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

Paul Floury[1,2]*, Jérôme Gaillardet[1], Eric Gayer[1], Julien Bouchez[1], Gaëlle Tallec[2], Patrick Ansart[2], Frédéric Koch[3], Caroline Gorge[1], Arnaud Blanchouin[2], and Jean-Louis Roubaty [1]

[1] Institut de Physique du Globe de Paris (IPGP), CNRS and Université Sorbonne Paris-Cité, 1 rue Jussieu, 75238 Paris, France

[2] UR HBAN, Institut national de recherche en sciences et technologies pour l'environnement et l'agriculture, Antony (IRSTEA), France

[3] Endress+Hauser SAS, Huningue, France

Corresponding author. E-mail: floury@ipgp.fr

**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 one every 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 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). The RL is able to capture the abrupt changes in dissolved species concentrations during a typical 6-days rain event, as well as daily oscillations during a hydrological low-flow period of summer drought. Using the measured signals as a benchmark, we numerically assess the effects of a lower sampling frequency (typical of conventional field sampling campaigns) and of a lower precision (typically reached in the laboratory) on the hydrochemical signal. The high-resolution, high-precision measurements made possible by the RL open new perspectives for understanding critical zone hydro-bio-geochemical cycles. Finally, the RL 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 (Calmels et al. 2011; Feng et al., 2004; Kirchner et al., 2000; Kirchner et al., 2001; Neal et al., 2012; Neal et al. 2013). 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, page 1358). Yet, taking high-frequency sample sets back to the laboratory is limited by the requirement of considerable human resources (Chapman et al., 1996; Danielsen et al., 2008; Halliday et al., 2015; Neal et al. 2013; Rozemeijer et al., 2014; Strobl and Robillard, 2008; Telci et al., 2009).

Thus far, high-frequency chemical measurements in catchments have been mostly reported during short periods such as a single storm event or a day (Beck et al., 2009;

Brick et al., 1996; Chapman et al., 1997; Gammons et al., 2007; Kurz et al., 2013; Liu et al., 2007; Morel et al., 2009; Montety et al., 2011; Neal et al., 2002; Nimick et al., 2011; Nimick et al., 2005; Takagi et al., 2015; Tercier-Weaber et al., 2009). 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). The authors demonstrate the "act of discovery" permitted by such sampling scheme, as the high sampling frequency of river hydrochemistry over sufficiently long time spans revealed patterns related to hydrological and biological drivers invisible at lower sampling frequency. However this study also highlights the practical limits of manual approaches relying on conventional field sampling combined with laboratory analyses. 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 suggested as an alternative to monitor water chemistry. To date, these systems have only been used to monitor 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., 2017). The RL prototype is one of the work packages of the French program CRITEX: “Innovative sensors for the temporal and spatial EXploration of the CRITical Zone at the catchment scale” (https://www.critex.fr). The ability of the RL is 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 temporal patterns of river chemistry, such as daily concentration variations. The RL opens thus new opportunities in the field of river chemistry research and operational monitoring.

## 2 Monitoring site

The RL was installed in the Orgeval, Critical Zone Observatory located 70 km eastward from Paris, France (https://gisoracle.irstea.fr/), a temperate agricultural catchment, within the Seine river watershed, and part of the French Critical Zone Research Infrastructure OZCAR (“Observatoires de la Zone Critique, Applications et Recherche”). Orgeval 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. The Avenelles River 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 an annual precipitation rate of ~650 mm on average. The Avenelles sub-catchment sits within the sedimentary carbonate-dominated Paris Basin. The river is perennial, supplied by groundwater from the Brie aquifer; with 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 (0.1 $m^3/s$) 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 it to 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 is needed 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 designed by IPGP (Institut de Physique du Globe de Paris, France) and IRSTEA (Institut national de Recherche en Sciences et Technologies pour l'Environnement et l'Agriculture, France) and assembled by Endress & Hauser (E+H®) (Fig. 1). A technical sketch is available in supplementary information (Fig. SI1).

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 every 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 probes are developed and provided by Endress & Hauser (E+H®).

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). Our tests show that the frequency for a complete and uncontaminated analyse of cation and anion is actually limited by the filtration device (see part 4.3).
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 $Ca^{2+}$, and 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 water (see section 4). Pure distilled water is regularly (every two weeks) introduced to check the residual noise. 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 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. Analytical 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 errors in concentration measurements. We evaluated this effect using a set of injections of the “River x1” solutions, over one week and over two months, (Tab. 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 random nature. Therefore, the standard deviation of the concentration measurements of a given solution 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 lower than 1 % over one week and lower than 1.7 % over two months (Tab.1). The agreement between the calculated concentrations of the "River x1" solution and the RL measurements also demonstrate the accuracy of the prototype (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. SI2). Our results show that a lapse of 2 hours at least is 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 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 relative derivative of the concentration with respect to time is lower than 1% per hour for 90% of the time for all species. In this case, the 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 (21st of July 2015 for cations and 19th 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 conducted hourly sampling of the river by collecting 5 litres of water and filtering it immediately using a Teflon® frontal filtration unit (Sartorius®) with 0.2-µm porosity polysulfonether filters. Bottles of acidified (at pH = 2) and unacidified river water were transported to the laboratory at IPGP for measurement of major cations and anions, respectively, using IC devices similar to those installed in the RL (Thermo Fisher® ics 2100). In the laboratory, measurements were performed using Thermo Fisher® ics 5000 for cations measurements and Dionex® 120 from Thermo Fisher® for anions measurements. The calibration procedure in both laboratory and RL is the same using the same set of calibration solutions. The error measurement reached in the laboratory is estimated at 1% through repeated injections of the standard solution “River x1” (every 5 samples). Comparison between the RL and the laboratory for the seven measured species are shown in Figure 4. First, the measurements made by the RL are more precise than those performed in the laboratory, a feature that can be primarily attributed to the greater stability of the continuously working injection system of the RL. Second, the fine variations measured by the RL are reproduced in the laboratory, validating the observed diurnal variations and supporting the reliability of the RL to detect changes on the order of a percent within a day. The third observation is that small yet systematic offsets between the two sets of data exist, up to 3% for Mg. One possible explanation for this difference is that the filtration procedures differed between the RL and the manual sampling, which may have led to a discrepancy in the concentration measurements related to the potential for some elements to be hosted in the colloidal phase (Dupré et al., 1999). In addition, the most accurate measurements were obtained with the RL ratther than with the laboratory equipment because (1) the calibration curve of the RL was made from a series of solutions (dilutions of the "River x1" solution) having the same element ratios as the solution used for the accuracy test (the "River x1" solution); (2) the RL is continuously processing solutions with a similar matrix, thereby minimizing memory effects and cross-contamination that can compromise measurements if widely differing samples are run successively on the same instrument. These two conditions were not met with our in-lab IC instruments, where we used a series of calibration solutions having the same concentration for all elements, and for which the measurement sessions took place between other sessions with very different samples. These features of the measurement protocol, representative of most laboratory workflows for hydrochemical measurements, are likely to lead to inaccuracies. Regardless of the observed discrepancy between the two sets of measurements, we note that variations in concentration recorded by the RL and measured at the IPGP laboratory have the same amplitudes and are synchronous.

## 5. Discussion

### 5.1 What are the benefits of bringing the lab into the field?

The RL presented above allows us to record continuously, at a high frequency and over long spans of time, the concentration of 7 major dissolved species in a river system.

Although this is beyond the scope of the present paper , the RL presented here opens new possibilities for the exploration of the fine structure of hydrochemical evolution at the catchment scale and for improved understanding of the associated hydrological, geochemical, and biological processes. From a technical point of view, our study shows that deploying the conventional laboratory measurement techniques in the field adds significant value. The tests performed and reported above clearly demonstrate an improvement in precision compared to the analysis of bottled samples taken back to the lab. We see three main reasons for this improvement.

1) In a given river, dissolved concentrations typically vary by less than one order of magnitude when water discharge changes by several orders of magnitude (Godsey et al., 2009). This constancy allows us to select a relatively narrow range of concentration for establishing specific calibration curves of the IC instruments, a condition which is rarely possible in the laboratory where different kinds of samples are analyzed.

2) While in the laboratory samples are injected discretely, in the RL river water samples are injected as a continuous flow. Thus, the primary circuit and the filtration system operate continuously at a constant pressure, which supports stable and accurate analyses.

3) The third factor is the experimental conditions in the bungalow. The temperature is maintained at 24°C ± 2° (in addition to the 40°C thermostatically-controlled temperature in the column, precolumn and detection device of the ICs) allowing for better stability of the IC measurements. Moreover, the RL IC instruments are never stopped, which favours stability.

## 5.2 What is revealed by a higher sampling frequency?

To our knowledge, the high frequency of measurements (one measurement every 40 minutes) reached by 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: every 7 hours (starting October 5th, 2015 at 10 pm) and every 24 h. The 7-hourly frequency was chosen to reproduce the sampling frequency of Neal et al., (2012) made in the Plynlimon watershed, Wales. The daily sampling frequency is typically what is achievable on the long term 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. We describe the PDF by 3 statistical parameters: mean, standard deviation and skweness. Skewness indicates the distribution asymmetry, both in magnitude and direction (a positive skewness means that most values are higher than the mean). Altogether, the three parameters account, at first-order, for the structure of a concentration signal. We compared these three parameters for the computed PDFs to quantify the signal degradation induced by artificial sub-sampling.

We applied this statistical approach to two representative periods of the hydrological cycle of the Orgeval Critical Zone Observatory: a typical 6-day rain event caused by the arrival of a wet, Atlantic meteorological front (in October 2015) and a dry summer low water stage period (July 2015) where the stream is essentially sustained by groundwater, during an apparently steady hydrological period. We first present the behaviour of calcium and sulphate concentrations as an example during the two considered periods (Fig. 5 and 6), before generalizing to all measured species (Supplementary information and Fig. SI 3, SI 5 and SI 6).

**Rain event**. The Ca concentration time series recorded at a 40-minutes frequency shows that minimum Ca concentrations are recorded at maximum water discharge, but this relationship is invisible at lower sampling frequency (Fig. 5). Narrow peaks during the maximum of the stream flow are unresolved at a daily or 7-hourly frequency. The comparison of the calculated PDF shows that a bimodal character is captured at all frequencies. The average and standard deviation are not significantly affected by the sampling frequency, with a relative difference of less than 2% for the values of these parameters between the three distributions. However, the skewness values vary among the different records. From the 40-minutes frequency to the daily frequency signals, the skewness is weaker, which means that even if the overall concentration variability is well captured at the lower sampling frequencies, the concentration signal is clearly degraded. This degradation is particularly intense during the middle of the rain event, where the concentration signal evolves quickly.

**Summer event.** Despite the absence of rain events during the 2015 summer, the River Lab recorded high frequency variations revealing a diurnal structure with 7% relative variations between day and night. Each element exhibits its own type of daily variation in terms of amplitude and regularity. The Figure 6 shows that the structure of this signal is altered when the sampling frequency decreases. While these daily variations are still captured when sampling occurs every 7 hours, their amplitude is somewhat altered (5%) compared to the 40-minutes sampling frequency (8%). The daily variability of the signal is absent on the daily 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 40-minutes frequency 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 is generalized and expanded to other elements for both the summer and rain events. The generalization to all species measured is presented in supplementary information. In Figures 5 and 6, we arbitrarily chose the hour of sampling (10 a.m. and 2 p.m. for Figures 5 and 6, respectively). In figure SI 3, SI 5 and SI 6, the sub-sampling is performed at each of the possible sampling hours. This statistical analysis quantitatively demonstrates that such 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 (Supplementary information; Fig. SI 3, SI 5 and SI 6).

### 5.3 What is revealed by better analytical precision?

As shown above, the Orgeval RL not only achieves high-frequency measurements but also results in 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 al., 2013a). The same representative periods as in the previous section (summer and rain events) were utilized for these tests. In this section we present the example of one element for each characteristic period ($Ca^{2+}$ for rain event Fig. 7 and $SO_4^{2+}$ for summer event Fig. 8. The generalization for all elements is detailed in the supplementary information section (Supplementary information and Fig. SI 4, SI 7 and SI 8).

**Rain event.** The Figure 7 illustrates the concentration PDF obtained after degradation of the analytical precision for the Ca concentration. The narrow peaks recorded during the maximum of the stream flow are virtually invisible in the signal at a 4%-precision, and strongly smoothed in the signal at a 2%-precision. The original bimodal characteristic of the PDF is still visible in the 2%-precision signal but no longer in the 4%-precision signal. The mean and standard deviation appear to be insensitive to these changes in analytical precision, while the skewness is strongly impacted, reflecting significant alteration of the concentration PDF at lower precision.

**Summer event.** Figure 8 shows how the sulphate concentration signal is affected when the precision is degraded. Day-night variations are only visible in the original RL signal because of its high analytical precision. The effect of degraded precision on the PDFs is more important than for the rain event (Fig. 7). While the mean value is robust, the standard deviation is altered (+150% from the RL signal to the 4% precision signal). The skewness decreases (but keeps the same sign) by up to 90% for the signal at 4%-precision compared to the original signal and 74% for the signal at 2%-precision, indicating that the original RL signal asymmetry is lost as precision is worsened. These changes in the parameters of the concentration PDF show that the structure of the concentration signal in the Orgeval River would be significantly altered if the measurements were made with analytical precision lower than that of the RL prototype.

**Generalization**. This approach has been expanded to other elements for both the summer and rain events, as shown in the supplementary information, confirming that concentration PDFs are strongly sensitive to the analytical precision for all species (Fig. SI 4, SI 7 and SI 8).

## 6 Conclusion

This paper demonstrates the feasibility of deploying conventional laboratory instruments in the field to measure the concentration of major dissolved anions and cations in rivers ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, $SO_4^{2-}$, $NO_3^-$) at a high frequency (one measurement every 40 minutes) and at a high analytical precision (better than 1%) over several months. The River Lab prototype was installed in the Avenelles stream at the Orgeval Critical Zone Observatory, France. The RL features physico-chemical probes, an on-line 0.2-µm pore size filtration system, and two ionic chromatographic devices, all installed in a closed, air-conditioned bungalow. The RL is autonomous, remotely operable and data can be transmitted automatically. Human intervention is required only 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 capabilities of 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 (every 40 minutes) appears to be limited by the turnover time of water in the filtered water circuit, which is itself imposed by the filtration unit. However, the high frequency and high precision of the RL enabled precise and accurate observations on 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 rain event, as well as daily oscillations during a hydrological steady period of summer drought.

Using the high frequency RL signal as a benchmark, it is possible to artificially alter the sample frequency and the analytical precision and study the resulting effect on the hydrochemical 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 James Kirchner's quote: "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, page 1359). The improvements made possible by the RL allow us to hear the full potamological symphony.

Future work will explore the relationships between the desired measurement frequency and the timescales characterizing the complex interactions between primary and secondary minerals, biotic processes and hydrological processes in catchments. Recording such fine stream hydrochemical variations has the potential to offer a new perspective in Critical Zone Science development.

## Author's information

Corresponding author: *E-mail: floury@ipgp.fr and gaillardet@ipgp.fr

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## Table Captions

**Table 1. Assessment of the RL accuracy and instrumental drift based on concentration measurements made after several injections of the standard solution "River x1". The uncertainty on the calibration solution is the quadratic sum of the uncertainty on the standard solutions (provided by the manufacturer) and the overall uncertainty for weighing during solution preparation. Measurement errors over one week and over two months are expressed as the relative standard deviation (RSD) calculated based on the injections of the solution "River x1" directly into the IC instruments via the multiport valve (see Fig. 1).**

**Table 2. Precision on concentration measurements of the whole RL system calculated as the relative standard deviation (RSD) of concentration measurements made over three 24-hour closed loop experiments, during which the inlet and the outlet of the primary circuit are connected through a 300-L tank of river water.**

## Figure Captions

**Figure 1. Sketch of the River Lab. Bold blue arrows indicate the primary circuit of unfiltered water. Dashed arrows indicate filtered water supplied to IC instruments. 1: The inlet of the primary circuit samples the river at a constant 20-cm depth maintained by buoys. Water is filtered at < 2 mm using a strainer. The distance between the mouth and the pump is 6 m. The primary circuit assembly is almost entirely composed of polyvinyl chloride (PVC) pipes. 2: The electric pump runs continuously at a constant power, leading to a rate of 700 liters per hour. 3: Almost all the river water just flows through the pipe and remains unfiltered. A fraction is filtered at < 2 µm through a tangential stainless steel filtration unit, then filtered through a cellulose acetate frontal filter at < 0.2 µm and finally delivered to IC instruments at a flow rate of 1 liter per hour. 4: A multiport valve before introduction to the IC instruments allows for switching between filtered river water and standard or blank solutions. 5: All probes are deployed in an overflow tank of 5 liters of unfiltered river water. 6: The outlet of the primary circuit is downstream in the river.**

**Figure 2. Assessment of the precision of the whole RL system including the primary circuit, filtration systems and IC instruments. 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 system is then run for a period of 24 hours. The figure illustrates the relative variation of concentration (C) of four dissolved species in percentage of relative deviation compared to the mean concentration ($C_{mean}$). This test was performed on the 17th of April 2016. The time between two IC analyses is 40 minutes. The purple curve represents data of temperature of the water in the tank. We do not consider the 2 first hours (3 first measurements), corresponding to the homogenization of water in the circuit and tank (see conductivity measurements in Fig. SI 2) for the calculation of precision.**

**Figure 3. Assessment of the effects of cross-contamination and response time in concentration measurements of the RL system using a tracer (NaCl) injection experiment. A closed system is established on the primary circuit of the RL by connecting the inlet and outlet through a 300-L tank of river water. Then, 200 g of salt previously dissolved in a small amount of river water are injected instantaneously right after one measurement in the closed system to generate a "spike". The conductivity measurement frequency is 1 per minute, whereas the time between two measurements of chloride concentration is 40 minutes. Error bars for conductivity and $Cl^-$ concentration measurements are smaller than their symbols. Results are normalized to the difference between the minimum value,**

**before the tracer injection (0%) and the maximum value, at the end of the experiment (100%).**

**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 rain event (from the 1st to the 25th of October 2015), sampled every 40 minutes (RL original signal at 40-minutes frequency) and artificially sub-sampled every 7 hours and every day at 10 a.m. Black dots represent data during the rain 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.), and skewness (Skew.). Gray dots represent concentration values outside of the rain event and are not considered in the corresponding PDF. The two statistical parameters standard deviation (Std D.) and skewness (Skew.) are not available for the daily subsampling because of the too small number of points.**

**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) and artificially sub-sampled every 7 hours, and every day 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.), and skewness (Skew.).**

**Figure 7. Calcium concentration and stream flow in the Orgeval river during a rain 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 rain 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.) and skewness (Skew.). Gray dots represent concentration values outside of the rain event, which are not considered for the analysis presented on the right panels.**

**Figure 8. 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.), and skewness (Skew.) are calculated for each PDF.**

Figure 1

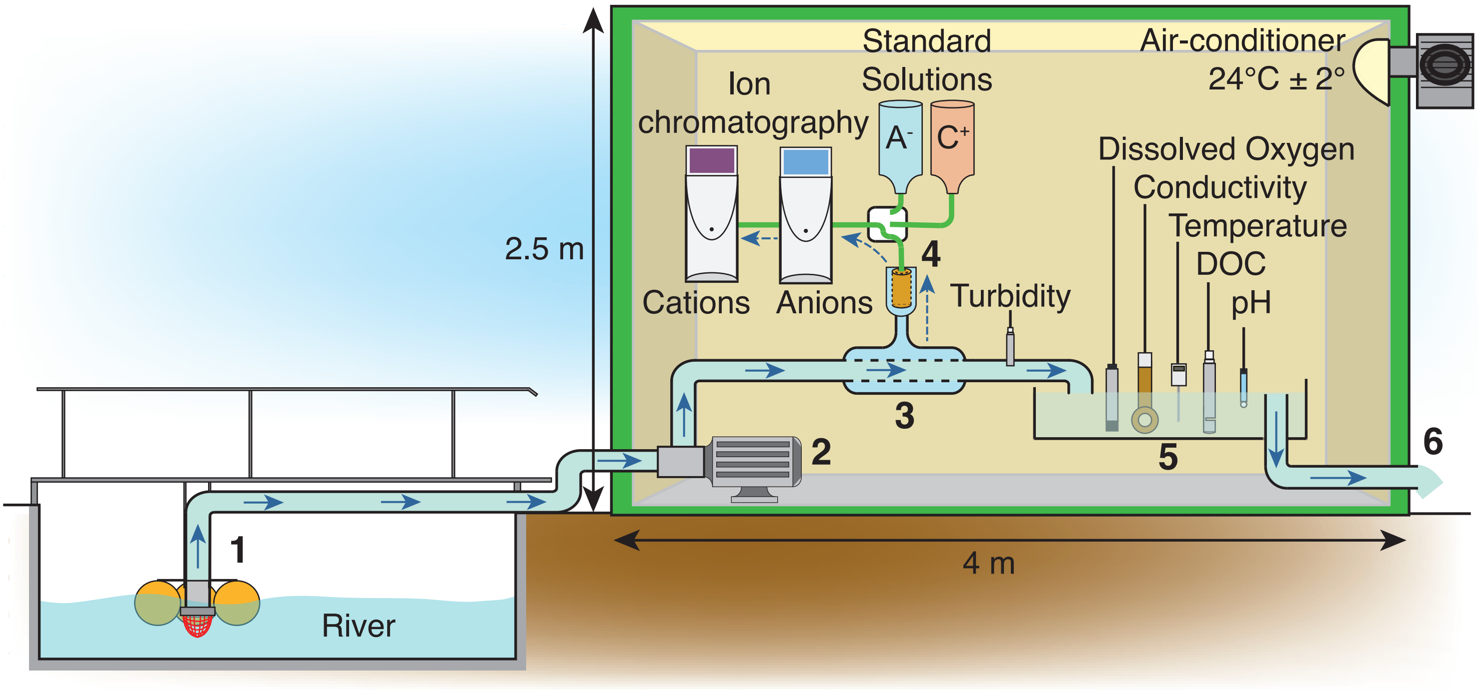
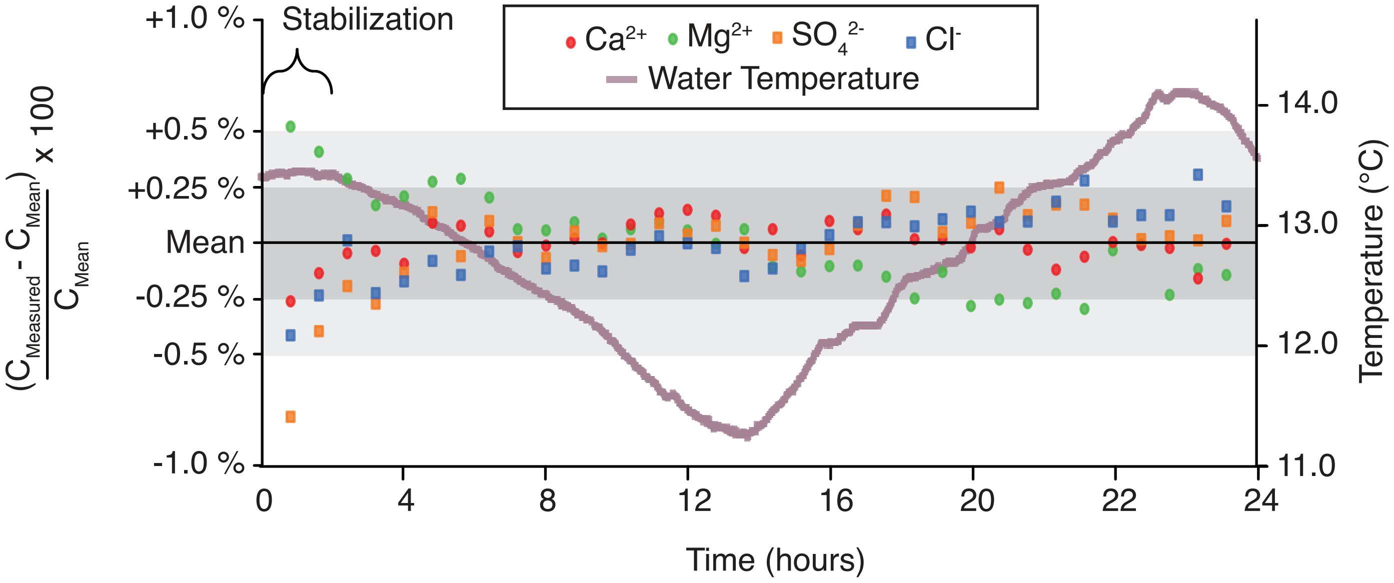

Standard
Solutions
Air-conditioner
24°C ± 2°
Ion
chromatography
A-
C+
Dissolved Oxygen
Conductivity
Temperature
DOC
pH
2.5 m
4
Cations
Anions
Turbidity
3
5
2
6
1
River
4 m

Figure 2



Stabilization
Ca2+
Mg2+
SO4 2-
Cl-
Water Temperature
+1.0 %
+0.5 %
+0.25 %
Mean
-0.25 %
-0.5 %
-1.0 %
(C Measured - C Mean) / C Mean x 100
0
4
8
12
16
20
22
24
Time (hours)
14.0
13.0
12.0
11.0
Temperature (°C)

Figure 3

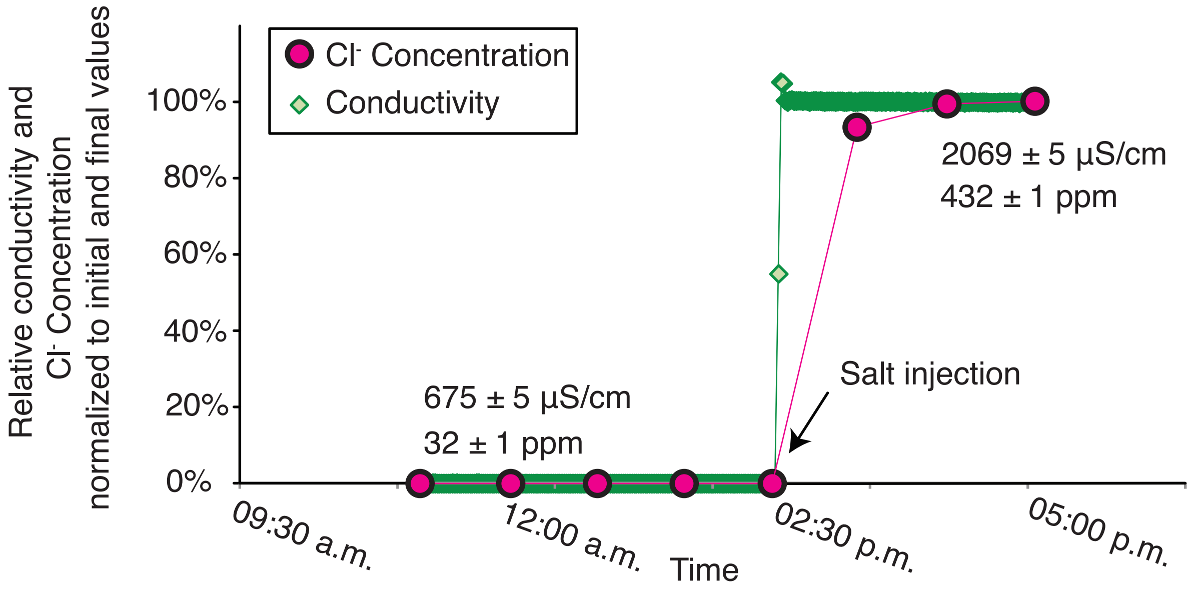

Relative conductivity and
Cl- Concentration
normalized to initial and final values
100%
80%
60%
40%
20%
0%
Cl- Concentration
Conductivity
2069 ± 5 µS/cm
432 ± 1 ppm
Salt injection
675 ± 5 µS/cm
32 ± 1 ppm
09:30 a.m.
12:00 a.m.
Time
02:30 p.m.
05:00 p.m.

Figure 4

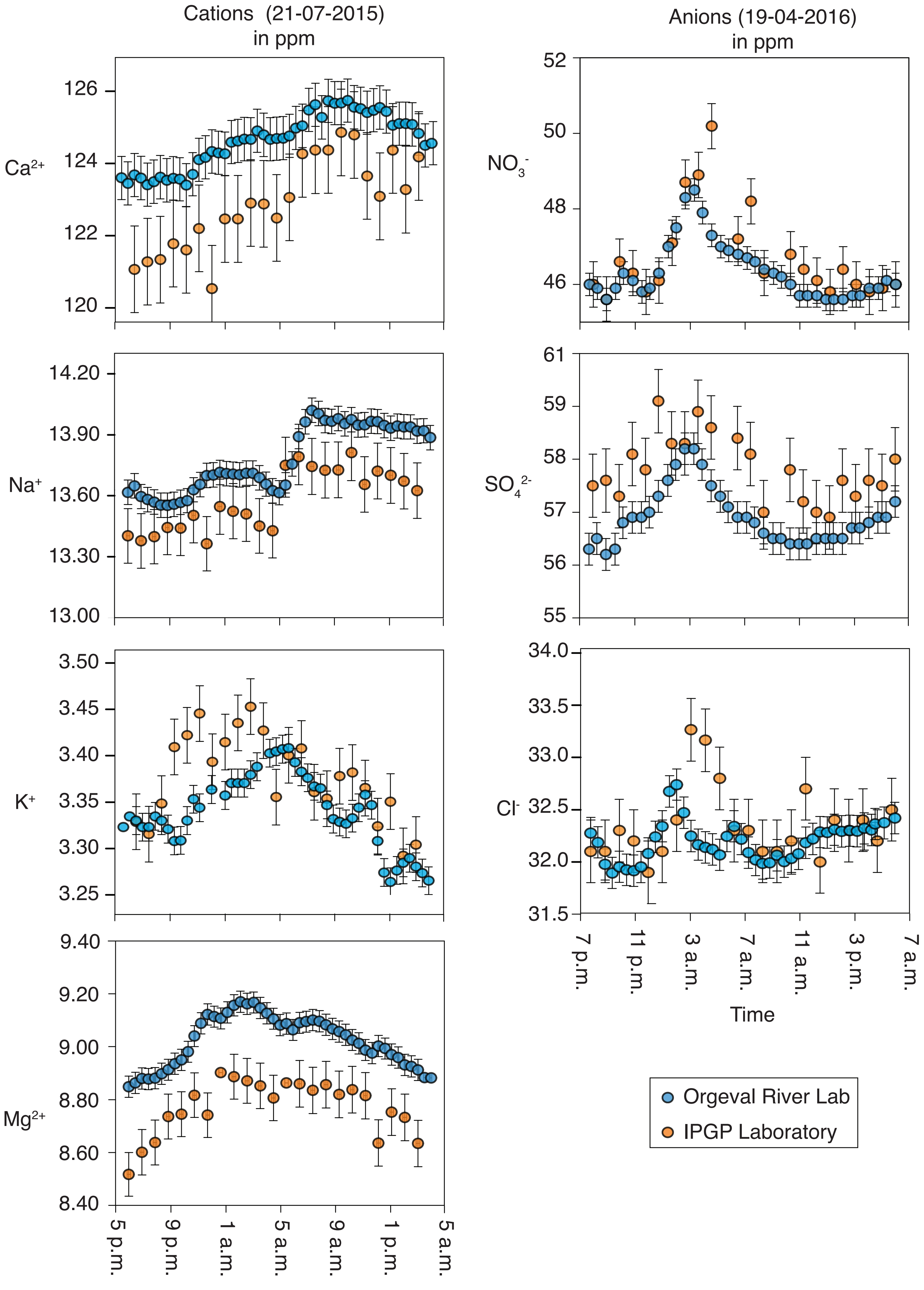
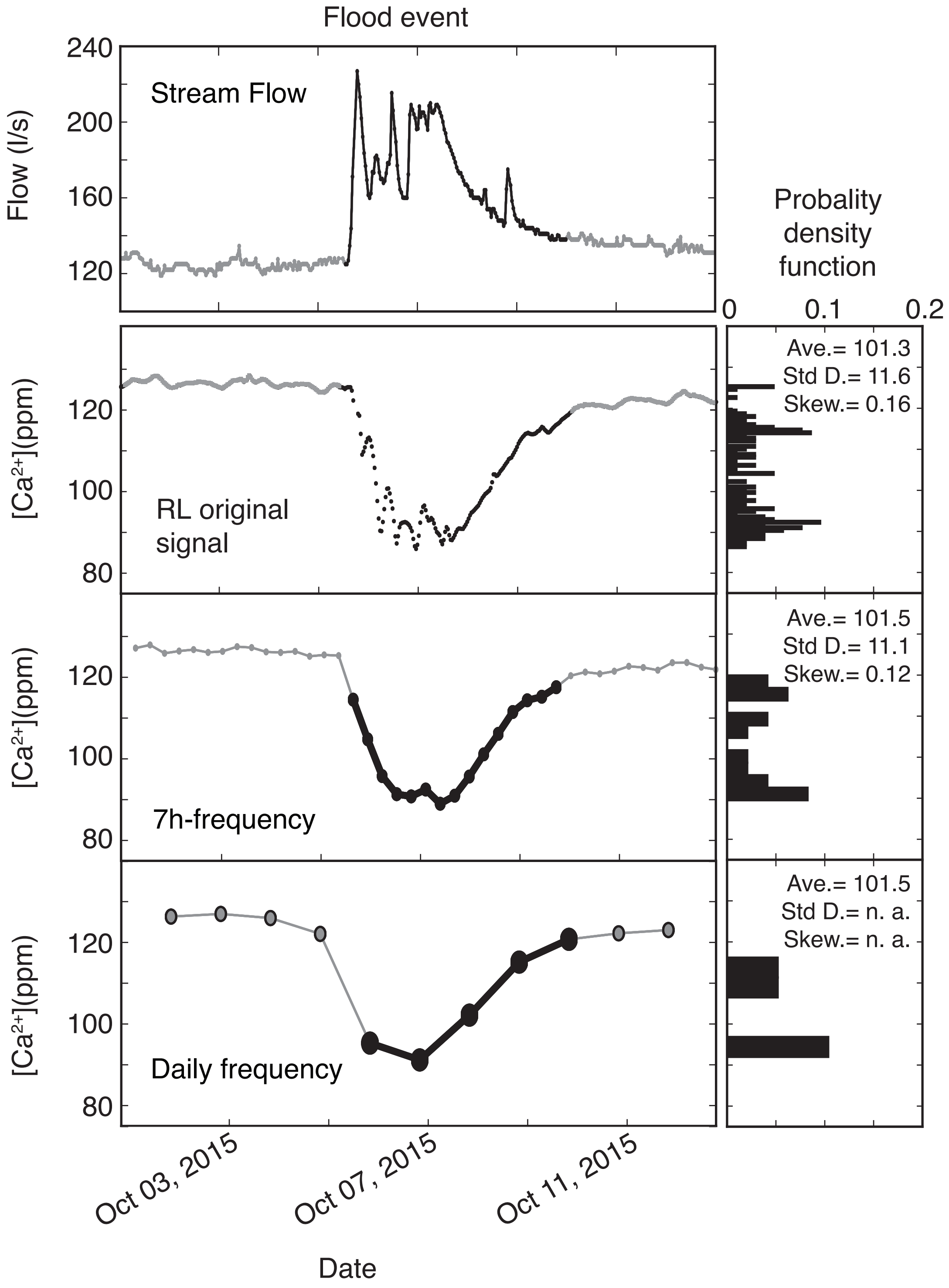

Cations (21-07-2015)
in ppm
Anions (19-04-2016)
in ppm
Ca$^{2+}$
126
124
122
120
$NO_3^-$
52
50
48
46
Na$^+$
14.20
13.90
13.60
13.30
13.00
$SO_4^{2-}$
61
59
58
57
56
55
K$^+$
3.50
3.45
3.40
3.35
3.30
3.25
Cl$^-$
34.0
33.5
33.0
32.5
32.0
31.5
7 p.m.
11 p.m.
3 a.m.
7 a.m.
11 a.m.
3 p.m.
7 a.m.
Time
Mg$^{2+}$
9.40
9.20
9.00
8.80
8.60
8.40
5 p.m.
9 p.m.
1 a.m.
5 a.m.
9 a.m.
1 p.m.
5 a.m.
Time
● Orgeval River Lab
● IPGP Laboratory

Figure 5


Flood event
Stream Flow
Flow (l/s)
240
200
160
120
Probality density function
0
0.1
0.2
[Ca2+](ppm)
120
100
80
RL original signal
Ave.= 101.3
Std D.= 11.6
Skew.= 0.16
7h-frequency
Ave.= 101.5
Std D.= 11.1
Skew.= 0.12
Daily frequency
Ave.= 101.5
Std D.= n. a.
Skew.= n. a.
Oct 03, 2015
Oct 07, 2015
Oct 11, 2015
Date

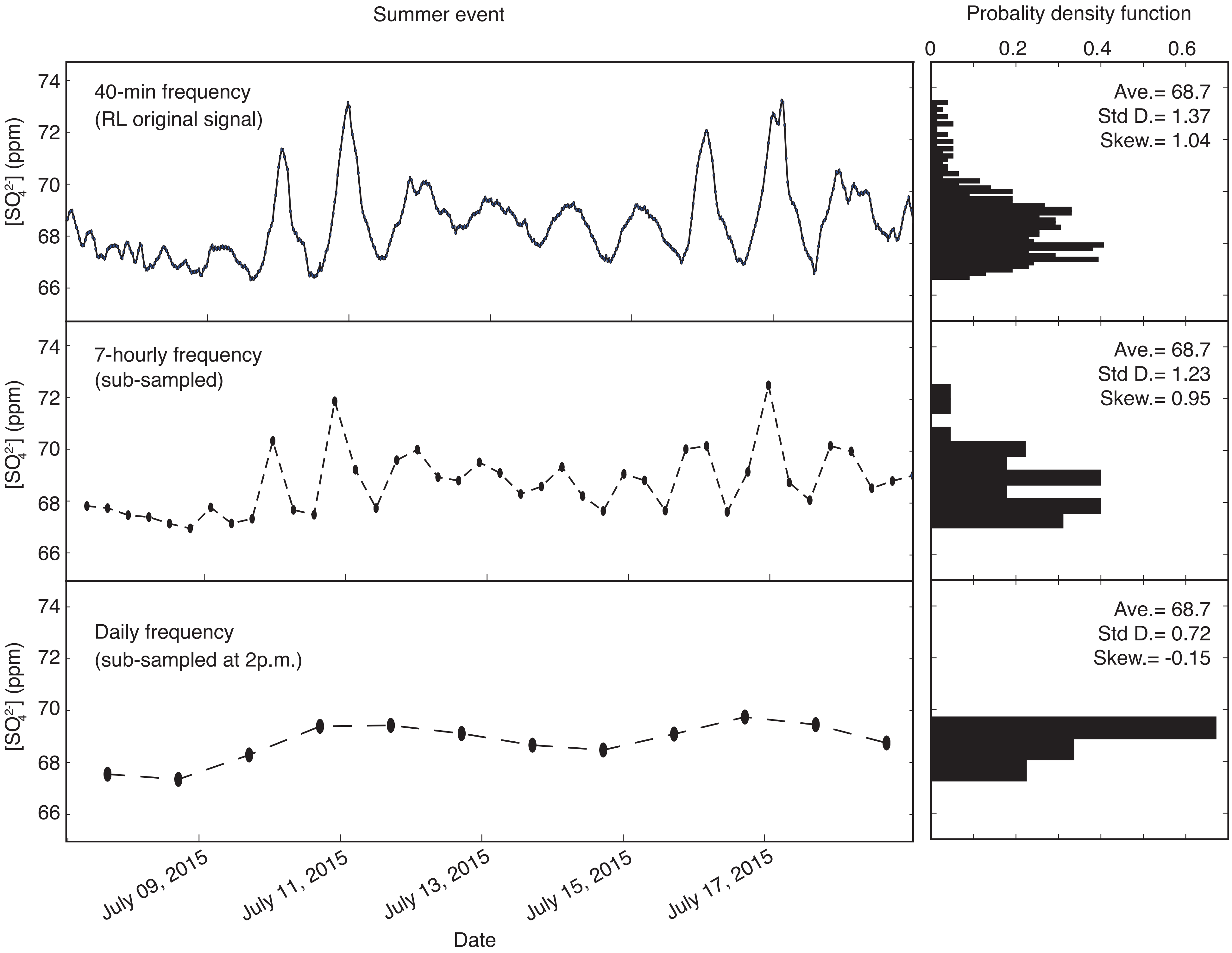
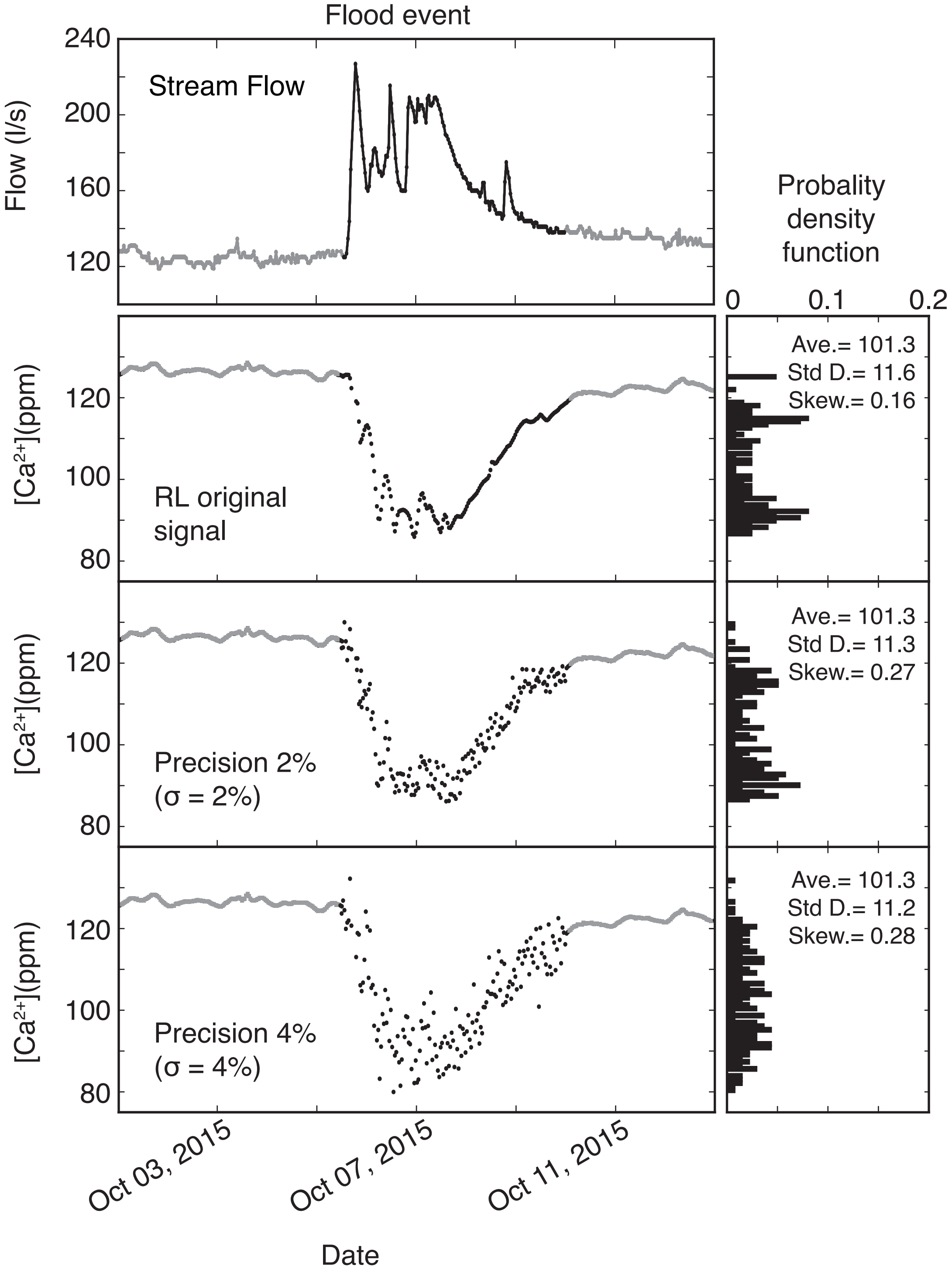

Summer event
Probality density function
0
0.2
0.4
0.6
40-min frequency
(RL original signal)
Ave.= 68.7
Std D.= 1.37
Skew.= 1.04
7-hourly frequency
(sub-sampled)
Ave.= 68.7
Std D.= 1.23
Skew.= 0.95
Daily frequency
(sub-sampled at 2p.m.)
Ave.= 68.7
Std D.= 0.72
Skew.= -0.15
[SO$_4^{2-}$] (ppm)
74
72
70
68
66
July 09, 2015
July 11, 2015
July 13, 2015
July 15, 2015
July 17, 2015
Date

Figure 6

Figure 7


Flood event
Stream Flow
Flow (l/s)
240
200
160
120
Probality density function
0
0.1
0.2
[Ca2+](ppm)
120
100
80
RL original signal
Ave.= 101.3
Std D.= 11.6
Skew.= 0.16
Precision 2%
(σ = 2%)
Ave.= 101.3
Std D.= 11.3
Skew.= 0.27
Precision 4%
(σ = 4%)
Ave.= 101.3
Std D.= 11.2
Skew.= 0.28
Oct 03, 2015
Oct 07, 2015
Oct 11, 2015
Date

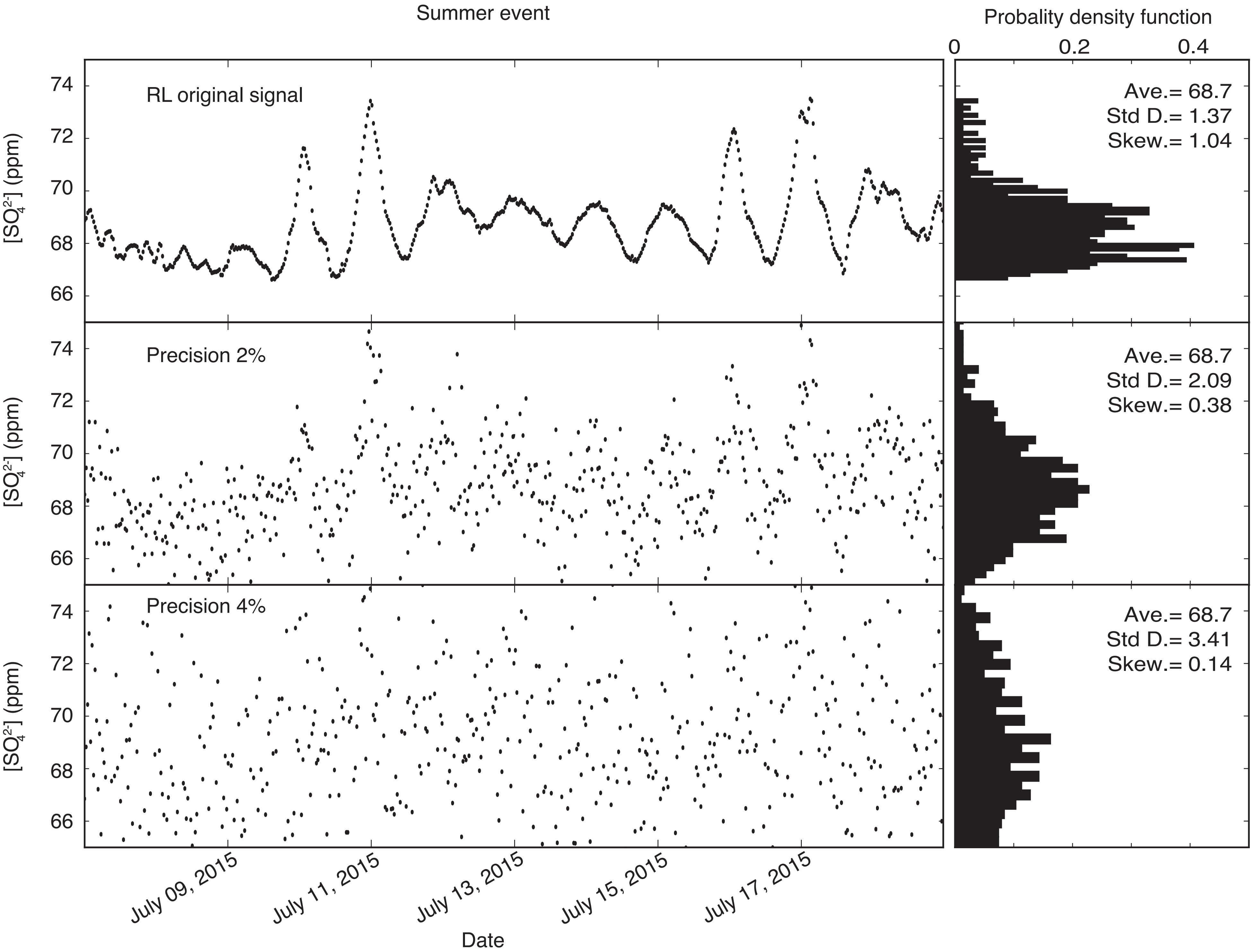

Summer event
Probality density function
0
0.2
0.4
RL original signal
Precision 2%
Precision 4%
[SO$_4^{2-}$] (ppm)
74
72
70
68
66
Ave.= 68.7
Std D.= 1.37
Skew.= 1.04
Ave.= 68.7
Std D.= 2.09
Skew.= 0.38
Ave.= 68.7
Std D.= 3.41
Skew.= 0.14
July 09, 2015
July 11, 2015
July 13, 2015
July 15, 2015
July 17, 2015
Date

Figure 8

Table 1

| | $Mg^{2+}$ | $K^+$ | $Ca^{2+}$ | $Na^+$ | $SO_4^{2-}$ | $NO_3^-$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|
| Calibration Concentration | 10.0 | 3.0 | 130.0 | 10.0 | 70.0 | 60.0 | 40.0 |
| Uncertainty ($mg.L^{-1}$) | 0.03 | 0.01 | 0.39 | 0.03 | 0.84 | 0.84 | 0.28 |
| **Uncertainty (%)** | **0.3** | **0.45** | **0.3** | **0.3** | **1.2** | **1.4** | **0.7** |
| | **One Measurement (Injection of "River x1" solution 4 times succsessivly)** | | | | | | |
| Number of measurements | *(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 |
| SD ($mg.L^{-1}$) | 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 of "River x1" solution every 8h)** | | | | | | |
| Number of measurements | *(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 |
| SD ($mg.L^{-1}$) | 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 of "River x1" solution every 2 days)** | | | | | | |
| Number of measurements | *(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 |
| SD ($mg.L^{-1}$) | 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** |

Table 2

| Date | Number of measurements | $Mg^{2+}$ | $K^+$ | $Ca^{2+}$ | $Na^+$ | $SO_4^{2-}$ | $NO_3^-$ | $Cl^-$ |
|---|---|---|---|---|---|---|---|---|
| | | 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 |