
0.60
0.50
Chloride
0.70
Calcium
0.50
0.30
0.10
-0.10
Sodium
1.00
0.80
0.60
0.40
0.20
0.00
Skew.< 0
Skew.> 0
Skew.=0
Rain Event

Figure SI 8


Nitrate
Skewness
0.40
0.20
0.00
-0.20
-0.40
RL value
4%
2%
RL precision
Sampling Precision
Magnesium
Skewness
0.60
0.40
0.20
0.00
-0.20
-0.40
RL value
4%
2%
RL precision
Sampling Precision
Sulfate
Skewness
1.50
1.00
0.50
0.00
-0.50
RL value
4%
2%
RL precision
Sampling Precision
Potassium
Skewness
0.40
0.20
0.00
-0.20
-0.40
RL value
4%
2%
RL precision
Sampling Precision
Chloride
Skewness
1.00
0.50
0.00
-0.50
RL value
4%
2%
RL precision
Sampling Precision
Calcium
Skewness
0.50
0.00
-0.50
-1.00
RL value
4%
2%
RL precision
Sampling Precision
Skew.< 0
Skew.> 0
Skew.=0
Summer Event
Sodium
Skewness
1.00
0.50
0.00
-0.50
RL value
4%
2%
RL precision
Sampling Precision