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Hydrology and Earth System Sciences
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The Potamochemical symphony: new progresses in the high frequency acquisition of stream chemical data

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Abstract

Our understanding of hydrological and chemical processes at a catchment scale is limited by our capacity to record the full breadth of the information carried by river chemistry, both in terms of sampling frequency and in precision. Here, we present the proof-of-concept of a new system of water quality monitoring that we called the "River Lab" (RL), based on the idea of permanently installing a suite of laboratory instruments in the field. Confined in a bungalow next to the river, this set of instruments performs analyses at a frequency of 40-minutes for major dissolved species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-) through continuous sampling and filtration of the river water using automated ion chromatographs. The RL was deployed in the Orgeval Critical Zone Observatory, France for over a year of continuous analyses. Results show that the RL is able to capture long-term fine chemical variations with no drift and a precision a significantly better than conventionally achieved in the laboratory (up to ± 0.5 % for all major species for over a day and up to 1.7 % over two months).

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Using chemical signals obtained as a benchmark, we assess the effects of a lower sampling frequency (typical of traditional field sampling campaigns) and of a lower precision (typically reached in the laboratory) on the chemical river signal. The RL is able to capture the abrupt changes in dissolved species concentrations during a typical 6-days flood event, as well as unexpected daily oscillations during a hydrological 'boring' period of summer drought.

The unprecedented, high-resolution, high precision measurements made possible by the RL open new perspectives for understanding critical zone hydro-bio-geochemical cycles. This approach also offers a solution for operational agencies to monitor the water quality in quasi real-time.

1 Introduction

River chemistry offers a window into the multiple processes that control the nature and the abundance of solutes in continental waters and thus represents a tool to study the Critical Zone (Neal et al. 2013; Calmels et al. 2011; Feng et al., 2004; Kirchner et al., 2000; Kirchner et al., 2001; Neal et al., 2012). Moreover, understanding the parameters that control river water geochemistry is one of the major challenges for humanity to access and preserve drinkable water (Bain et al., 2012; Banna et al., 2013; Bartam and Ballance, 1996), but our understanding is limited by the temporal resolution of sampling (Whitehead et al., 2009). As summarized by J. Kirchner: "If we want to understand the full symphony of catchment hydrochemical behaviour, then we need to be able to hear every note." (Kirchner et al., 2004). Yet, taking high-frequency sample sets back to the laboratory is limited by the requirement of considerable human resources (Danielsen et al., 2008; Rozemeiler et al., 2014; Strobl and Robillard, 2008; Telci et al., 2009; Chapman et al., 1996; Halliday et al., 2015).

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Thus far, high-frequency chemical measurements in catchments have been mostly reported during short periods such as a single storm events or a day (Chapman et al., 1997; Morel et al., 2009; Takagi et al., 2015,Nimick et al., 2011; Beck et al., 2009; Brick et al., 1996; Kurz et al., 2013; Nimick et al., 2005; Gammons et al., 2007; Montety et al., 2011; Neal et al., 2002; Tercier-Weaber et al., 2009; Liu et al., 2007). These studies highlight the wealth of information provided by sampling at sub-hourly frequency, however, such strategies underestimate the legacy of past hydrological episodes (Kirchner 2006; Jasechko et al., 2016).

To date, the best combination of high frequency and long term monitoring ever reported for river chemistry is a 7-hourly frequency sampling over 18 months (Neal et al., 2012). This study demonstrated the "act of discovery" permitted by such sampling schemes, but also highlights the practical limits of "manual approaches". However, automated approaches, developed using probes installed directly in the river (Rozemeijer et al., 2010a; Macintosh et al., 2011; Cassidy and Jordan 2011; Dabakk et al., 1999; Glasgow et al., 2004; Zhu et al., 2010; Yang et al., 2008) or online instrumental devices in which continuously pumped water is injected (Rozemeijer et al., 2010b; Zabiegala et al., 2010; Jordan and Cassidy 2011) have been demonstrated as a novel alternative to monitor water chemistry. Thus far, these systems have only been applied to nutrients such as dissolved N or P (Kunz et al., 2012; Clough et al., 2007; Aubert et al., 2013a; Aubert et al., 2013b).

In this paper, we present a novel apparatus designed to bring the chemical laboratory to the field: the River Lab (RL). This approach overcomes traditional limitations on the number of samples and avoids several issues related to sample transport, filtration and storage (von Freyberg et al., In review). RL prototype is one of the work packages of the French program CRITEX: "Innovative sensors for the Temporal and spatial

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EXploration of the CRITical Zone at the catchment scale". The breakthrough of the RL lies in its ability to perform a complete chemical analysis of all inorganic major anionic and cationic species in the dissolved load of river water using ion chromatography (IC), to a frequency of up to one complete measurement every 40 minutes.

This article describes the analytical design of the RL and its performance by evaluating the precision, reproducibility and accuracy of concentration measurements. The first results from the RL reveal a significant improvement in reproducibility compared to conventional sampling and analysis techniques. Leveraging these optimal analytical conditions, the RL is able to reveal unsuspected temporal patterns of river chemistry, such as daily concentration variations. Thus, the RL opens new opportunities in the field of river chemistry research and operational monitoring.

2 Monitoring site

The RL was installed on the Orgeval river, a Critical Zone Observatory located 70 km eastward from Paris, France. The Orgeval is a temperate agricultural catchment, within the Seine river watershed, and is part to the French Critical Zone Observatory network RBV ("Réseau des bassins versants"). This catchment is one of the most instrumented and documented river observatories in France, with 50 years of hydrological data (Garnier et al., 2014). Catchment hydrologic data are available on the ORACLE website (https://bdoh.irstea.fr/ORACLE/).

The RL is installed at the outlet of the Avenelles river, a sub-catchment in the Orgeval watershed, which drains an area of 45 km^2. The climate is temperate and oceanic, with cool winters (mean temperature 3°C), warm summers (20°C in average) and a mean annual precipitation rate of ~ 650 mm. The Avenelles sub-catchment sits within the sedimentary carbonate-dominated Paris Basin. The river is perennial, supplied by

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groundwater from the Brie aquifer, with a water chemistry dominated by Ca^{2+}, SO_4^{2-}, HCO_3^{2-} and NO_3^- ions. The water level at the Avenelles gauging station shows an average daily volumetric flow rate of 0.2 m^3/s (from 1962 to 2016) with low water period in summer (0.01 m^3/s) and flash flood events reaching 10.4 m^3/s in spring.

3 Design of the River Lab

The concept of the RL is to pump river water and feed a set of physico-chemical probes and ion chromatography instruments (IC) for a complete analysis of major dissolved species continuously at high frequency (40 minutes for a complete analysis). All the instruments of the RL fit into an isolated bungalow of 4 m length by 2.5 m width, kept at 24°C ± 2°C. The RL was conceptualized by IPGP and IRSTEA and assembled by Endress & Hauser (E+H®).

The RL has been designed around a primary circuit, which pumps the river water at 700 liters per hour. First, the unfiltered river water sampled in the middle of the stream (Fig. 1) continuously supplies an overflow tank where 6 parameters are measured: pH, conductivity, dissolved O_2, dissolved organic carbon (DOC), turbidity and temperature. The water is then released into the river downstream from the RL. The turnover time of water in this primary circuit is 2 minutes. The turbidity probe is installed upstream of the overflow tank in a pipe perpendicular to the flow to provide more accurate measurements. The turbidity and DOC probes benefit from an automatic self-cleaning each 5 minutes using compressed air. For all probes, the frequency of acquisition is one measurement per minute. The tank and each probe are hand-cleaned weekly. All information about characteristics and calibration for each probe are available as supplementary information “SI Probes characteristics”.

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Second, a fraction of water pumped through the primary circuit feeds another circuit directed toward two IC instruments for the measurement of major dissolved species concentrations. A filtration system is deployed between the primary circuit and the IC instruments, consisting of a tangential filter with a 2 µm pore size, followed by a 0.2 µm frontal filtration system through cellulose acetate filters (Fig. 1) crucial for the IC instruments. Cation and anion chromatographs, connected in series, are fed simultaneously every 40 minutes from the filtered water circuit through a injection valve. Between two injections, the water in the filtered circuit is constantly renewed (1 L per hour).

The IC analysis is performed using two Dionex® ICS-2100 (Thermo Fisher Scientific®) instruments using eluent produced with concentrated eluent cartridges and ultra-pure water (Fig. 1). The cationic species measured are Na^+, K^+, Mg^{2+} and Ca^{2+}, while anionic species are Cl^-, NO_3^- and SO_4^{2-}. The chosen analysis time is 30 minutes (40 minutes if Sr^{2+} concentration measurements are included; see details in SI "Ion Chromatographs characteristics"). The multiport valve installed upstream of the ICs allows us to check the drift of the instruments and the background signal by regular introduction of calibration solutions and pure distilled (see section 4). Both cationic and anionic chromatographs are calibrated every two months using synthetic solutions mimicking the river chemistry, made from 1000-ppm mono-elemental standard solutions. Two sets of calibration solutions are prepared, one for anions and the second for cations. The first solution (called "River x1") is prepared based on concentrations of the river water during summer, i.e. with the highest measured concentrations for most species. In the second solution, these concentrations are doubled (called "River x2"). Further solutions are produced out of River x1 and x2 through dilution by up to ten fold to achieve lower concentrations ("River x0.5; x0.25; x0.1"). The resulting five calibration solutions cover

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the entire range of possible natural variability of each species observed for the Orgeval river, including flood events.

Data from probes and ICs are collected, merged and updated in a single database in real time. Data from the gauging station (flow discharge and precipitation level) are automatically added to the database. Several parameters of the RL can be remotely monitored such as pump activity, pressure, flow and temperature in the primary circuit; activation of the tangential filtration cleaning system, instrument connection, and temperature in the bungalow. A set of alarms and sensors controls each key point of the system. An email is automatically sent in case of dysfunction. Under normal operating conditions, the RL needs human intervention only once per week.

4 Performances of the River Lab

RL data acquisition started on the 12th of June 2015. The reliability of the system was assessed through 5 different tests involving IC measurements and the sampling procedure (accuracy, drift, precision of the whole system, cross-contamination and reproducibility). We refer to the 3rd edition of JCGM 200-2012 (JCGM 2012) for the terminology used in assessing the performance criteria.

4.1 Accuracy and instrumental drift

The aim of the RL is to achieve very high frequency measurements of river chemistry over long periods of time (pluriannual). To compensate for any long-term drift in the IC calibration, instruments are calibrated with a new set of solutions every two months or after each maintenance operation on the IC instruments. However, calibration drift can occur over timescales shorter than two months, resulting in systematic and / or random

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errors in concentration measurements. Using a set of injections of the "River x1" solutions, over one week and over two months, we evaluated this effect (Table 1). For all species measured, no systematic variation was observed in the measured concentration of the solution "River x1", showing that at the two timescales, instrumental drift does not induce any systematic bias on concentration measurements, and that most of the error is of a random nature. Therefore, the standard deviation of the concentration measurement can be used as a reliable measure of the error due to instrumental drift. The measurement error over one week is calculated as the standard deviation of concentration measurements over 19 injections of solution "River x1" performed every 8 hours during one week (from the 5th to the 12th of November 2015). The measurement error over two months is calculated as the standard deviation of concentration measurements over a series of injections performed every two days during two months (from the 28th December 2015 to the 26th February 2016). These error estimates are better than 1 % over one week and better than 1.7 % over two months (Tab. 1).

4.2 Precision of the whole system

In order to estimate the precision of the whole system (IC instruments combined with the sampling device including the primary circuit, the pump and the filtration units), we performed a "closed loop" experiment over the course of one day by connecting the inlet and the outlet of the primary circuit to a 300-L tank containing river water. The test was performed three times over two different seasons (the 20th of July 2015, the 28th of August 2015, and the 17th of April 2016). The conductivity probe (one measurement every minute) was used to check the stability of the water chemistry during the course of the experiment (Fig. SI 2). Our results show that a lapse of 2 hours at least is

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necessary for the system to stabilize, corresponding to the homogenization time of the water within the closed loop (Fig. 2). After two hours, major anion and cation concentrations show a remarkable stability indicating the absence of drift over of 24-hour time lapse despite the temperature variations in the river water, and allowing us to estimate the precision of the whole system over one day using the standard deviation of the measurements performed during the test. The results of the test are presented in Table 2. The precision reached is lower than 0.5% for all species except for potassium, for which it is lower than 1.2%.

4.3 Cross contamination

The ability of the RL to detect rapid variations in river chemistry (typically expected during storm events) depends on 1) the response time of the RL to a perturbation in the river and 2) the potential cross contamination from one sample to the next one. We assessed these two effects by a tracer injection experiment. After establishing a closed loop experiment (on the 29th of August 2015) and allowing for the period of stabilization, we introduced a known amount of NaCl (200 g previously dissolved in a small amount of river water) into the 300-L tank of river water in order to simulate a "spike" in the river chemistry. The monitoring of conductivity in the primary circuit allowed us to follow the propagation of the spike injection into the primary circuit while Cl^- concentrations measured by the IC every 40 minutes allowed us to follow its propagation through the filtration devices and IC instruments (Fig. 3). The conductivity probe shows that the salinity spike is detected very quickly and stabilized after 5 minutes. This indicates that the water in the primary circuit is quickly homogenized (in agreement with the high flow rate of the primary circuit: 700 l/h). Conversely, the Cl^- and Na^+ concentrations only reach the expected concentration at the second IC

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measurement i.e. after 80 minutes.

The first IC measurement following the spike injection indicates that only 93% of the final steady-state concentration is reached, revealing a contamination of the $(n)^{th}$ sample by 7% of the $(n-1)^{th}$ sample. In practice, such a contamination will only be significant if the instantaneous derivative of river concentration with time is important. In the case of the Orgeval River, where the RL is deployed, the derivative of the concentration with respect to time is lower than 1% per hour for 90% of the time for all species. In the case, identified cross contamination induces an error of 0.07% compared to the true concentration, which means that the effect of cross contamination is negligible compared to the precision of the RL (see section 4.2). However, in the case of flood events, when the stream flow increases quickly, the derivative of concentration can change by more than 10% per hour. In such cases, cross contamination will induce an error of 1% or more. The injection test shows that the time resolution of the RL is limited by the transfer time of the water between sampling and injection into the IC instruments. This transfer time of the water in the RL is mainly due to the design of the filtration system, which may be improved in the future.

4.4 Reproducibility: RL *vs* Laboratory

As a final test for assessing the ability of the RL to record fine natural variations of river chemistry in comparison to conventional techniques of filtration and analyses in the laboratory, we focused on two days in the summer of 2015 following long periods without rain (21^{st} of July 2015 for cations and 19^{th} of April 2016 for anions) which showed very high resolution diurnal variations (<5% relative) in chemical composition of the Orgeval river. In addition to the analyses made by the RL every 40 minutes, we

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252 conducted hourly sampling of the river by collecting 5 litres of water and filtering it
253 immediately using a Teflon® frontal filtration unit (Sartorius®) with 0.2 µm
254 polysulfonether filters. Bottles of acidified (at pH = 2) and unacidified river water were
255 transported to the laboratory at IPGP for measurement of major cations and anions,
256 respectively, using IC devices similar to those installed in the RL and calibrated using
257 the same calibration procedure. The error measurement reached in the laboratory is
258 calculated at 1%, estimated through repeated injections of the standard solution "River
259 x1" (every 5 samples). Comparison between the RL and the laboratory for the seven
260 measured species are shown in Figure 4. First, the measurements made by the RL are
261 more precise than those performed in the laboratory, a feature that can be primarily
262 attributed to the greater stability of the continuously working injection system of the
263 RL. Second, the fine variations measured by the RL are reproduced in the laboratory,
264 validating the observed diurnal variations and supporting the reliability of the RL to
265 detect changes on the order of a percent within a day. The third observation is that small
266 yet systematic offsets between the two sets of data exist, up to 3% for Mg. One possible
267 explanation for this difference is that the filtration procedures differed between the RL
268 and the manual sampling, which may have led to a discrepancy in the concentration
269 measurements related to the behaviour of the colloidal phase (Dupré et al., 1999).
270 Regardless of this yet-unexplained discrepancy, we note that variations in concentration
271 recorded by the RL and measured at the IPGP laboratory have the same amplitudes and
272 are synchronous.
273
274 **5 Discussion**
275 **5.1 What are the benefits of bringing the lab into the field?**
276 The RL presented above is a technological breakthrough allowing us to record

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277 continuously, at a high frequency and over long spans of time, the concentration of 7
278 major dissolved species in a river system. From a scientific point of view - beyond the
279 scope of the present paper - the RL presented here opens new possibilities for the
280 exploration of the fine structure of hydrochemical evolution at the catchment scale and
281 for improved understanding of the associated hydrological, geochemical, and biological
282 processes. From a technical point of view, our study shows that deploying the
283 conventional laboratory measurement techniques in the field adds significant value. The
284 tests performed and reported above clearly demonstrate an improvement in precision
285 compared to the analysis of bottled samples taken back to the lab. We see three main
286 reasons for this improvement.
287 1) In a given river, dissolved concentrations typically vary by less than one order of
288 magnitude when water discharge changes by several orders of magnitude (Godsey et al.,
289 2009). This constancy allows us to select a relatively narrow range of concentration for
290 establishing specific calibration curves of the IC instruments, a condition which is rarely
291 possible in the laboratory where different kinds of samples are analyzed.
292 2) While in the laboratory samples are injected discreetly, in the RL river water samples
293 are injected as a continuous flow. Thus, the primary circuit and the filtration system
294 operate continuously at a constant pressure, which supports stable and accurate
295 analyses.
296 3) The third factor is the experimental conditions in the bungalow. The temperature is
297 maintained at 24°C ± 2° (in addition to the 40°C thermostatically-controlled
298 temperature in the column, precolumn and detection device of the ICs) allowing for
299 better stability of the IC measurements. Moreover, the IC instrument is never stopped,
300 which favours stability.
301

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5.2 What is revealed by a higher sampling frequency?

To our knowledge, the high frequency of measurements (one measurement every 40 minutes, 0.42 mHz) demonstrated above for the RL installed on the Orgeval River is the highest ever reported for stream chemistry over several months. To highlight the corresponding improvement in the recorded concentration signal, we tested the effect of sampling frequency on the concentration signal. First, we artificially sub-sampled the RL original signal at two lower sampling frequencies: 0.04 mHz (every 7 hours, starting October 5th, 2015 at 10 pm) and 0.01 mHz (every 24 h). The 0.04-mHz frequency was chosen to reproduce the sampling frequency of Neal et al., (2012) made in the Plynlimon watershed, Wales. The 0.01-mHz frequency is typically what is achievable by "human grab-sampling" in the field. Second, we calculated the probability density function (PDF) of concentration measurements over a given time interval.

The use of PDFs allows us to explore the structure of concentration signals beyond the mean concentration, which constitutes an important metric for river solute budget, but lacks any insight into the variations in concentrations that can be used to retrieve information on catchment processes. A PDF can be described by 4 statistical parameters (mean, standard deviation, skweness, and kurtosis) that account, at first-order, for the fine structure of a concentration signal. We compared these four parameters for the computed PDFs to quantify the signal degradation induced by artificial sub-sampling. Skewness indicates the distribution asymmetry, both in magnitude and direction (positive skewness means that most values are higher than the mean), while Kurtosis is a measure of the "tailedness" of the distribution. For a given distribution (*i.e.* a given standard deviation and skewness), a lower kurtosis indicates fewer extreme outliers.

We applied this statistical approach to two representative periods of the hydrological cycle of the Orgeval Critical Zone Observatory: a typical 6-day flood event caused by

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327 the arrival of a wet, Atlantic meteorological front (in October 2015) and a dry summer
328 low water stage period (July 2015) where the stream is essentially sustained by
329 groundwater (an apparently "boring" hydrological period). We first presented the
330 behaviour of calcium and sulphate concentrations as an example during the two
331 considered periods (Fig. 5 and 6), before generalizing to all measured species (Fig. 7).
332
333 **Flood event**. The Ca concentration time series recorded at 0.42 mHz (every 40-
334 minutes) shows that minimum Ca concentrations are recorded at maximum water
335 discharge, but this relationship is invisible at lower sampling frequency (Fig. 5). Narrow
336 peaks during the maximum of the stream flow are unresolved at a daily or 7-hourly
337 frequency. The comparison of the calculated PDF shows that a bimodal character is
338 captured at all frequencies. The average and standard deviation are not significantly
339 affected by the sampling frequency, with a relative difference of less than 2% for the
340 values of these parameters between the three distributions. However, the skewness and
341 kurtosis values vary among the different records. From the 0.42 mHz to 0.01 mHz
342 signals, skewness values decrease by about 50%, which means that even if the overall
343 concentration variability is well captured at the lower sampling frequencies, the
344 concentration signal is clearly degraded. This degradation is particularly intense during
345 the maximum flood event, where the concentration signal evolves quickly.
346
347 **Summer event.** Despite the absence of rain events during the 2015 summer, the River
348 Lab recorded high frequency variations revealing a diurnal structure with 7% relative
349 variations between day and night and specific to each element. The figure 6 shows that
350 the structure of this signal is altered when the sampling frequency decreases. While
351 these daily variations are still captured when sampling occurs every 7 hours, their

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amplitude is somewhat altered (5%) compared to the 0.42 Hz sampling frequency (8%). The daily structure of the signal is absent on the 0.01 mHz sampling frequency. While the mean remains the same over the range of sampling frequency, the variability quantified by the relative standard deviation decreases with lower sampling frequency, by up to 50% for the daily frequency compared to the 0.42 mHz signal, indicating a significant loss of information. The skewness of the concentration distribution recorded at a sub-sampled daily frequency has a value that is opposite in sign compared to the other two frequencies, indicating that there is an inversion of the measured asymmetry of the PDF at lower sampling frequencies. Therefore, too coarse of a sampling frequency can yield a strongly altered signal compared to higher frequencies, resulting in a biased shape of the distribution of the concentrations.

Generalization. The resampling approach applied above can be generalized and expanded to other elements for both the summer and flood events. In figures 5 and 6, we arbitrarily chose the hour of sampling (10 a.m. and 2p.m. for Figures 5 and 6, respectively). In figure 7, the sub-sampling is performed at each of the possible sampling hours: 24 for the 0.01 mHz sampling frequency (one time a day) and at each of the 7 for the 0.04 mHz sampling frequency (every 7 hours). For each of these sampling hours we computed the PDF of every element concentration and presented the average and the standard deviation (Fig. 7) of the four statistical parameters already discussed above.

Figure 7 shows that the concentration PDF 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. This consequence of sampling frequency on signal variability is

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more important during the summer event compared to the flood event, where the amplitude of flood event concentration variations are much higher (30-40%) compared to the summer event (8%). Skewness and kurtosis are clearly the most affected parameters when the sampling frequency is decreased. Depending on the element, skewness varies as a function of sampling frequency, from +100% to -300% for the summer event and from +50% to -100% for the flood event, indicating complete changes in the asymmetry of the PDFs. Changes in the kurtosis are even more pronounced between 0.42 and 0.01mHz, ranging from +1000% to -2600% in summer and 0 to 700% for the flood event. 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 flood events in the catchment, the alteration of the signal by lowering the sampling frequency is less critical but still significant during these periods.

5.3 What is revealed by better analytical precision?

As shown above, the Orgeval RL not only achieves high frequency measurements but also produces improved precision compared to conventional lab analysis following manual sampling. Therefore, any sampling procedure, even at a high frequency, involving conventional lab analysis induces a loss of precision. We demonstrate this effect through a numerically generated artificial degradation of the precision. Using the original RL concentration signal as a reference, we artificially degraded the signals by adding a normally distributed noise onto the concentration signals recorded by the RL. Noise levels of 4% and 2% were tested; as they are representative of the relative analytical precision reported for most laboratory IC devices (Neal et al. 2011; Aubert et

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401 al., 2013a). The same representative periods as in the previous section (summer and
402 flood events) were utilized for these tests.
403
404 **Flood event.** The figure 8 illustrates the concentration PDF obtained after degradation
405 of the analytical precision for the Ca concentration. The narrow peaks recorded during
406 the maximum of the stream flow are virtually invisible in the signal at a 4%-precision,
407 and strongly smoothed in the signal at a 2%-precision. The original bimodal
408 characteristic of the PDF is still visible in the 2%-precision signal but no longer in the
409 4%-precision signal. The mean and standard deviation appear to be insensitive to these
410 changes in analytical precision, while skewness and kurtosis are strongly impacted,
411 reflecting significant alteration of the concentration PDF at lower precision.
412
413 **Summer event.** Figure 9 shows how the sulphate concentration signal is affected when
414 the precision is degraded. Day-night variations are only visible in the original RL signal
415 because of its high analytical precision. The effect of degraded precision on the PDFs is
416 more important than for the flood event (Fig. 8). While the mean value is robust, the
417 standard deviation is altered (+150% from the RL signal to the 4% precision signal).
418 The skewness decreases by up to 90% for the signal at 4%-precision compared to the
419 original signal and 74% for the signal at 2%-precision, indicating that the original RL
420 signal asymmetry is lost as precision is compromised. These changes in the parameters
421 of the concentration PDF show that the structure of the concentration signal in the
422 Orgeval River would be significantly altered if the measurements were made with
423 analytical precision lower than that of the RL prototype.
424

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425 **Generalization**. This approach has been expanded to other elements for both the
426 summer and flood events, as shown in the figure 10, indicating that concentration PDFs
427 are strongly sensitive to the analytical precision for all species. For both selected events
428 (flood and drought), changes in the four statistical parameters are more significant for
429 the 4% precision signal than for the 2% precision signal. The average is not sensitive to
430 analytical precision. The standard deviation systematically increases as the precision is
431 compromised, leading to a much larger variability at low precision. Skewness and
432 kurtosis decrease for all elements considered both for the flood and drought event.
433 Given that the concentration PDF calculated from the RL original signal is
434 asymmetrical with a positive skweness, this observation indicates that the PDFs become
435 more symmetrical and flatten at degraded analytical precision.
436 Based on the resampling test, the observed effects are more drastic for the summer
437 event than for the flood event, indicating that the high precision record is particularly
438 necessary in order to capture subtle day-night variations.
439

440 **6 Conclusion**

441 This paper demonstrates the feasibility of deploying conventional laboratory
442 instruments in the field to measure the concentration of major dissolved anions and
443 cations in rivers (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-) at a high frequency (0.42 mHz,
444 i.e. one measurement every 40 minutes) and at a high analytical precision (better than
445 1%) over several months. The RL prototype was installed in the Avenelles stream at the
446 Orgeval Critical Zone Observatory, France. The RL features physico-chemical probes,
447 an on-line 0.2-µm-filtration system, and two ionic chromatographic devices, all
448 installed in a closed, air-conditioned bungalow. The RL is autonomous, operable at
449 distance and data can be transmitted automatically. Human intervention is required only

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once a week. Therefore, the RL also allows for an efficient attribution of human resources, as well as considerable saving of consumables.

A suite of tests performed on the RL to assess quality measurement and to compare with more conventional "grab sampling" followed by laboratory measurements revealed only a minor drift in the instrument calibration, leading to improved precision. This precision is not easily achieved in the laboratory under standard analysis conditions, showing the benefit of transporting the laboratory devices to the field. The analytical breakthrough made possible by the RL for major dissolved elements could theoretically be extended to other elements separable by ion chromatography. Preliminary tests demonstrate that species present in trace amounts in river water (down to the ppb, such as strontium or lithium) could be measured with the same gain in precision.

For this particular prototype, the measurement frequency (0.42 mHz) appears to be limited by the turnover time of water in the filtered water circuit, which is in turn imposed by the filtration unit. However, the high frequency and high precision of the RL enabled unprecedented observations of the fine structure in hydrochemical time series. Their interpretation is beyond the scope of the present proof-of-concept paper but the RL is able to capture the abrupt changes in dissolved species concentrations during a typical 6-days flood event, as well as unexpected daily oscillations during a hydrological ‘boring’ period of summer drought.

Using the high frequency signal as a benchmark, it is possible to artificially alter the sample frequency and the analytical precision and study the resulting effect on the geochemical distribution obtained for characteristic hydrological events. This analysis shows that in order to retrieve the fine structure of the hydrochemical signal, high sampling frequency and improved analytical precision are both necessary conditions. To paraphrase Jim Kirchner's quote: "If we want to understand the full symphony of

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475 catchment hydrochemical behaviour, then we need to be able to hear every note". The
476 improvements made possible by the RL make it, to date, the best orchestra available to
477 play the potamological symphony.
478 Our study opens a new era of investigation into the fine structure of the hydrochemical
479 signal in rivers. Future work will explore the relationships between the desired
480 measurement frequency and the timescales of the complex interactions between primary
481 and secondary minerals, biotic processes and hydrological processes that are taking
482 place in catchment systems. Recording such fine stream hydrochemical variations is
483 thus offering a new perspective on Critical Zone.
484

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487

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748 **Table**

749 **Table 1. Assessment of the RL accuracy and instrumental drift based on concentration**
750 **measurements made after several injections of the standard solution "River x1". The uncertainty**
751 **on the calibration solution is the quadratic sum of the uncertainty on the standard solutions**
752 **(provided by the manufacturer) and the overall uncertainty for weighing during solution**
753 **preparation. Measurement errors over one week and over two months are expressed as the relative**
754 **standard deviation (RSD) calculated based on the injections of the solution "River x1" directly into**
755 **the IC instruments via the multiport valve (see Fig. 1).**
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757
758 **Table 2. Precision on concentration measurements of the whole RL system**
759 **calculated as the relative standard deviation (RSD) of concentration measurements**
760 **made over three 24-hour closed loop experiments, during which the inlet and the**
761 **outlet of the primary circuit are connected through a 300-L tank of river water.**
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798 **Figure Captions**
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801 **Figure 1. Sketch of the River Lab. Bold blue arrows indicate the primary circuit of**
802 **unfiltered water. Dashed arrows indicate filtered water supplied to IC**
803 **instruments. 1: The inlet of the primary circuit samples the river at a constant 20-**
804 **cm depth maintained by buoys. Water is filtered at < 2 mm using a strainer. The**
805 **distance between the mouth and the pump is 6 m. The primary circuit assembly is**
806 **almost entirely composed of polyvinyl chloride (PVC) pipes. 2: The electric pump**
807 **runs continuously at a constant power, leading to a rate of 700 liters per hour. 3:**
808 **Almost all the river water just flows through the pipe and remains unfiltered. A**
809 **fraction is filtered at < 2 µm through a tangential stainless steel filtration unit, then**
810 **filtered through a cellulose acetate frontal filter at < 0.2 µm and finally delivered to**
811 **IC instruments at a flow rate of 1 liter per hour. 4: A multiport valve before**
812 **introduction to the IC instruments allows for switching between filtered river**
813 **water and standard or blank solutions. 5: All probes are deployed in an overflow**
814 **tank of 5 liters of unfiltered river water. 6: The outlet of the primary circuit is**
815 **downstream in the river.**
816
817
818 **Figure 2. Assessment of the precision of the whole RL system including the**
819 **primary circuit, filtration systems and IC instruments. A closed system is**
820 **established on the primary circuit of the RL by connecting the inlet and the outlet**
821 **through a 300-L tank of river water. The system is then run for a period of 24**
822 **hours. The figure illustrates the relative variation of concentration (C) of four**
823 **dissolved species in percentage of relative deviation compared to the mean**
824 **concentration (C_{mean}). This particular test was performed on the 17th of April 2016.**
825 **The time between two IC analyses is 40 minutes. The purple curve represents data**
826 **of temperature of the water in the tank. We do not consider the 2 first hours (3**
827 **first measurements), corresponding to the homogenization of water in the circuit**
828 **and tank (see conductivity measurements in Fig. SI 2) for the calculation of**
829 **precision.**
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832 **Figure 3. Assessment of the effects of cross contamination and response time in**
833 **concentration measurements of the RL system using a tracer (NaCl) injection**
834 **experiment. A closed system is established on the primary circuit of the RL by**
835 **connecting the inlet and outlet through a 300-L tank of river water. Then, 200 g of**
836 **salt previously dissolved in a small amount of river water are injected**
837 **instantaneously right after one measurement in the closed system to generate a**
838 **"spike". The conductivity measurement frequency is 1 per minute, whereas the**
839 **time between two measurements of chloride concentration is 40 minutes. Error**
840 **bars for conductivity and Cl^- concentration measurements are smaller than their**
841 **symbols. Results are normalized to the difference between the minimum value,**
842 **before the tracer injection (0%) and the maximum value, at the end of the**
843 **experiment (100%).**
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Figure 4. Assessment of the reproducibility of IC measurements made by the RL every 40 minutes (blue), based on concentration measurements made in the laboratory after conventional sampling every hour (orange), performed the 21st of July 2015 for the cationic species and the 19th of April 2016 for the anionic species. For measurements performed in the laboratory, the error measurement is 1% (except for K^+ at 2%) calculated as the standard deviation over repeated injection of the standard solutions "River x1". For RL measurements the error is given in table 2.

Figure 5. Calcium concentration and stream flow in the Orgeval river during a flood event (from the 1st to the 25th of October 2015), sampled every 40 minutes (RL original signal at 0.42 mHz) and artificially sub-sampled every 7 hours (0.04 mHz), and every day (0.01 mHz) at 10 a.m.. Dashed vertical lines indicate the three stream flow peaks. Black dots represent data during the flood event strictly (from the 5th of October 2015 to the 10th of October 2015 at 10 a.m.), over which probability density functions (PDFs) of concentration are calculated and represented as histograms (right panels). For each PDF, the following statistical parameters are calculated: average (Ave.), standard deviation (Std D.), skewness (Skew) and kurtosis (Kur.). Gray dots represent concentration values outside of the flood event and are not considered in the corresponding PDF.

Figure 6. Sulphate concentration in the Orgeval river during a summer event (from the 7th to the 19th of July 2015) sampled every 40 minutes (RL original signal at 0.42 mHz) and artificially sub-sampled every 7 hours (0.04 mHz), and every day (0.01 mHz) at 2 p.m.. Probability density functions (PDF) of concentration are represented as histograms (right panels). For each PDF, the following statistical parameters are calculated: average (Ave.), standard deviation (Std D.), skewness (Skew) and kurtosis (Kur.).

Figure 7. Values of the four statistical parameters obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL. From the top to the bottom: average, standard deviation, skewness and kurtosis. The statistical parameters are calculated from data collected over two periods: 'flood event' (left panels) and 'summer event' (right panels). Each statistical parameter is calculated for three sampling frequencies: every 40 minutes (RL original signal at 0.42 mHz) and artificially sub-sampled every 7 hours (0.04 mHz) and every day (0.01 mHz). For each statistical parameter, the value obtained from the RL original signal is considered the reference against which all values are compared. The figure thus shows the relative deviation of the four statistical parameter 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.

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Figure 8. Calcium concentration and stream flow in the Orgeval river during a flood event (from the 1st to the 25th of October 2015), as recorded by RL and for two artificially degraded signals using a normally distributed noise with standard deviation of 2% and 4%, to reflect the effect of decreased analytical precision. Black dots represent data during the flood event strictly from the 5th of October 2015 at 12 a.m. through 10th of October 2015). The probability density functions (PDF) of concentration are calculated and represented as histograms (right panels). For each PDF, the following statistical parameters are calculated: average (Ave.), standard deviation (Std D.), skewness (Skew) and kurtosis (Kur.). Gray dots represent concentration values outside of the flood event, which are not considered for the analysis presented on the right panels.

Figure 9. Sulphate concentration in the Orgeval river recorded by the RL during two weeks in summer (from 7th of July 2015 through 19th of July 2015), and for two artificially degraded signals, using a normally distributed noise with a standard deviation of 2% and 4%, to reflect the effect of degraded analytical precision. The probability density functions (PDF) of concentration are calculated and represented as histograms (right panels). The average (Ave.), standard deviation (Std D.), skewness (Skew) and kurtosis (Kur.) are calculated for each PDF.

Figure 10. Values of the four statistical parameters obtained from the Orgeval River concentration PDF for the seven dissolved species measured by the RL. From the top to the bottom: average, standard deviation, skewness and kurtosis. The statistical parameters are calculated from data collected over two periods (see text): 'Flood 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 concentration PDF were computed 10,000 times. For each statistical parameter, the value obtained from the RL original signal was considered as a reference value against which all numerical values are compared. We thus present the relative deviation of the value of the four statistical parameters for the artifically 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.

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Figure 1

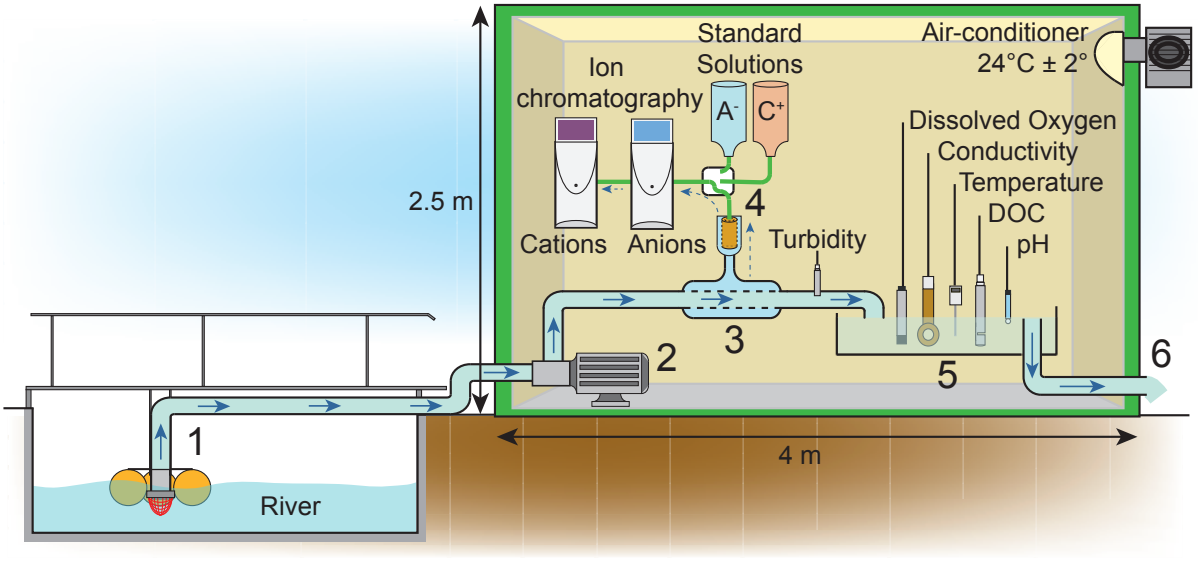

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Figure 2

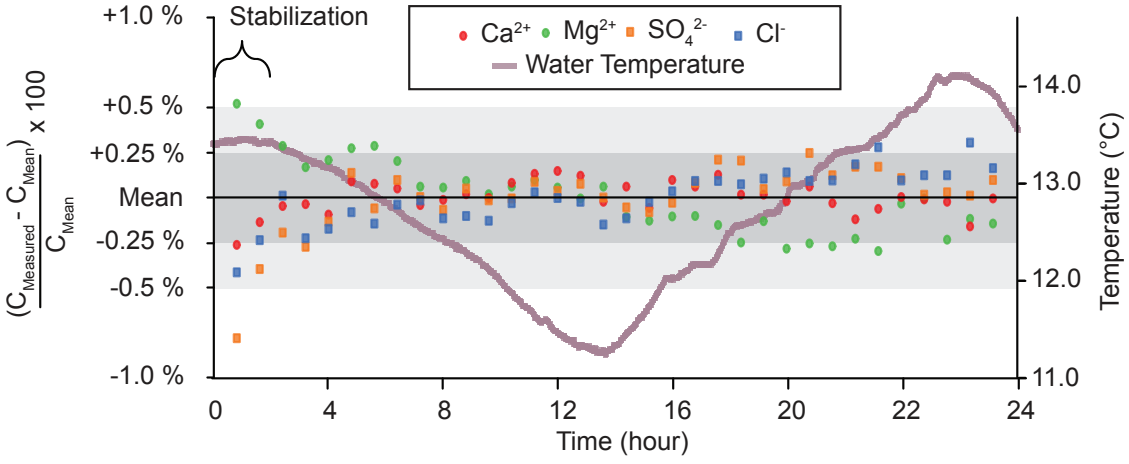

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Figure 3

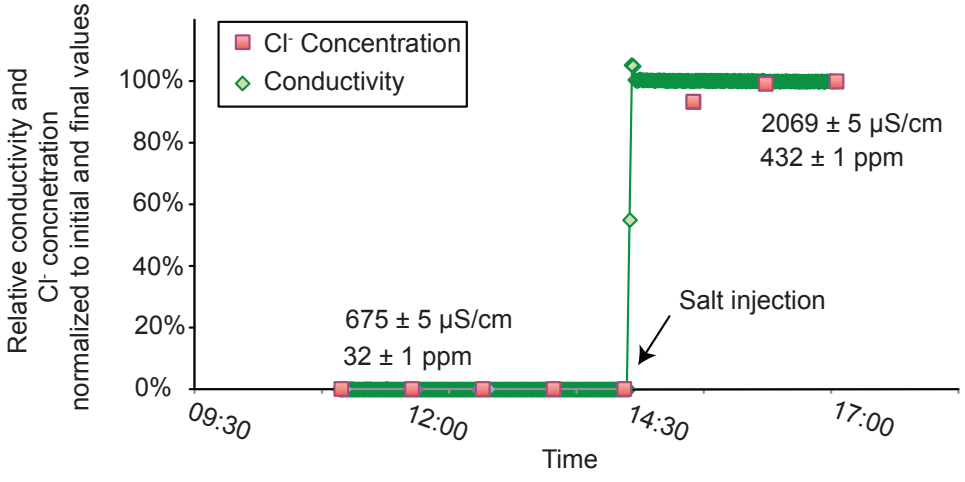

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Figure 4

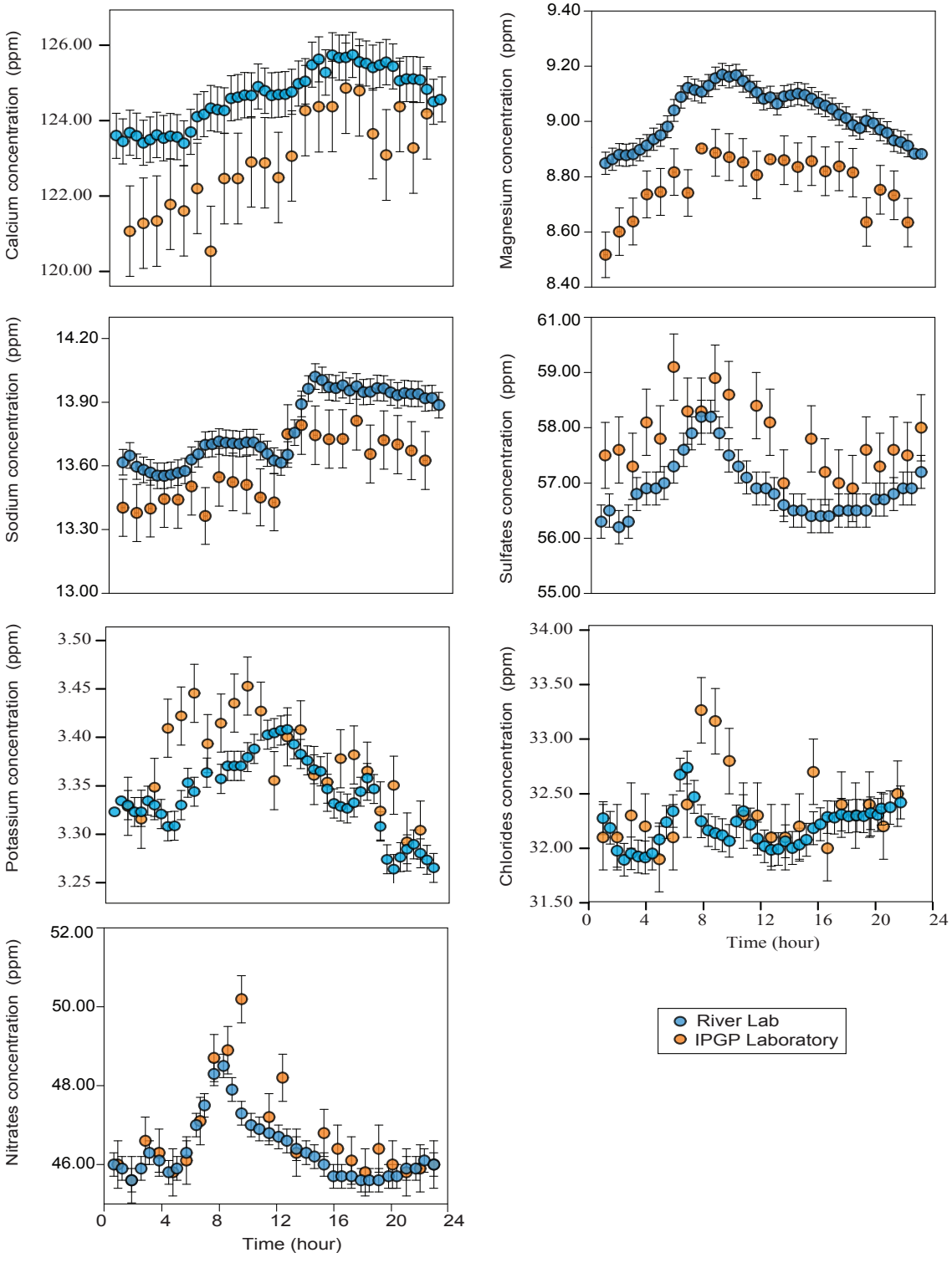

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Figure 5

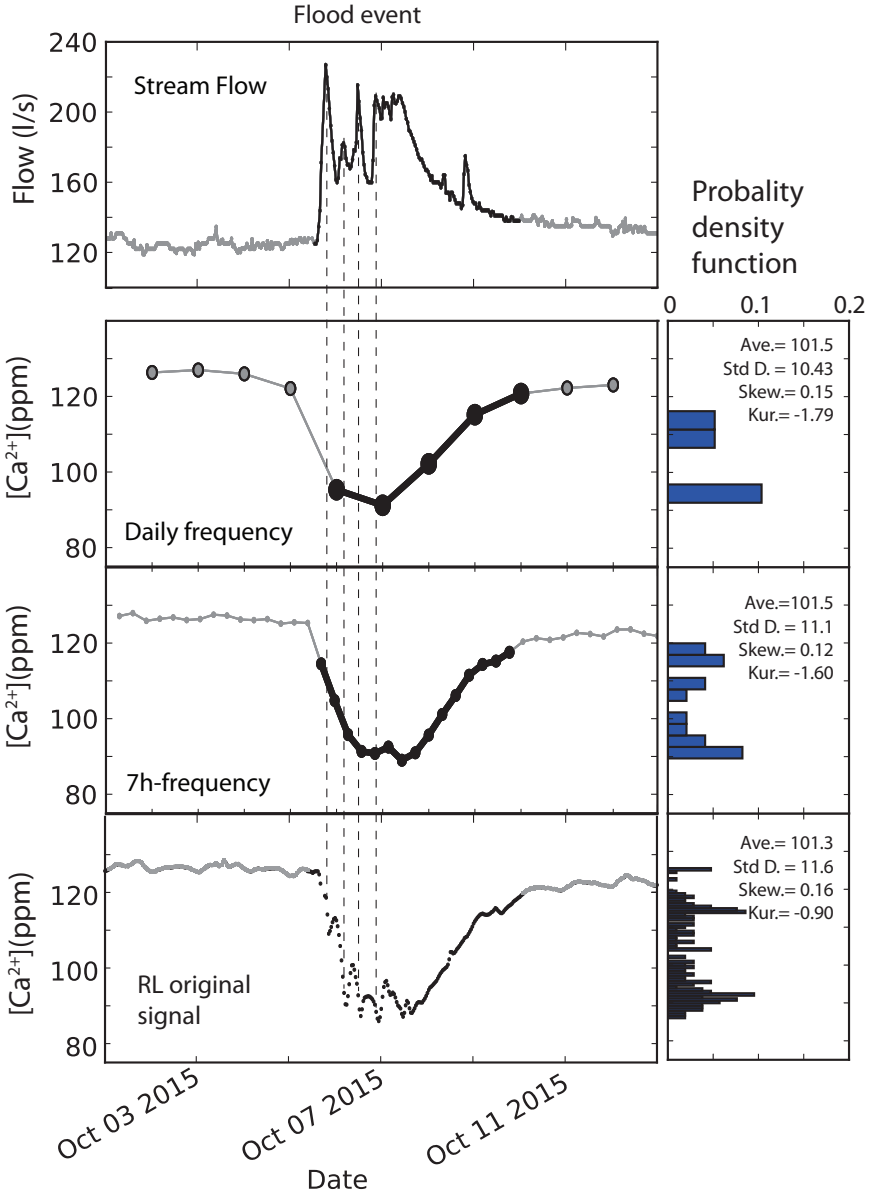

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Figure 6

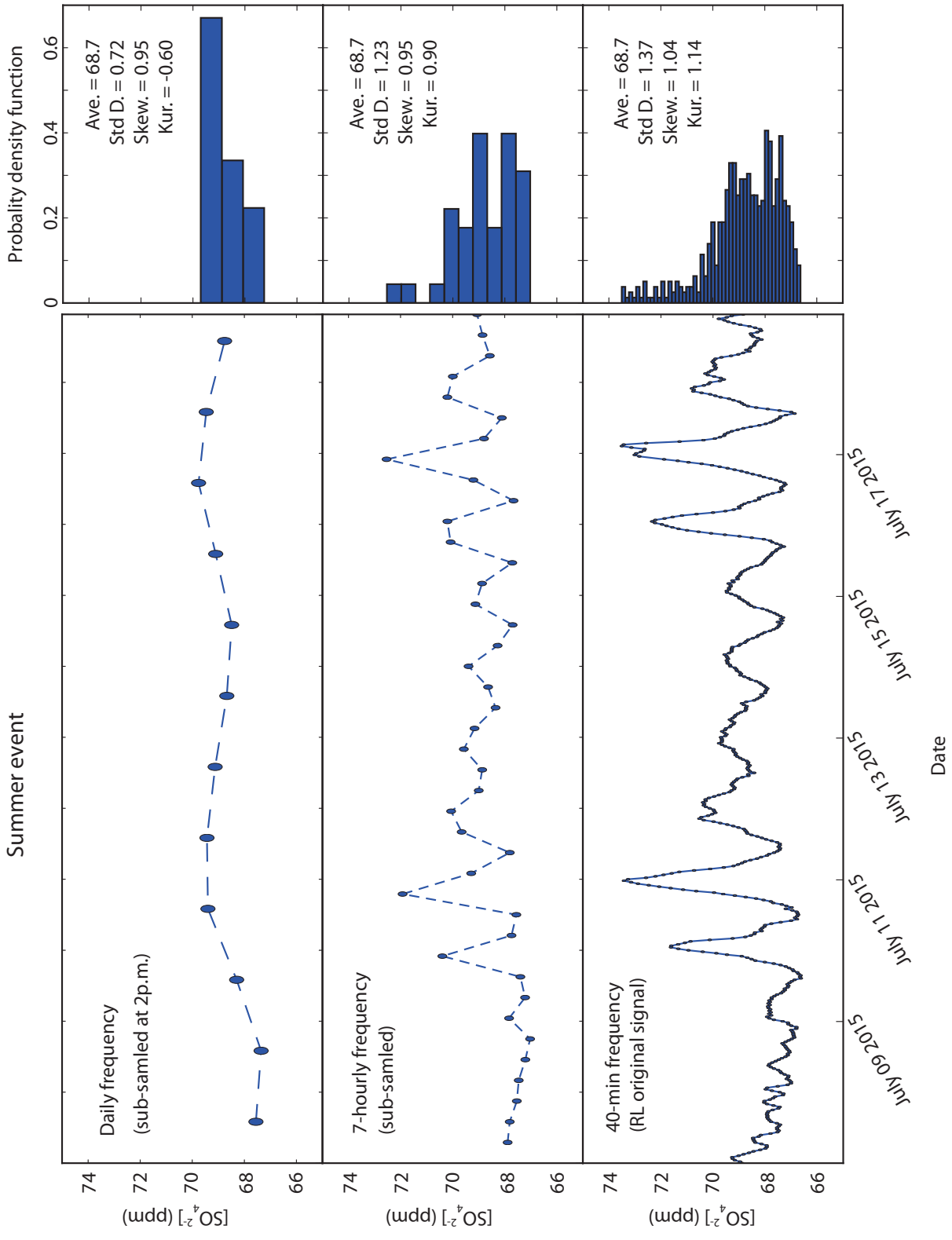

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Figure 7

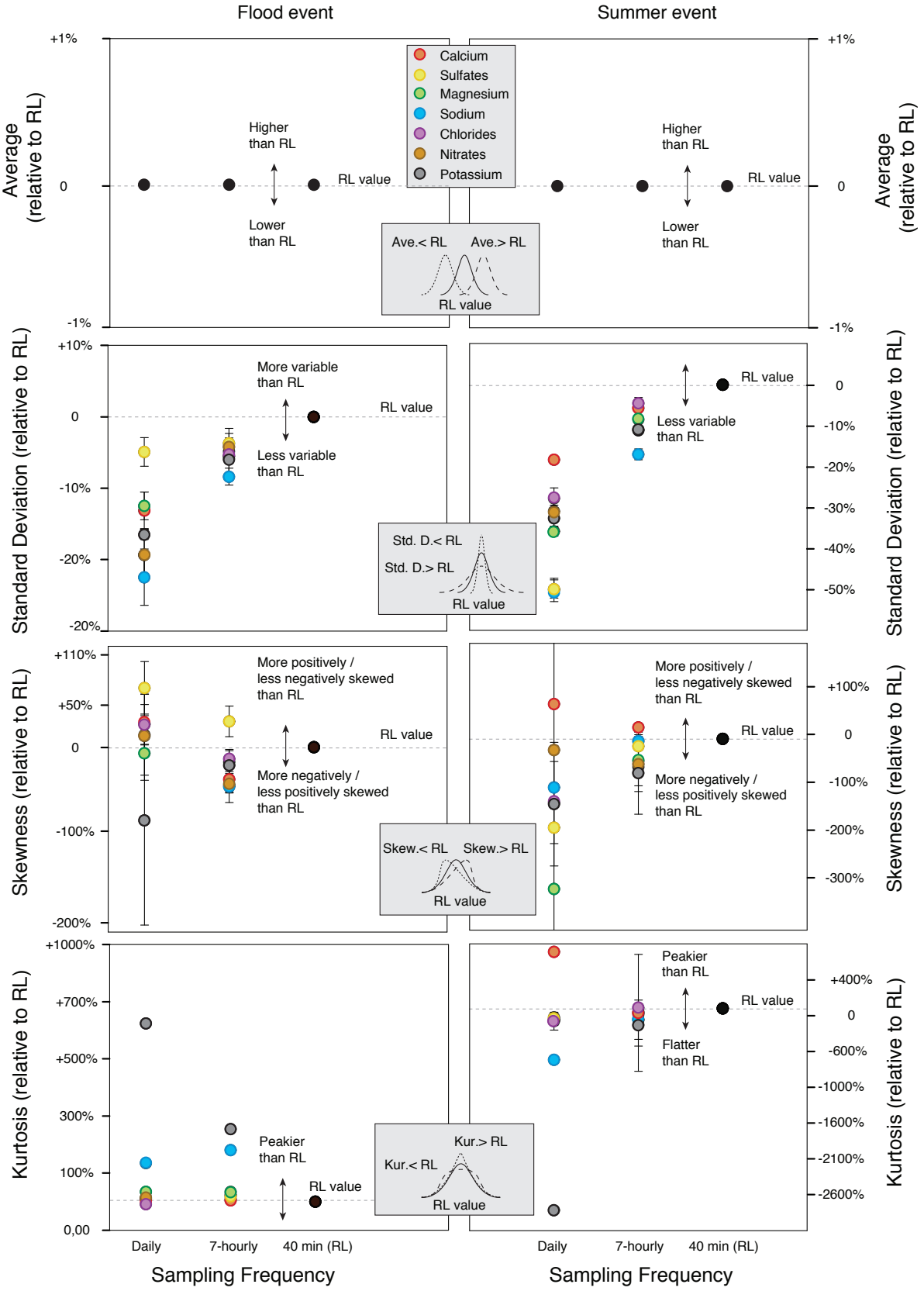

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Figure 8

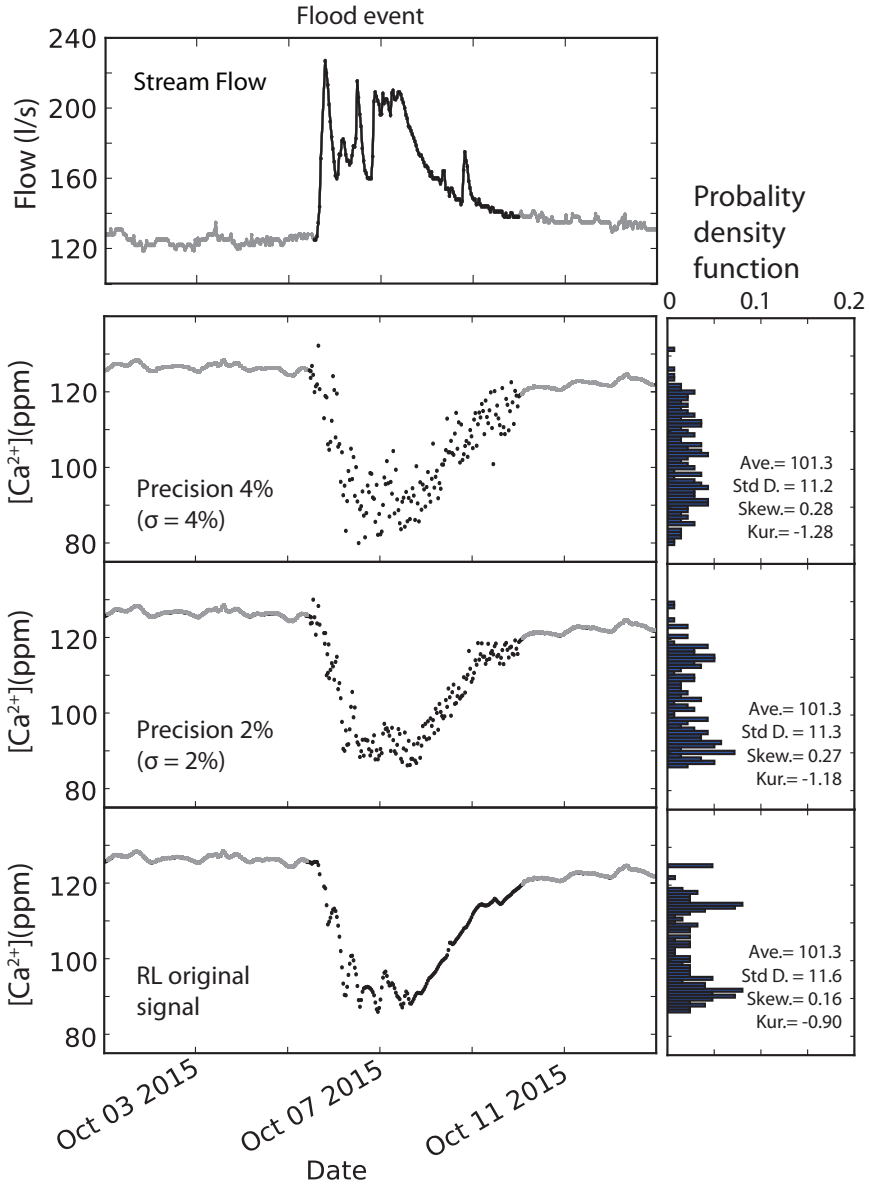

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Figure 9

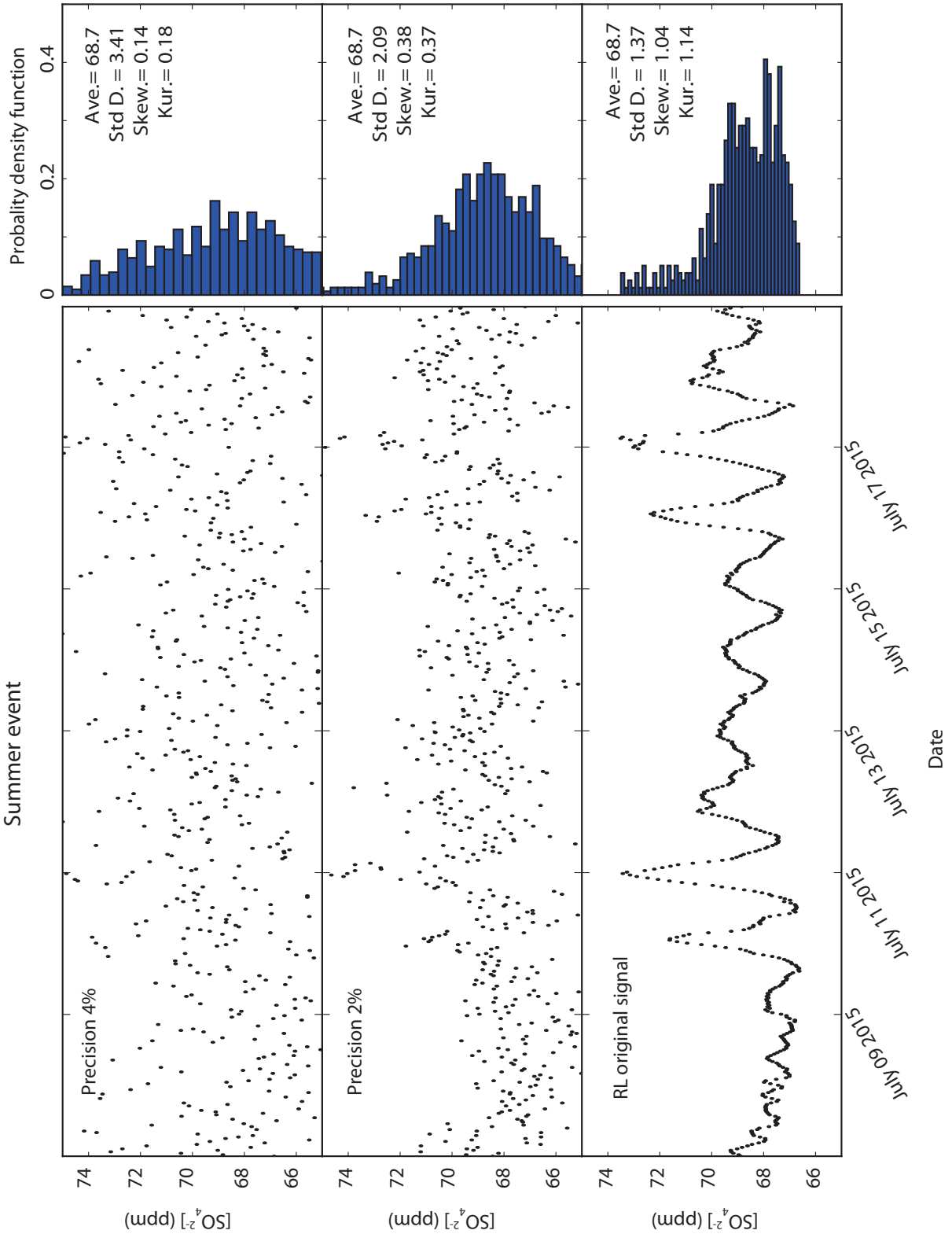

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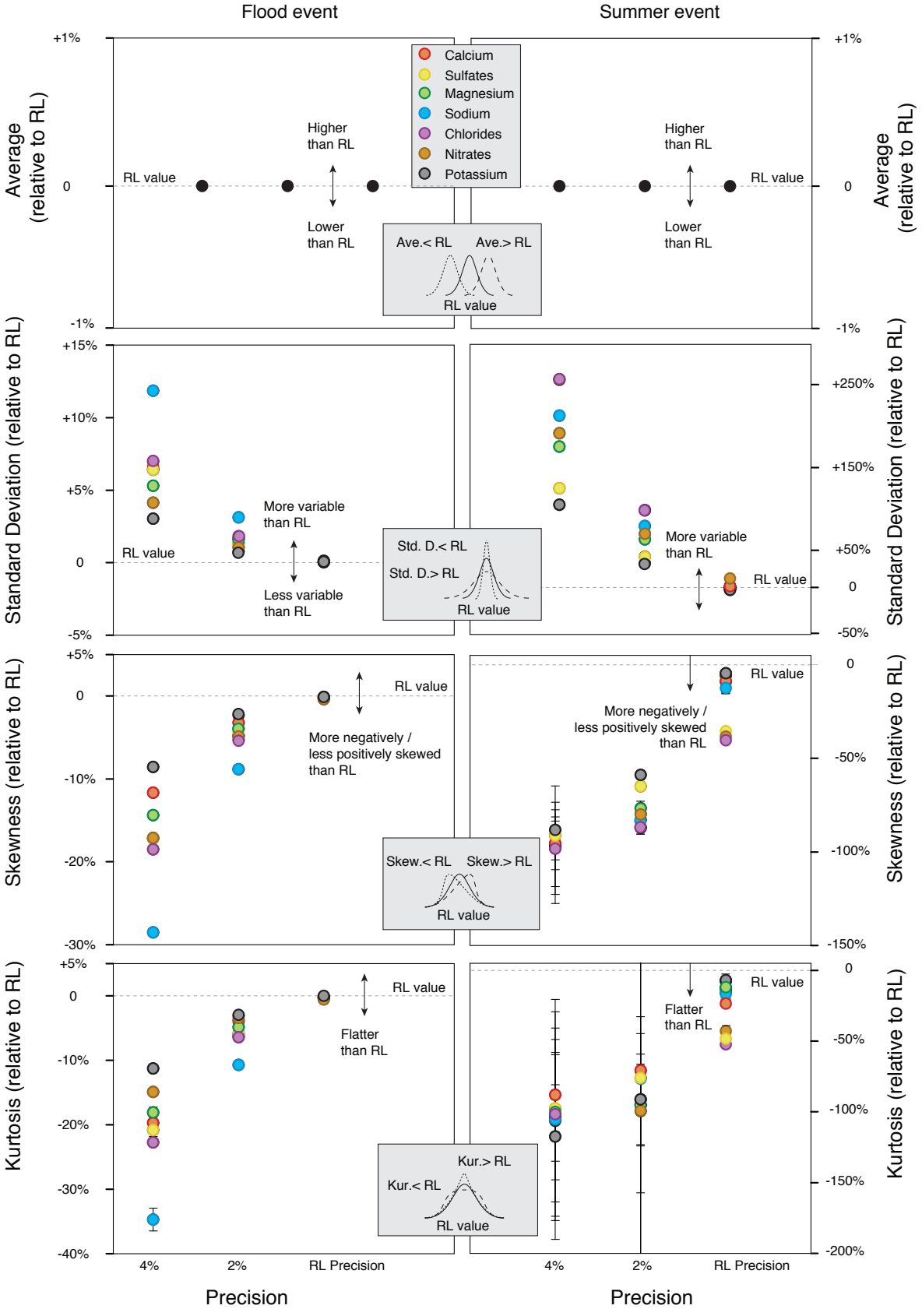
Figure 10



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	Mg^{2+}	K^{+}	Ca^{2+}	Na^{2+}	SO_4^{2-}	NO_3^{-}	Cl^{-}
Calibration Solution	10.0	3.0	130.0	10.0	70.0	60.0	40.0
($mg.L^{-1}$)	0.03	0.01	0.39	0.03	0.84	0.84	0.28
(%)	**0.3**	**0.45**	**0.3**	**0.3**	**1.2**	**1.4**	**0.7**
	One Measurement (Injection "River x1" solution 4 times)						
Number of measurement	*(4)*	*(4)*	*(4)*	*(4)*	*(4)*	*(4)*	*(4)*
Average ($mg.L^{-1}$)	10.08	3.00	129.86	9.98	70.26	60.31	40.32
Std. Dev. ($mg.L^{-1}$)	0.02	0.01	0.16	0.02	0.69	0.63	0.27
RSD (%)	**0.16**	**0.27**	**0.12**	**0.21**	**0.86**	**0.74**	**0.33**
	One Week (Injection "River x1" solution every 8h)						
Number of measurement	*(19)*	*(19)*	*(19)*	*(19)*	*(19)*	*(19)*	*(19)*
Average ($mg.L^{-1}$)	10.13	3.02	130.64	10.01	70.54	60.63	40.44
Std. Dev. ($mg.L^{-1}$)	0.03	0.01	0.39	0.02	0.67	0.44	0.22
RSD (%)	**0.28**	**0.32**	**0.30**	**0.22**	**0.96**	**0.72**	**0.54**
	Two months (Injection "River x1" solution every 2 days)						
Number of measurement	*(28)*	*(28)*	*(28)*	*(28)*	*(25)*	*(25)*	*(25)*
Average ($mg.L^{-1}$)	10.33	3.14	134.34	10.05	70.05	62.33	40.57
Std. Dev. ($mg.L^{-1}$)	0.06	0.04	0.80	0.05	1.17	0.55	0.43
RSD (%)	**0.54**	**1.34**	**0.59**	**0.50**	**1.68**	**0.92**	**1.07**

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Date	*Number of measurements*	Mg^{2+}	K^{+}	Ca^{2+}	Na^{2+}	SO_4^{2-}	NO_3^{-}	Cl^{-}
		RSD (%)						
20th July 2015	*(22)*	0.17	0.90	0.21	0.22	0.39	0.47	0.24
28th August 2015	*(20)*	0.32	0.63	0.31	0.36	0.20	0.25	0.19
17th April 2016	*(35)*	0.38	1.20	0.17	0.31	0.31	0.38	0.30