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

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Abstract. Our understanding of hydrological and chemical processes at the 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 precision. Here, we present a proof-of-concept study of a "lab in the field" called the "River Lab" (RL), based on the idea of permanently installing a suite of laboratory instruments in the field next to a river. Housed in a small shed, 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-day rain event, as

27 well as daily oscillations during a hydrological low-flow period of summer drought.

28 Using the measured signals as a benchmark, we numerically assess the effects of a

29 lower sampling frequency (typical of conventional field sampling campaigns) and of a

30 lower precision (typically reached in the laboratory) on the hydrochemical signal. The

31 high-resolution, high-precision measurements made possible by the RL open new

32 perspectives for understanding critical zone hydro-bio-geochemical cycles. Finally, the

33 RL also offers a solution for management agencies to monitor water quality in quasi

34 real-time.

35

36 **1 Introduction**

37 Rivers are messengers from the Critical Zone. The chemical composition of rivers

38 offers a window into the multiple processes that operate among water, organic matter,

39 primary and secondary minerals and living organisms at the Earth's surface. (Calmels et

40 al. 2011; Feng et al., 2004; Kirchner et al., 2000; Kirchner et al., 2001; Neal et al., 2012;

41 Neal et al. 2013). Understanding the parameters that control the composition of river

42 water is not only a scientific challenge, but also one of the major challenges for

43 humanity to access and preserve drinkable water (Bain et al., 2012; Banna et al., 2013;

44 Bartam and Ballance, 1996). A limit in our understanding of water geochemistry at the

45 Earth's surface is limited by the temporal resolution at which sampling can be operated

46 (Whitehead et al., 2009). As summarized by J. Kirchner: "If we want to understand the

47 full symphony of catchment hydrochemical behaviour, then we need to be able to hear

48 every note." (Kirchner et al., 2004, page 1358). Yet, taking high-frequency sample sets

49 back to the laboratory, filtering and analysing them for several elements is limited by

50 the requirement of considerable human resources (Chapman et al., 1996; Danielsen et

51   al., 2008; Halliday et al., 2015; Neal et al. 2013; Rozemeijer et al., 2014; Strobl and

52   Robillard, 2008; Telci et al., 2009).

53   A significant number of studies have reported high-frequency chemical measurements

54   in watersheds. Thus far, these data have been mostly acquired during limited periods of

55   time such as single storm events or a day (Beck et al., 2009; Brick et al., 1996;

56   Chapman et al., 1997; Gammons et al., 2007; Kurz et al., 2013; Liu et al., 2007; Morel

57   et al., 2009; Montety et al., 2011; Neal et al., 2002; Nimick et al., 2011; Nimick et al.,

58   2005; Takagi et al., 2015; Tercier-Weaber et al., 2009). Although these studies clearly

59   highlighted the wealth of information provided by sampling rivers at sub-hourly

60   frequency, they underestimate the legacy of past hydrological episodes (Kirchner 2006;

61   Jasechko et al., 2016; Rode et al., 2016) and are of limited use when mass budgets are to

62   be calculated for a typical hydrological cycle.

63   To date, the best combination of high-frequency and long-term monitoring ever

64   reported for river chemistry is a 7-hourly frequency sampling over 18 months (Neal et

65   al., 2012). In this study, the authors demonstrate the "act of discovery" permitted by

66   such sampling scheme, by showing that the high sampling frequency of river

67   hydrochemistry over sufficiently long time spans reveals patterns related to

68   hydrological and biological drivers that are imperceptible at lower sampling frequency.

69   Automated approaches, developed using probes installed directly in the river

70   (Rozemeijer et al., 2010a; Macintosh et al., 2011; Cassidy and Jordan 2011; Dabakk et

71   al., 1999; Glasgow et al., 2004; Zhu et al., 2010; Yang et al., 2008) or online

72   instrumental devices in which continuously pumped water is injected (Rozemeijer et al.,

73   2010b; Zabiegala et al., 2010; Jordan and Cassidy 2011) are alternatives to sampling

74   methods requiring human intervention. Several papers have been published over the last

75   decade reporting existing devices mostly focused on monitoring dissolved N or P and

76 organic matter (Clough et al., 2007; Kunz et al., 2012; Aubert et al., 2013a; Aubert et

77 al., 2013b, Escoffier et al., 2016). A recent overview of the potential of available

78 conductivity, dissolved oxygen and carbon dioxide, nutrients, dissolved organic matter,

79 chlorophyll in situ probes is given by Rode et al. (2016).

80 A new solution for high-frequency measurement of river chemistry is offered by

81 bringing the laboratory's measuring devices to the field (the "lab in the field" concept).

82 A Swiss group has recently developed such a system (von Freyberg et al., 2017) by

83 installing ionic chromatography devices in a hut next to a stream. In this paper, we

84 present a parallel initiative named the River Lab (RL) and funded by the French

85 program CRITEX: "Innovative sensors for the temporal and spatial EXploration of the

86 CRITical Zone at the catchment scale" (https://www.critex.fr). This approach, like the

87 previously published one, overcomes traditional limitations on the number of samples

88 and avoids several issues related to sample transport, filtration and storage. The RL is

89 able to perform a complete chemical analysis of all inorganic major anionic and cationic

90 species in the dissolved load of river water using ion chromatography (IC), with a

91 frequency of up to one complete measurement every 40 minutes.

92 This article is a proof-of-concept paper that describes the analytical design of the RL

93 and its performance by evaluating the precision, reproducibility and accuracy of

94 concentration measurements. The first results from the RL reveal a significant

95 improvement in reproducibility compared to conventional sampling and analysis

96 techniques. Leveraging these optimal analytical conditions, the RL is able to reveal

97 temporal patterns of river chemistry, such as daily concentration variations. The RL

98 opens thus new opportunities in the field of river chemistry research and environmental

99 monitoring.

100

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"). The 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

126 du Globe de Paris, France) and IRSTEA (Institut national de Recherche en Sciences et

127 Technologies pour l'Environnement et l'Agriculture, France) and assembled by Endress

128 & Hauser (E+H®) (Fig. 1). A technical sketch is available in supplementary information

129 (Fig. SI1).

130

131 The RL has been designed around a primary circuit, which pumps the river water at 700

132 liters per hour. First, the unfiltered river water sampled in the middle of the stream (Fig.

133 1) continuously supplies an overflow tank where 6 parameters are measured: pH,

134 conductivity, dissolved O_2, dissolved organic carbon (DOC), turbidity and temperature.

135 The water is then released into the river downstream from the RL. The turnover time of

136 water in this primary circuit is 2 minutes. The turbidity probe is installed upstream of

137 the overflow tank in a pipe perpendicular to the flow to provide more accurate

138 measurements. The turbidity and DOC probes benefit from an automatic self-cleaning

139 every 5 minutes using compressed air. For all probes, the frequency of acquisition is

140 one measurement per minute. The tank and each probe are hand-cleaned weekly. All

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

142

143 Second, a fraction of water pumped through the primary circuit feeds another circuit

144 directed toward two IC instruments for the measurement of major dissolved species

145 concentrations. A filtration system is deployed between the primary circuit and the IC

146 instruments, consisting of a tangential filter with a 2-µm pore size, followed by a 0.2-

147 µm frontal filtration system through cellulose acetate filters (Fig. 1) crucial for the IC

148 instruments. Cation and anion chromatographs, connected in series, are fed

149 simultaneously every 40 minutes from the filtered water circuit through a injection

150 valve. Between two injections, the water in the filtered circuit is constantly renewed (1

151   L per hour). Our tests show that the frequency for a complete and uncontaminated

152   analyse of cation and anion is actually limited by the filtration device (see part 4.3).

153   The IC analysis is performed using two Dionex[®] ICS-2100 (Thermo Fisher Scientific[®])

154   instruments using eluent produced with concentrated eluent cartridges and ultra-pure

155   water (Fig. 1). The cationic species measured are Na^+, K^+, Mg^{2+} and Ca^{2+}, and anionic

156   species are Cl^-, NO_3^- and SO_4^{2-}. The chosen analysis time is 30 minutes (40 minutes if

157   Sr^{2+} concentration measurements are included; see details in SI "Ion Chromatographs

158   characteristics"). The multiport valve installed upstream of the ICs allows us to check

159   the drift of the instruments and the background signal by regular introduction of

160   calibration solutions and pure distilled water (see section 4). Pure distilled water is

161   regularly (every two weeks) introduced to check the residual noise. Both cationic and

162   anionic chromatographs are calibrated every two months using synthetic solutions

163   mimicking the river chemistry, made from 1000-ppm mono-elemental standard

164   solutions. Two sets of calibration solutions are prepared, one for anions and the second

165   for cations. The first solution (called "River x1") is prepared based on concentrations of

166   the river water during summer, i.e. with the highest measured concentrations for most

167   species. In the second solution, these concentrations are doubled (called "River x2").

168   Further solutions are produced out of River x1 and x2 through dilution by up to ten-fold

169   to achieve lower concentrations ("River x0.5; x0.25; x0.1"). The resulting five

170   calibration solutions cover the entire range of possible natural variability of each species

171   observed for the Orgeval River, including flood events.

172

173   Data from probes and ICs are collected, merged and updated in a single database in real

174   time. Data from the gauging station (flow discharge and precipitation level) are

175   automatically added to the database. Several parameters of the RL can be remotely

176 monitored such as pump activity, pressure, flow and temperature in the primary circuit;

177 activation of the tangential filtration cleaning system, instrument connection, and

178 temperature in the bungalow. A set of alarms and sensors controls each key point of the

179 system. An email is automatically sent in case of dysfunction. Under normal operating

180 conditions, the RL needs human intervention only once per week.

181

182 **4 Analytical performances of the River Lab**

183 RL data acquisition started on the 12th of June 2015. The reliability of the system was

184 assessed through 5 different tests involving IC measurements and the sampling

185 procedure (accuracy, drift, precision of the whole system, cross-contamination and

186 reproducibility). We refer to the 3rd edition of JCGM 200-2012 (Joint Committee for

187 Guides in Metrology) (JCGM 2012) for the terminology used in assessing the

188 performance criteria.

189

190 **4.1 Accuracy and instrumental drift**

191 The aim of the RL is to achieve very high-frequency measurements of river chemistry

192 over long periods of time (pluriannual). To compensate for any long-term drift in the IC

193 calibration, instruments are calibrated with a new set of solutions every two months or

194 after each maintenance operation on the IC instruments. However, calibration drift can

195 occur over timescales shorter than two months, resulting in systematic and / or random

196 errors in concentration measurements. We evaluated this effect using a set of injections

197 of the "River x1" solutions, over one week and over two months, (Tab. 1). For all

198 species measured, no systematic variation was observed in the measured concentration

199 of the solution "River x1", showing that at the two timescales, instrumental drift does

200 not induce any systematic bias on concentration measurements, and that most of the

201 error is of random nature. Therefore, the standard deviation of the concentration

202 measurements of a given solution can be used as a reliable measure of the error due to

203 instrumental drift. The measurement error over one week is calculated as the standard

204 deviation of concentration measurements over 19 injections of solution "River x1"

205 performed every 8 hours during one week (from the 5th to the 12th of November 2015).

206 The measurement error over two months is calculated as the standard deviation of

207 concentration measurements over a series of injections performed every two days

208 during two months (from the 28th December 2015 to the 26th February 2016). These

209 error estimates are lower than 1 % over one week and lower than 1.7 % over two

210 months (Tab.1). The agreement between the calculated concentrations of the "River x1"

211 solution and the RL measurements also demonstrate the accuracy of the prototype (Tab.

212 1).

213

214 **4.2 Precision of the whole system**

215 In order to estimate the precision of the whole system (IC instruments combined with

216 the sampling device including the primary circuit, the pump and the filtration units), we

217 performed a "closed-loop experiment" over the course of one day by connecting the

218 inlet and the outlet of the primary circuit to a 300-L tank containing river water. The test

219 was performed three times over two different seasons (the 20th of July 2015, the 28th of

220 August 2015, and the 17th of April 2016). The conductivity probe (one measurement

221 every minute) was used to check the stability of the water chemistry during the course

222 of the experiment (Fig. SI 2). Our results show that a lapse of 2 hours at least is

223 necessary for the system to stabilize, corresponding to the homogenization time of the

224 water within the closed loop (Fig. 2). After two hours, major anion and cation

225 concentrations show a remarkable stability indicating the absence of drift over of 24-

226 hour time lapse despite the temperature variations in the river water, and allowing us to

227 estimate the precision of the whole system over one day using the standard deviation of

228 the measurements performed during the test. The results of the test are presented in

229 Table 2. The precision reached is lower than 0.5% for all species except for potassium,

230 for which it is lower than 1.2%.

231

232 **4.3 Cross-contamination**

233 The ability of the RL to detect rapid variations in river chemistry (typically expected

234 during storm events) depends on 1) the response time of the RL to a perturbation in the

235 river and 2) the potential cross contamination from one sample to the next one. We

236 assessed these two effects by a tracer injection experiment. After establishing a closed-

237 loop experiment (on the 29th of August 2015) and allowing for the period of

238 stabilization, we introduced a known amount of NaCl (200 g previously dissolved in a

239 small amount of river water) into the 300-L tank of river water in order to simulate a

240 "spike" in the river chemistry. The monitoring of conductivity in the primary circuit

241 allowed us to follow the propagation of the spike injection into the primary circuit while

242 Cl^- concentrations measured by the IC every 40 minutes allowed us to follow its

243 propagation through the filtration devices and IC instruments (Fig. 3). The conductivity

244 probe shows that the salinity spike is detected very quickly and stabilized after 5

245 minutes. This indicates that the water in the primary circuit is quickly homogenized (in

246 agreement with the high flow rate of the primary circuit: 700 l/h). Conversely, the Cl^-

247 and Na^+ concentrations only reach the expected concentration at the second IC

248 measurement i.e. after 80 minutes.

249

250 The first IC measurement following the spike injection indicates that only 93% of the

251 final steady-state concentration is reached, revealing a contamination of the $(n)^{th}$ sample

252 by 7% of the $(n-1)^{th}$ sample. In practice, such a contamination will only be significant if

253 the instantaneous derivative of river concentration with time is important. In the case of

254 the Orgeval River, where the RL is deployed, the relative derivative of the concentration

255 with respect to time is lower than 1% per hour for 90% of the time for all species. In

256 this case, the cross-contamination induces an error of 0.07% compared to the true

257 concentration, which means that the effect of cross contamination is negligible

258 compared to the precision of the RL (see section 4.2). However, in the case of flood

259 events, when the stream flow increases quickly, the derivative of concentration can

260 change by more than 10% per hour. In such cases, cross contamination will induce an

261 error of 1% or more. The injection test shows that the time resolution of the RL is

262 limited by the transfer time of the water between sampling and injection into the IC

263 instruments. This transfer time of the water in the RL is mainly due to the design of the

264 filtration system, which may be improved in the future.

265

266 **4.4 Reproducibility: RL *vs* Laboratory**

267 As a final test for assessing the ability of the RL to record fine natural variations of river

268 chemistry in comparison to conventional techniques of filtration and analyses in the

269 laboratory, we focused on two days in the summer of 2015 following long periods

270 without rain (21st of July 2015 for cations and 19th of April 2016 for anions) which

271 showed very high resolution diurnal variations (<5% relative) in chemical composition

272 of the Orgeval river. In addition to the analyses made by the RL every 40 minutes, we

273 conducted hourly sampling of the river by collecting 5 litres of water and filtering it

274 immediately using a Teflon$^{®}$ frontal filtration unit (Sartorius$^{®}$) with 0.2-μm porosity

275 polysulfonether filters. Bottles of acidified (at pH = 2) and unacidified river water were

276   transported to the laboratory at IPGP for measurement of major cations and anions,

277   respectively, using IC devices similar to those installed in the RL (Thermo Fisher® ics

278   2100). In the laboratory, measurements were performed using Thermo Fisher® ics 5000

279   for cations measurements and Dionex® 120 from Thermo Fisher® for anions

280   measurements. The calibration procedure in both laboratory and RL is the same using

281   the same set of calibration solutions. The error measurement reached in the laboratory is

282   estimated at 1% through repeated injections of the standard solution "River x1" (every 5

283   samples). Comparison between the RL and the laboratory for the seven measured

284   species are shown in Figure 4. First, the measurements made by the RL are more precise

285   than those performed in the laboratory, a feature that can be primarily attributed to the

286   greater stability of the continuously working injection system of the RL. Second, the

287   fine variations measured by the RL are reproduced in the laboratory, validating the

288   observed diurnal variations and supporting the reliability of the RL to detect changes on

289   the order of a percent within a day. The third observation is that small yet systematic

290   offsets between the two sets of data exist, up to 3% for Mg. One possible explanation

291   for this difference is that the filtration procedures differed between the RL and the

292   manual sampling, which may have led to a discrepancy in the concentration

293   measurements related to the potential for some elements to be hosted in the colloidal

294   phase (Dupré et al., 1999). In addition, the most accurate measurements were obtained

295   with the RL rather than with the laboratory equipment because the RL is continuously

296   processing solutions with a similar matrix, thereby minimizing memory effects and

297   cross-contamination that can compromise measurements if widely differing samples are

298   run successively on the same instrument. These features of the measurement protocol,

299   representative of most laboratory workflows for hydrochemical measurements, are

300   likely to lead to inaccuracies. Regardless of the observed discrepancy between the two

301   sets of measurements, we note that variations in concentration recorded by the RL and

302   measured at the IPGP laboratory have the same amplitudes and are synchronous.

303

304   **5. Discussion**

305   **5.1 What are the benefits of bringing the lab into the field?**

306   The RL presented above allows us to record continuously, at a high frequency and over

307   long spans of time, the concentration of 7 major dissolved species in a river system.

308   Although this is beyond the scope of the present paper , the RL presented here opens

309   new possibilities for the exploration of the fine structure of hydrochemical evolution at

310   the catchment scale and for improved understanding of the associated hydrological,

311   geochemical, and biological processes. From a technical point of view, our study shows

312   that deploying the conventional laboratory measurement techniques in the field adds

313   significant value. The tests performed and reported above clearly demonstrate an

314   improvement in precision compared to the analysis of bottled samples taken back to the

315   lab. We see three main reasons for this improvement.

316   1) In a given river, dissolved concentrations typically vary by less than one order of

317   magnitude when water discharge changes by several orders of magnitude (Godsey et al.,

318   2009). This constancy allows us to select a relatively narrow range of concentration for

319   establishing specific calibration curves of the IC instruments, a condition which is rarely

320   possible in the laboratory where different kinds of samples are analyzed.

321   2) While in the laboratory samples are injected discretely, in the RL river water samples

322   are injected as a continuous flow. Thus, the primary circuit and the filtration system

323   operate continuously at a constant pressure, which supports stable and accurate

324   analyses.

325   3) The third factor is the experimental conditions in the bungalow. The temperature is

326   maintained at 24°C ± 2° (in addition to the 40°C thermostatically-controlled

327   temperature in the column, precolumn and detection device of the ICs) allowing for

328   better stability of the IC measurements. Moreover, the RL IC instruments are never

329   stopped, which favours stability.

330

331   **5.2 What is revealed by a higher sampling frequency?**

332   To our knowledge, the high frequency of measurements (one measurement every 40

333   minutes) reached by the RL installed on the Orgeval River is the highest ever reported

334   for stream chemistry over several months. To highlight the corresponding improvement

335   in the recorded concentration signal, we tested the effect of sampling frequency on the

336   concentration signal. First, we artificially sub-sampled the RL original signal at two

337   lower sampling frequencies: every 7 hours (starting October 5th, 2015 at 10 pm) and

338   every 24 h. The 7-hourly frequency was chosen to reproduce the sampling frequency of

339   Neal et al., (2012) made in the Plynlimon watershed, Wales. The daily sampling

340   frequency is typically what is achievable on the long term by "human grab-sampling" in

341   the field. Second, we calculated the probability density function (PDF) of concentration

342   measurements over a given time interval. The use of PDFs allows us to explore the

343   structure of concentration signals beyond the mean concentration, which constitutes an

344   important metric for river solute budget, but lacks any insight into the variations in

345   concentrations that can be used to retrieve information on catchment processes. We

346   describe the PDF by 3 statistical parameters: mean, standard deviation and skweness.

347   Skewness indicates the distribution asymmetry, both in magnitude and direction (a

348   positive skewness means that most values are higher than the mean). Altogether, the

349   three parameters account, at first-order, for the structure of a concentration signal. We

350 compared these three parameters for the computed PDFs to quantify the signal

351 degradation induced by artificial sub-sampling.

352 We applied this statistical approach to two representative periods of the hydrological

353 cycle of the Orgeval Critical Zone Observatory: a typical 6-day rain event caused by the

354 arrival of a wet, Atlantic meteorological front (in October 2015) and a dry summer low

355 water stage period (July 2015) where the stream is essentially sustained by groundwater,

356 during an apparently steady hydrological period. We first present the behaviour of

357 calcium and sulphate concentrations as an example during the two considered periods

358 (Fig. 5 and 6), before generalizing to all measured species (Supplementary information

359 and Fig. SI 3, SI 5 and SI 6).

360

361 **Rain event**. The Ca concentration time series recorded at a 40-minutes frequency shows

362 that minimum Ca concentrations are recorded at maximum water discharge, but this

363 relationship is invisible at lower sampling frequency (Fig. 5). Narrow peaks during the

364 maximum of the stream flow are unresolved at a daily or 7-hourly frequency. The

365 comparison of the calculated PDFs shows that a bimodal character is captured at all

366 frequencies. The average and standard deviation are not significantly affected by the

367 sampling frequency, with a relative difference of less than 2% for the values of these

368 parameters between the three distributions. However, the skewness values vary among

369 the different records. From the 40-minutes frequency to the daily frequency signals, the

370 skewness is weaker, which means that even if the overall concentration variability is

371 well captured at the lower sampling frequencies, the concentration signal is clearly

372 degraded. This degradation is particularly intense during the middle of the rain event,

373 where the concentration signal evolves quickly.

374

375   **Summer event.** Despite the absence of rain events during the 2015 summer, the River

376   Lab recorded high frequency variations revealing a diurnal structure with 7% relative

377   variations between day and night. Each element exhibits its own type of daily variation

378   in terms of amplitude and regularity. The Figure 6 shows that the structure of this signal

379   is altered when the sampling frequency decreases. While these daily variations are still

380   captured when sampling occurs every 7 hours, their amplitude is somewhat altered (5%)

381   compared to the 40-minutes sampling frequency (8%). The daily variability of the

382   signal is absent on the daily sampling frequency. While the mean remains the same over

383   the range of sampling frequency, the variability quantified by the relative standard

384   deviation decreases with lower sampling frequency, by up to 50% for the daily

385   frequency compared to the 40-minutes frequency signal, indicating a significant loss of

386   information. The skewness of the concentration distribution recorded at a sub-sampled

387   daily frequency has a value that is opposite in sign compared to the other two

388   frequencies, indicating that there is an inversion of the measured asymmetry of the PDF

389   at lower sampling frequencies. Therefore, too coarse of a sampling frequency can yield

390   a strongly altered signal compared to higher frequencies, resulting in a biased shape of

391   the distribution of the concentrations.

392

393   **Generalization.** The resampling approach applied above is generalized and expanded to

394   other elements for both the summer and rain events. The generalization to all species

395   measured is presented in supplementary information. In Figures 5 and 6, we arbitrarily

396   chose the hour of sampling (10 a.m. and 2 p.m. for Figures 5 and 6, respectively). In

397   figure SI 3, SI 5 and SI 6, the sub-sampling is performed at each of the possible

398   sampling hours. This statistical analysis quantitatively demonstrates that such high

399   frequency measurements are able to capture the day-night chemical cycles of the

400   Orgeval River. Given the amplitude and duration of typical rain events in the catchment,

401   the alteration of the signal by lowering the sampling frequency is less critical but still

402   significant during these periods (Supplementary information; Fig. SI 3, SI 5 and SI 6).

403

404   **5.3 What is revealed by better analytical precision?**

405   As shown above, the Orgeval RL not only achieves high-frequency measurements but

406   also results in improved precision compared to conventional lab analysis following

407   manual sampling. Therefore, any sampling procedure, even at a high frequency,

408   involving conventional lab analysis induces a loss of precision. We demonstrate this

409   effect through a numerically generated artificial degradation of the precision. Using the

410   original RL concentration signal as a reference, we artificially degraded the signals by

411   adding a normally distributed noise onto the concentration signals recorded by the RL.

412   Noise levels of 4% and 2% were tested as they are representative of the "standard'

413   analytical precision reported for most laboratory IC devices. The same representative

414   periods as in the previous section (summer and rain events) were utilized for these tests.

415   In this section we present the example of one element for each characteristic period

416   (Ca^{2+} for rain event Fig. 7 and SO_4^{2+} for summer event Fig. 8. The generalization for all

417   elements is detailed in the supplementary information section (Supplementary

418   information and Fig. SI 4, SI 7 and SI 8).

419

420   **Rain event.** The Figure 7 illustrates the concentration PDF obtained after degradation

421   of the analytical precision for the Ca concentration. The narrow peaks recorded during

422   the maximum of the stream flow are virtually invisible in the signal at a 4%-precision,

423   and strongly smoothed in the signal at a 2%-precision. The original bimodal

424   characteristic of the PDF is still visible in the 2%-precision signal but no longer in the

425   4%-precision signal. The mean and standard deviation appear to be insensitive to these

426   changes in analytical precision, while the skewness is strongly impacted, reflecting

427   significant alteration of the concentration PDF at lower precision.

428

429   **Summer event.** Figure 8 shows how the sulphate concentration signal is affected when

430   the precision is degraded. Day-night variations are only visible in the original RL signal

431   because of its high analytical precision. The effect of degraded precision on the PDFs is

432   more important than for the rain event (Fig. 7). While the mean value is robust, the

433   standard deviation is altered (+150% from the RL signal to the 4% precision signal).

434   The skewness decreases (but keeps the same sign) by up to 90% for the signal at 4%-

435   precision compared to the original signal and 74% for the signal at 2%-precision,

436   indicating that the original RL signal asymmetry is lost as precision is worsened. These

437   changes in the parameters of the concentration PDF show that the structure of the

438   concentration signal in the Orgeval River would be significantly altered if the

439   measurements were made with analytical precision lower than that of the RL prototype.

440

441   **Generalization**. This approach has been expanded to other elements for both the

442   summer and rain events, as shown in the supplementary information, confirming that

443   concentration PDFs are strongly sensitive to the analytical precision for all species (Fig.

444   SI 4, SI 7 and SI 8).

445

446   **6 Conclusion**

447   This paper demonstrates the feasibility of deploying conventional laboratory

448   instruments in the field to measure the concentration of major dissolved anions and

449   cations in rivers $(Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-)$ at a high frequency (one

450   measurement every 40 minutes) and at a high analytical precision (better than 1%) over

451   several months. The River Lab prototype was installed in the Avenelles stream at the

452   Orgeval Critical Zone Observatory, France. The RL features physico-chemical probes,

453   an on-line 0.2-μm pore size filtration system, and two ionic chromatographic devices,

454   all installed in a closed, air-conditioned bungalow. The RL is autonomous, remotely

455   operable and data can be transmitted automatically. Human intervention is required only

456   once a week. Therefore, the RL also allows for an efficient attribution of human

457   resources, as well as considerable saving of consumables.

458   A suite of tests performed on the RL to assess quality measurement and to compare

459   with more conventional "grab sampling" followed by laboratory measurements revealed

460   only a minor drift in the instrument calibration, leading to improved precision. This

461   precision is not easily achieved in the laboratory under standard analysis conditions,

462   showing the benefit of transporting the laboratory devices to the field. The analytical

463   capabilities of the RL for major dissolved elements could theoretically be extended to

464   other elements separable by ion chromatography. Preliminary tests demonstrate that

465   species present in trace amounts in river water (down to the ppb, such as strontium or

466   lithium) could be measured with the same gain in precision.

467   For this particular prototype, the measurement frequency (every 40 minutes) appears to

468   be limited by the turnover time of water in the filtered water circuit, which is itself

469   imposed by the filtration unit. However, the high frequency and high precision of the

470   RL enabled precise and accurate observations on the fine structure in hydrochemical

471   time series. Their interpretation is beyond the scope of the present proof-of-concept

472   paper but the RL is able to capture the abrupt changes in dissolved species

473   concentrations during a typical 6-days rain event, as well as daily oscillations during a

474   hydrological steady period of summer drought.

475 Using the high frequency RL signal as a benchmark, it is possible to artificially alter the

476 sample frequency and the analytical precision and study the resulting effect on the

477 hydrochemical distribution obtained for characteristic hydrological events. This analysis

478 shows that in order to retrieve the fine structure of the hydrochemical signal, high

479 sampling frequency and improved analytical precision are both necessary conditions. To

480 paraphrase James Kirchner's quote: "If we want to understand the full symphony of

481 catchment hydrochemical behaviour, then we need to be able to hear every note"

482 (Kirchner et al., 2004). The improvements made possible by the RL here or

483 concomitantly by von Freyberg et al. (2017) allow us to consider hearing the full

484 potamological symphony.

485 Future work will explore the relationships between the desired measurement frequency

486 and the timescales characterizing the complex interactions between primary and

487 secondary minerals, biotic processes and hydrological processes in catchments.

488 Recording such fine stream hydrochemical variations has the potential to offer a new

489 perspective in Critical Zone Science development.

490

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509   **References**

510
511   Aubert, A. H., Gascuel-Odoux, C., Gruau, G., Akkal, N. et al. Solute transport
512   dynamics in small, shallow groundwater-dominated agricultural catchments: insights
513   from a high-frequency, multisolute 10 yr-long monitoring study. *Hydrol. Earth Syst.*
514   *Sci*. 2013a, 17, 1379–1391.

515
516   Aubert, A. H., Gascuel-Odoux, C., Merot P. Annual hysteresis of water quality: A
517   method to analyse the effect of intra- and inter-annual climatic conditions.
518   *Journal of Hydrology.* 2013b, 478, 29–39.

519
520   Aubert, A.H., Kirchner, J. W., Gascuel-Odoux, C., Faucheux, M. et al. Fractal Water
521   Quality Fluctuations Spanning the Periodic Table in an Intensively Farmed Watershed.
522   *Environ. Sci. Technol*. 2014, 48, 930−937.

523
524   Azzaro F., Galletta M. Automatic colorimetric analyzer prototype for high frequency
525   measurement of nutrients in seawater . *Marine Chemistry.* 2006, 99, 191–198.

526
527   Bain R., Gundry S., Wright J., Yang H., Pedleyc S., Bartramd J. Accounting for water
528   quality in monitoring access to safe drinking-water as part of the Millennium
529   Development Goals: lessons from five countries. *Bull World Health Organ.* 2012, 90,
530   228–235.

531
532   Banna M., Imran S., Francisque A., Najjaran H., Sadiq R., Rodriguez M., Hoorfar M.
533   Online Drinking Water Quality Monitoring: Review on Available and Emerging
534   Technologies. *Environ. Sci. Technol.* 2014, 44, 1370-1421.

535
536   Bartram J., Ballance R. Water Quality Monitoring. A practical guide to the design and
537   implementation of freshwater quality studies and monitoring programmes. *United*
538   *Nations Environment Programme.* 1996, 400 pages.
539

540 Beck A. J., Janssen F., Polerecky L., Herlory O., De Beer D. Phototrophic Biofilm
541 Activity and Dynamics of Diurnal Cd Cycling in a Freshwater Stream. *Environ. Sci.*
542 *Technol*. 2009, 43, 7245−7251.
543
544 Brick, CM., Moore J. N. Diel variation of trace metals in the upper Clark Fork River,
545 Montana. *Environ Sci Technol* .1996, 30, 1953–1960.
546
547 Calmels D., Galy A., Hovius N., Bickle M., West A., Chen M., Chapman H.
548 Contribution of deep groundwater to the weathering budget in a rapidly eroding
549 mountain belt, Taiwan. *Earth and Planetary Science Letters.* 2011, 303 48–58.
550
551 Cassidy R., Jordan P. Limitations of instantaneous water quality sampling in surface-
552 water catchments: Comparison with near-continuous phosphorus time-series data.
553 *Journal of Hydrology,* 2011, 405, 182–193.
554
555 Chan E. , Kessler J., Shiller A., Joung D., Colombo F. Aqueous Mesocosm Techniques
556 Enabling the Real-Time Measurement of the Chemical and Isotopic Kinetics of
557 Dissolved Methane and Carbon Dioxide. *Environ. Sci. Technol.* 2016, 50, 3039−3046.
558
559 Chapman D. Water Quality Assessments - A Guide to Use of Biota, Sediments and
560 Water in Environmental Monitoring - Second Edition. *United Nations Environment*
561 *Programme,* 1996, 651 pages.
562
563 Chapman, P. J., Reynolds, B., Wheater, H. S. Sources and controls of calcium and
564 magnesium in storm runoff: the role of groundwater and ion exchange reactions along
565 water flowpaths. *Hydrol Earth Syst Sci.* 1997, 1, 671–685.
566 283, 3–17.
567
568 Clough T., Buckthought L., Kelliher F., Sherlock R. Diurnal fluctuations of dissolved
569 nitrous oxide (N_2O) concentrations and estimates of N_2O emissions from a spring-fed
570 river: implications for IPCC methodology. *Global Change Biology.* 2007. 13, 1016–
571 1027.
572
573 Dåbakk E., Nilsson M., Geladi P., Wold S., Renberg I. Sampling reproducibility and
574 error estimation in near infrared calibration of lake sediments for water quality
575 monitoring. *Journal of Near Infrared Spectroscopy,* 1999 , 7, 241–250.
576
577 Danielsen F., Burgess N.et al. Local Participation in Natural Resource Monitoring: a
578 Characterization of Approaches. *Conservation Biology,* 2008, 23, 31–42.
579
580 de Montety, V., Martin, J.B., Cohen, M.J., Foster, C., Kurz, M.J., Influence of diel
581 biogeochemical cycles on carbonate equilibrium in a karst river. *Chemical Geology.*
582 2011, 283, 31–43.
583
584 Dupré B., Viers J., Dandurand J.L., Polve M., Bénézeth P., Vervier P., Braun J.J.. Major
585 and trace elements associated with colloids in organic-rich river waters: ultrafiltration of
586 natural and spiked solutions. *Chemical Geology,* 1999, 160, 63-80.
587

588 Escoffier, N., Bensoussan, N., Vilmin, L., Flipo, N., Rocher, V., David, A., ... &
589 Groleau, A. (2016). Estimating ecosystem metabolism from continuous multi-sensor
590 measurements in the Seine River. *Environmental Science and Pollution Research*, 1-17.
591
592 Feng, X. H., Kirchner, J. W., Neal, C. Measuring catchment-scale chemical retardation
593 using spectral analysis of reactive and passive chemical tracer time series. *Journal of*
594 *Hydrology*. 2004, 292, 296–307.
595
596 Gammons, C. H., Grant T. M., Nimick, D. A., Parker, S. R., DeGrandpre, M. D. Diel
597 changes in water chemistry in an arsenic-rich stream and treatment-pond system.
598 *Science of the Total Environment*. 2007, 384, 433–451.
599
600 Garnier J., Billen, G., Vilain, G., Benoit, M., Passy, P., Tallec, G., Tournebize, J., et al.
601 Curative vs. preventive management of nitrogen transfers in rural areas: Lessons from
602 the case of the Orgeval watershed (Seine River basin, France). *Journal of*
603 *Environmental Management*. 2014, 144, 125–134.
604
605 Glasgow H., Burkholder J., Reed R., Lewitus A., Kleinman J. Real-time remote
606 monitoring of water quality: a review of current applications, and advancements in
607 sensor, telemetry, and computing technologies. *Journal of Experimental Marine*
608 *Biology and Ecology,* 2004, 300, 409–448.
609
610 Halliday S., Skeffington R., Wade A., Bowes M., Gozzard E., Newman J., Loewenthal
611 M., Palmer-Felgate E., Jarvie H. High-frequency water quality monitoring in an urban
612 catchment: hydrochemical dynamics, primary production and implications for the Water
613 Framework Directive. *Hydrological Processes*. 2015, 29, 3388–3407.
614
615 Huang K., Cassar N., Jonsson B., Cai W ., Bender M. An Ultrahigh Precision, High-
616 Frequency Dissolved Inorganic Carbon Analyzer Based on Dual Isotope Dilution and
617 Cavity Ring-Down Spectroscopy. *Environ. Sci. Technol.* 2015, 49, 8602−8610.
618
619 Jasechko, S., Kirchner, J. W., Welker, J. M., McDonnell, J. J. Substantial proportion of
620 global streamflow less than three months old. Nature Geoscience. 2016, 9, 126–130.
621
622 JCGM 200:2012. International vocabulary of metrology − Basic and general concepts
623 and associated terms (VIM). 2012.
624
625 Jones T., Chappell N., Tych W. First Dynamic Model of Dissolved Organic Carbon
626 Derived Directly from High-Frequency Observations through Contiguous Storms.
627 *Environ. Sci. Technol.* 2014, 48, 13289−13297.
628
629 Jordan P., Cassidy R. Technical Note: Assessing a 24/7 solution for monitoring water quality loads in
630 small river catchments. *Hydrol. Earth Syst. Sci.,* 2011, 15, 3093–3100.
631
632 Kirchner, J. W., Feng, X., Neal, C. Fractal stream chemistry and its implications for
633 contaminant transport in catchments. *Nature* 2000, 403, 524–527.
634
635 Kirchner, J. W., Feng, X., Neal, C. Catchment-scale advection and dispersion as a
636 mechanism for fractal scaling in stream tracer concentrations. *J Hydrol.* 2001, 254, 81-
637 100.

638
639 Kirchner, J. W., Feng, X., Neal, C., Robson, A. J. The fine structure of water-quality
640 dynamics: the (high-frequency) wave of the future. *Hydrological Processes*. 2004, 18,
641 1353–1359.
642
643 Kirchner, J. W. Getting the right answers for the right reasons: Linking measurements,
644 analyses, and models to advance the science of hydrology. *Water Resour. Res*. 2006, 42,
645 1–5.
646
647 Kurz, M. J., de Montety, V., Martin, J. B., Cohen, M. J., Foster, C. R. Controls on diel
648 metal cycles in a biologically productive carbonate-dominated river. *Chemical Geology*.
649 2013, 358, 61–74.
650
651 Liu, Z., Liu, X., Liao, C., Daytime deposition and nighttime dissolution of calcium
652 carbonate controlled by submerged plants in a karst spring-fed pool: insights from high
653 time-resolution monitoring of physico-chemistry of water. *Environ Geol*. 2008, 55,
654 1159–1168.
655
656 Macintosh K., Jordan P., Cassidy R., Arnscheidt J., Ward C. Low flow water quality in
657 rivers, septic tank systems and high-resolution phosphorus signals. *Science of the Total
658 Environment*, 2011, 412, 58–65.
659
660 Morel, B., Durand, P. , Jaffrezic, A., Gru   au, G., Molenat, J. Sources of dissolved
661 organic carbon during storm flow in a head- water agricultural catchment, *Hydrological
662 Processes*. 2009, 23, 2888–2901.
663
664 Neal, C., Watts, C., Williams, R. J., Neal, M., Hill, L., Wickham, H. Diurnal and longer
665 term patterns in carbon dioxide and calcite saturation for the River Kennet, south-
666 eastern England. *The Science of the Total Environment*. 2002, 205–231.
667
668 Neal, C., Reynolds, B., Norris, D., Kirchner, J. W., Neal, M., Rowland, P., et al. Three
669 decades of water quality measurements from the Upper Severn experimental catchments
670 at Plynlimon, Wales: an openly accessible data resource for research, modelling,
671 environmental management and education. *Hydrological Processes*. 2011. 25, 3818–
672 3830.
673
674 Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J. W., Neal, M., Sleep, D.,
675 Lawlor, A., Woods, C., Thacker, S., Guyatt, H., Vincent, C., Hockenhull, K., Wickham,
676 H., Harman, S., Armstrong, L. High-frequency water quality time series in precipitation
677 and streamflow: From fragmentary signals to scientific challenge. *Sci. Total Environ*.
678 2012, 434, 3−12.
679
680 Neal, C; Reynolds, B; Kirchner, J. W.; Rowland, P; Norris, D; Sleep, D; Lawlor, A;
681 Woods, C; Thacker, S; Guyatt, H; Vincent, C; Lehto, K; Grant, S; Williams, J; Neal, M;
682 Wickham, H; Harman, S; Armstrong, L. High- frequency precipitation and stream water
683 quality time series from Plynlimon, Wales: an openly accessible data resource spanning
684 the periodic table. *Hydrological Processes*, 2013, 27, 2531-2539.
685

686 Nimick, D. A., Cleasby, T. E., McCleskey, R. B. Seasonality of diel cycles of dissolved
687 trace metal concentrations in a Rocky Mountain stream. *Environ Geol.* 2005, 47, 603–
688 614.
689
690 Nimick, D. A., Gammons, C. H. , Parker, S. R. Diel biogeochemical processes and their
691 effect on the aqueous chemistry of streams: A review. *Chemical Geology.* 2011, 283, 3-
692 17.
693
694 Rode, M., Wade, A.J., Cohen, M.J., Hensley, R.T., Bowes, M.J., Kirchner, J.W.,
695 Arhonditsis, G.B., Jordan, P., Kronvang, B., Halliday, S.J., Ske, R.A., Rozemeijer, J.C.,
696 Aubert, A.H., Rinke, K., 2016. Sensors in the Stream : The High-Frequency Wave of
697 the Present. *Environ. Sci. Technol.* 2016, 50, 10297−10307.
698
699 Rozemeijer J., Klein J. , Broers H., van Tol-Leenders T., van der Grift B. Water quality
700 status and trends in agriculture-dominated headwaters, a national monitoring network
701 for assessing the effectiveness of national and European manure legislation in The
702 Netherlands. *Environ Monit Assess,* 2014, 186, 8981–8995.
703
704 Rozemeijer J., van der Velde Y., van Geer F., Bierkens M., Broers H. Direct
705 measurements of the tile drain and groundwater flow route contributions to surface
706 water contamination: From field-scale concentration patterns
707 in groundwater to catchment-scale surface water quality. Environmental Pollution,
708 2010, 158, 3571-3579.
709
710 Rozemeijer J., van der Velde Y., de Jonge H., van Geer F., Broers H., Bierkens M.
711 Application and Evaluation of a New Passive Sampler for Measuring Average Solute
712 Concentrations in a Catchment Scale Water Quality Monitoring Study. *Environ. Sci.
713 Technol.* 2010, 44, 1353–1359.
714
715 Strobl R., Robillard P. Network design for water quality monitoring of surface
716 freshwaters: A review. *Journal of Environmental Management*, 2008, 87, 639–648.
717
718 Takagi, M. Water chemistry of headwater streams under storm flow conditions in
719 catchments covered by evergreen broadleaved forest and by coniferous plantation
720 Landscape Ecol Eng. 2015, 11, 293–302.
721
722 Telci I., Nam K., Guan J., Aral M. Optimal water quality monitoring network design for
723 river systems. *Journal of Environmental Management,* 2009, 90, 2987–2998.
724
725 Tercier-Waeber M., Hezard T., Masson M., Schäfer J. In Situ Monitoring of the Diurnal
726 Cycling of Dynamic Metal Species in a Stream under Contrasting Photobenthic Biofilm
727 Activity and Hydrological Conditions. *Environ. Sci. Technol.* 2009, 43, 7237–7244.
728
729 Vuillemin R., Le Roux D., Dorval P., Bucas K., Sudreau J. P., Hamon M., Le Gall C.,
730 Sarradin P. M. CHEMINI: A new in situ CHEmical MINIaturized analyzer. *Deep-Sea
731 Research I.* 2009, 56, 1391–1399.
732
733 von Freyberg, J., Studer, B., and Kirchner, J. W.: A lab in the field: high-frequency
734 analysis of water quality and stable isotopes in streamwater and precipitation, Hydrol.
735 Earth Syst. Sci. Discuss., 2017 doi:10.5194/hess-2016-585.

736
737 Wang Z., Sonnichsen F., Bradley A., Hoering K., Lanagan T., Chu S., Hammar T.,
738 Camilli R. In Situ Sensor Technology for Simultaneous Spectrophotometric
739 Measurements of Seawater Total Dissolved Inorganic Carbon and pH. *Environ. Sci.*
740 *Technol.* 2015, 49, 4441−4449.
741
742 Whitehead P., Wilby R., Battarbee R., Kerman M., Wade A. A review of the potential
743 impacts of climate change on surface water quality. *Hydrological Sciences–Journal–des*
744 *Sciences Hydrologiques,* 2009, 54, 101-121.
745
746 Yang W., Nan J., Sun D. An online water quality monitoring and management system
747 developed for the Liming River basin in Daqing, China. *Journal of Environmental*
748 *Management*, 2008, 88, 318–325.
749
750 Zabiegała B., Kot-Wasik A., Urbanowicz M., Namieśnik J. Passive sampling as a tool
751 for obtaining reliable analytical information in environmental quality monitoring. *Anal*
752 *Bioanal Chem,* 2010, 396, 273–296.
753 Kunz A., Steinmetz R., Damasceno S., Coldebela A. Nitrogen removal from swine
754 wastewater by combining treated effluent with raw manure. *Sci. Agric.,* 2012, 69, 352-
755 356.
756
757 Zhu X., Li D., He D., Wang J., Ma D., Li F. A remote wireless system for water quality
758 online monitoring in intensive fish culture. *Computers and Electronics in Agriculture,*
759 2010, 71, 3–9.
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786   **Table Captions**

787   **Table 1. Assessment of the RL accuracy and instrumental drift based on**
788   **concentration measurements made after several injections of the standard solution**
789   **"River x1". The uncertainty on the calibration solution is the quadratic sum of the**
790   **uncertainty on the standard solutions (provided by the manufacturer) and the**
791   **overall uncertainty for weighing during solution preparation. Measurement errors**
792   **over one week and over two months are expressed as the relative standard**
793   **deviation (RSD) calculated for repeated injections of the solution "River x1"**
794   **directly into the IC instruments via the multiport valve (see Fig. 1).**
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797   **Table 2. Precision on concentration measurements of the whole RL system**
798   **calculated as the relative standard deviation (RSD) of concentration measurements**
799   **made over three 24-hour closed loop experiments, during which the inlet and the**
800   **outlet of the primary circuit are connected through a 300-L tank of river water.**
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Figure Captions

Figure 1. Sketch of the Orgeval 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 first filtered through a < 2 mm pore size 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 through a 2 µm tangential stainless steel filtration unit, then filtered through a 0.2 µm cellulose acetate frontal filter prior to being 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 (in deviation from the mean for 4 dissolved species) of the whole RL system including the primary circuit, filtration systems and IC instruments (April, 17th, 2016). 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 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. Cross-contamination assessment and response time of the RL system after a spike injection of 200 g of NaCl. 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 prior to the injection. 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 within symbols size. 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. Reproducibility assessment of IC measurements made by the RL every 40 minutes (blue), compared with concentration measurements made in the laboratory after conventional hourly river sampling (orange). Tests were performed on July 21st, 2015 and April 19th, 2016 for the cationic and ionic species respectively. For measurements performed in the laboratory, the error measurement is 1% (except for K$^+$ at 2%) calculated as the standard deviation

884 **over repeated injection of the standard solutions "River x1". For RL**
885 **measurements the error is given in Table 2.**
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887
888 **Figure 5. Calcium concentration and stream flow in the Orgeval river during a**
889 **rain event (from 1 to 25 October 2015), sampled every 40 minutes (RL original**
890 **signal at 40-minutes frequency) and artificially sub-sampled every 7 hours and**
891 **every day at 10 a.m. Black dots represent data during the rain event strictly (from**
892 **5 to 10 October 2015 at 10 a.m.), over which probability density functions (PDFs)**
893 **of concentration are calculated and represented as histograms (right panels). For**
894 **each PDF, the following statistical parameters are calculated: average (Ave.),**
895 **standard deviation (Std D.), and skewness (Skew.). Gray dots represent**
896 **concentration values outside of the rain event and are not considered in the**
897 **corresponding PDF. The two statistical parameters standard deviation (Std D.)**
898 **and skewness (Skew.) are not calculated for the daily subsampling because of the**
899 **too small number of points.**
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901
902 **Figure 6. Sulphate concentration in the Orgeval river during a summer event**
903 **(from 7 to the 19 July 2015) sampled every 40 minutes (RL original signal) and**
904 **artificially sub-sampled every 7 hours, and every day at 2 p.m.. Probability density**
905 **functions (PDF) of concentration are represented as histograms (right panels). For**
906 **each PDF, the following statistical parameters are calculated: average (Ave.),**
907 **standard deviation (Std D.), and skewness (Skew.).**
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909
910 **Figure 7. Calcium concentration and stream flow in the Orgeval river during a**
911 **rain event (from 1 to the 25 October 2015), as recorded by RL and for two**
912 **artificially degraded signals using a normally distributed noise with standard**
913 **deviation of 2% and 4%, to reflect the effect of decreased analytical precision.**
914 **Black dots represent data during the rain event strictly from 5 (12 a.m.) to 10**
915 **October 2015. The probability density functions (PDF) of concentration are**
916 **calculated and represented as histograms (right panels). For each PDF, the**
917 **following statistical parameters are calculated: average (Ave.), standard deviation**
918 **(Std D.) and skewness (Skew.). Gray dots represent concentration values outside of**
919 **the rain event, which are not considered for the analysis presented on the right**
920 **panels.**
921
922
923 **Figure 8. Sulphate concentration in the Orgeval river recorded by the RL during**
924 **two weeks in summer (7 to 19 July 2015), and for two artificially degraded signals,**
925 **using a normally distributed noise with a standard deviation of 2% and 4%, to**
926 **reflect the effect of degraded analytical precision. The probability density**
927 **functions (PDF) of concentration are calculated and represented as histograms**
928 **(right panels). The average (Ave.), standard deviation (Std D.), and skewness**
929 **(Skew.) are calculated for each PDF.**
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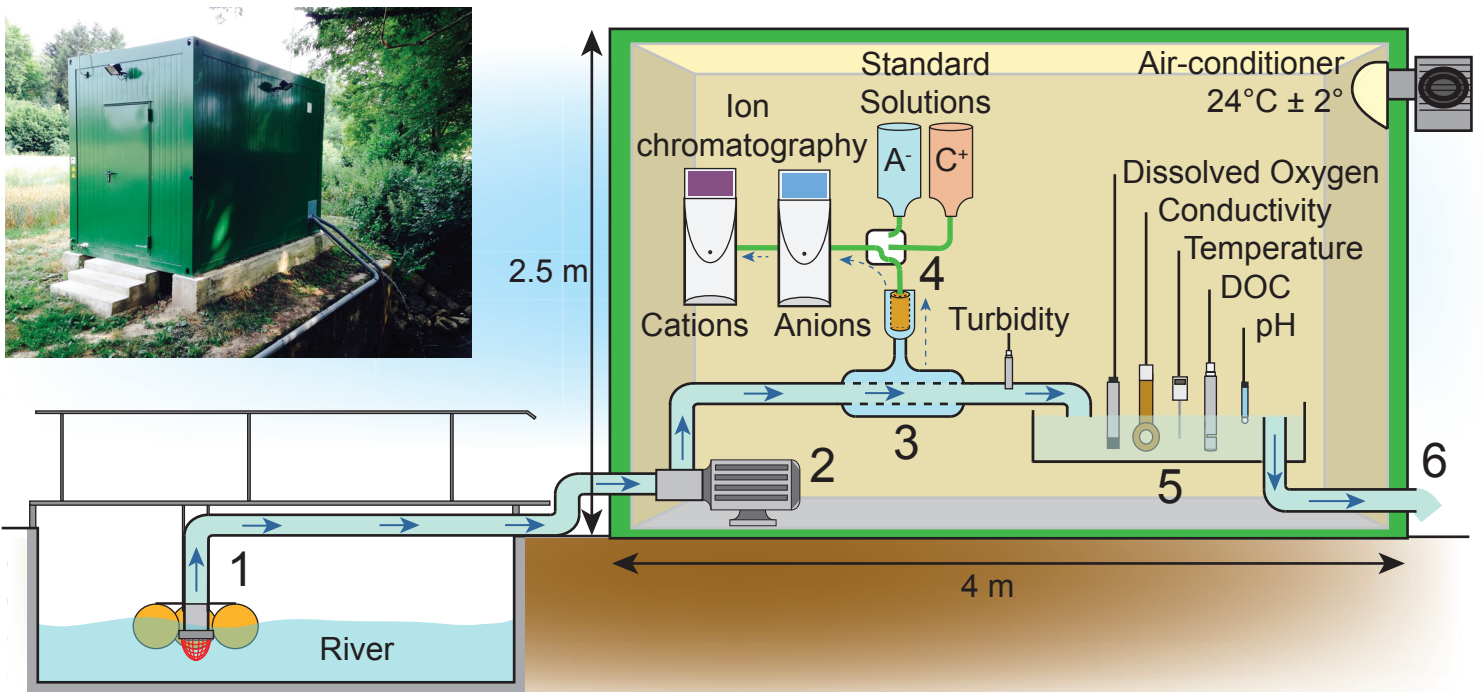931

Figure 1

Ion chromatography
Standard Solutions
A^- C^+
Air-conditioner
24°C ± 2°

Cations   Anions

Dissolved Oxygen
Conductivity
Temperature
DOC
pH

Turbidity

2.5 m

4

3

Turbidity

2

5

6

River

1

4 m

30

Figure 2

Figure 3

Figure 4

Cations (21-07-2015) in ppm

Anions (19-04-2016) in ppm

- Orgeval River Lab
- IPGP Laboratory

Figure 5

Flood event

Stream Flow — Flow (l/s): 120, 160, 200, 240

RL original signal — [Ca²⁺](ppm): 80, 100, 120
Ave.= 101.3
Std D.= 11.6
Skew.= 0.16

7h-frequency — [Ca²⁺](ppm): 80, 100, 120
Ave.= 101.5
Std D.= 11.1
Skew.= 0.12

Daily frequency — [Ca²⁺](ppm): 80, 100, 120
Ave.= 101.5
Std D.= n. a.
Skew.= n. a.

Probality density function: 0, 0.1, 0.2

Date: Oct 03, 2015 — Oct 07, 2015 — Oct 11, 2015

Summer event

Probality density function

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

Figure 6

Date

Figure 7

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