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Decomposing Bulk Electrical Conductivity of Streamflow to Recover Individual Solute Concentrations at High Frequency

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Abstract

The ability to evaluate stream hydrochemistry is often constrained by the capacity to sample streamwater at an adequate frequency. While technology is no longer a limiting factor, costs and sample management can still be a barrier to high-resolution water quality instrumentation. We propose a new framework to investigate the electrical conductivity (EC) of streamwater, which can be measured continuously through inexpensive sensors. We show that EC embeds information on individual ion content which can be isolated to retrieve solute concentrations at high resolution. The essence of the approach is the decomposition of the EC signal into its “harmonics”, i.e., the specific contributions of the major ions which conduct current in water. The ion contribution is used to explore water quality patterns and to develop algorithms that reconstruct solute concentrations starting from EC during periods where solute

13 measurements are not available. The approach is validated on a hydrochemical dataset
14 from Plynlimon, Wales, showing that improved estimates of high-frequency solute dy-
15 namics can be easily achieved. Our results support the installation of EC probes to
16 complement water quality campaigns and suggest that the potential of EC measure-
17 ments in rivers is currently far from being fully exploited.

18 **Introduction**

19 River hydrochemistry is characterized by marked time variability that typically depends
20 on hydrological and biogeochemical factors. In particular, one essential driver of water
21 quality dynamics is streamflow, which is characterized by frequent transitions between low
22 discharges (that typically reflect the composition of groundwater) and high discharges (that
23 can flush large portions of soil water). It is hence well known that capturing the structure of
24 hydrochemical behavior requires a sampling frequency comparable to — and possibly higher
25 than the typical timescale of the hydrologic response.¹ In most rivers this is equivalent to
26 a few hours, which makes the sufficient collection of water samples extremely challenging.
27 Instead, weekly, biweekly or monthly surveys are conducted, sometimes integrated by event-
28 based high-resolution campaigns. These surveys are fundamental for first-order estimates
29 of solute loads and long-term trends,^{2,3} but they may be insufficient to understand solute
30 dynamics and for a rigorous assessment of stream water quality.^{4,5} Transport and water-
31 quality models are widely employed as a complementary tool⁶ but they also strongly rely
32 on high-resolution data to calibrate and validate model results. The availability of high-
33 resolution hydrochemical datasets is thus crucial for both monitoring and modeling solute
34 hydrochemistry.

35 In the last years, high-resolution datasets have helped discover complex hydrochemical
36 patterns,^{7–12} and unprecedented technological advances have now made continuous water
37 quality measurements possible.^{13,14} In terms of costs and management, however, the collec-
38 tion of high-frequency hydrochemical data can still be a challenge. For this reason, recon-

39 structing high-frequency solute behavior through inexpensive “surrogate measures” of solute
40 concentration¹⁵ like electrical conductivity is a desirable opportunity.

41 Streamflow electrical conductivity (EC, also known as specific conductance) reflects the
42 presence of ions in flowing water and can be easily measured along with temperature by
43 relatively cheap and durable sensors. EC probes can acquire data at high frequency and
44 they have been long used to quantify the total amount of dissolved solids¹⁶ or as a quality
45 check for water chemistry analyses.¹⁷ However, EC measurements are seldom used to support
46 solute concentration measurements,¹⁸ with only few applications based on linear regressions
47 between EC and solute concentration^{19,20}.

48 The main research question that is investigated here is whether EC measurements can
49 be made useful for retrieving high-frequency water quality information. We propose a new
50 way to interpret EC signal in streamflow and use it to investigate the temporal evolution of
51 major ion concentrations. The driving hypothesis is that the use of continuous EC signal
52 to integrate low-frequency solute measurements is able to provide improved estimates of
53 high-frequency solute behavior.

54 **Materials and Methods**

55 The electrical conductivity of an aqueous solution is the capacity to transmit electrical
56 current through the movement of charged ions. Various forms exist to express EC as the
57 sum of the electrical conductivities of the individual ion species in water.²¹ In particular,
58 Parkhurst and Appelo²² propose:

$$EC = \sum_i EC_i = \sum_i (\Lambda^0 m \gamma_{EC})_i \quad (1)$$

59 where EC is expressed in S/m and for each solute species (denoted by subscript i): Λ^0 is the
60 molar conductivity [S/m/(mol/m³)], m is the molar concentration [mol/m³], and γ_{EC} [–] is
61 the electrochemical activity coefficient. To remove the temperature effect on Λ^0 and γ_{EC} ,

62 EC is typically reported at a standard temperature of 25°C. Further details on the terms
 63 of equation 1 are described in Section S2. Equation (1) can be reformulated to stress the
 64 time-variability of the individual terms. By denoting with t_k the times at which a water
 65 sample is collected, the relationship between EC and solute concentration C [mg/L] can be
 66 expressed as:

$$EC(t_k) = \sum_i EC_i(t_k) = \sum_i a_i(t_k) C_i(t_k) \quad (2)$$

67 where the coefficients $a_i = (\Lambda^0 \gamma_{EC} / M)_i$ [S/m/(g/m³)] (M indicating the solute molar mass
 68 [g/mol]) include known chemical properties of the solutes. The coefficients a_i have a mild
 69 dependence on the ionic strength of the solution, so they are not strictly constant and
 70 independent. However, in most environmental applications the ionic strength is rather low
 71 and with limited variability, so the coefficients a_i can be effectively considered as independent
 72 and with only minor time-variance.

73 For each solute species, we can define:

$$f_i(t_k) = \frac{EC_i(t_k)}{EC(t_k)} \quad (3)$$

74 which represents the relative contribution of each solute to total EC. The terms f_i can be
 75 seen as weights that describe how much an individual solute species influences the mea-
 76 sured EC, due to its chemical properties and concentration. Besides allowing a rank of
 77 the solutes according to their contribution to EC, the knowledge of weights f_i allows in-
 78 verting equation (2) and obtaining solute concentration starting from EC measurements as
 79 $C_i(t_k) = EC(t_k) f_i(t_k) / a_i(t_k)$. The key advantage of this inversion is that it can be extended
 80 to any time t where EC measurements and reliable estimates of the coefficients f_i and a_i are
 81 available:

$$C_i(t) = \frac{f_i(t)}{a_i(t)} EC(t) \quad (4)$$

82 Given that EC probes can provide almost continuous measurements and that the coefficients

83 a_i are rather constant, the ability to compute high-frequency solute concentration through
84 equation (4) translates into the capacity to properly estimate the individual contributions
85 $f_i(t)$.

86 **Proof of Concept**

87 To show the validity of the approach, we applied it to the water quality dataset publicly
88 available for the Upper Hafren (UHF) river in the Plynlimon area, mid-Wales (UK). The
89 dataset includes 7-hour frequency streamwater samples, analyzed for more than 40 elements
90 of the periodic table and for additional parameters like EC (at 25°C), pH and Alkalinity.^{8,23}
91 We selected 7 major ions (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} and NO_3^-), and obtained H^+
92 from pH and HCO_3^- from speciation calculation with Gran Alkalinity as input.²⁴ Some large
93 gaps in the Alkalinity series were filled through a linear regression with pH to allow extending
94 the analysis to a larger number of samples (Section S3).

95 **EC decomposition**

96 The first goal of the analysis is the decomposition of the bulk EC signal into its ion con-
97 tributions. To test the accuracy of equation (1), estimated EC was first compared to the
98 measured values (Section S4.1). All computations refer to the standard temperature of 25°C,
99 for consistency with measurements. The result (Figure S2) is generally accurate, with 95%
100 of the errors within $\pm 10\%$.

101 The good match between measured and calculated EC indicates that the estimated con-
102 tributions of the 9 major ions is generally appropriate. The weights $f_i(t)$ were then computed
103 through equation (3), where the terms $EC_i(t)$ were obtained as $a_i(t) C_i(t)$ and the term $EC(t)$
104 was set equal to the measured EC. The procedure is applied to each solute independently, so
105 it can be used to compute $f_i(t)$ for the available ion measurements even in case other major
106 ion concentrations are missing. The timeseries of weights f_i are shown in Figure 1, where so-

107 lutes are ranked according to their mean contribution to EC. Note that given the differences
 108 between measured and computed EC (Figure S2), the sum of the weights can occasionally
 be different from 1. Figure 1 shows the “harmonics” of the EC signal. Cl^- and Na^+ are the

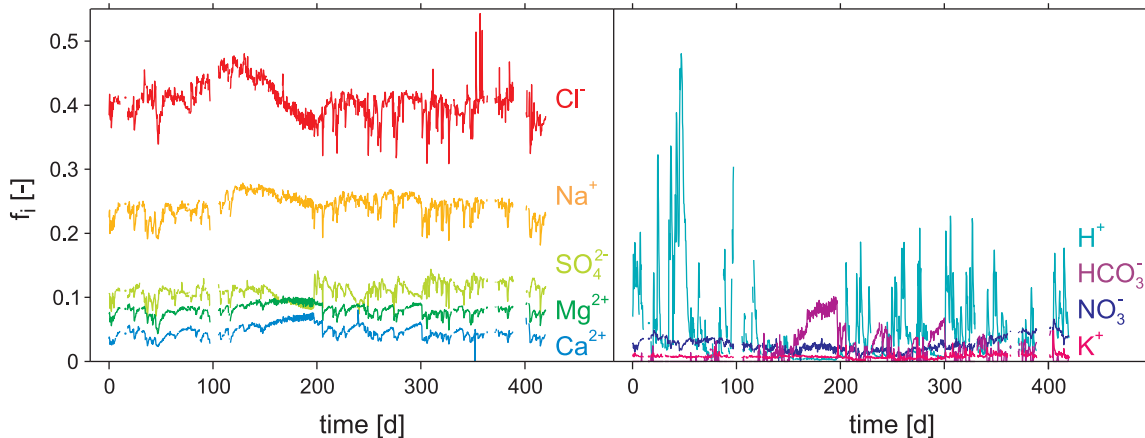


Figure 1: Relative contributions (f_i) of individual ions to the Electrical Conductivity (EC) signal at UHF, computed through equation 3. Cl and Na account for more than 60% of EC and have the lowest relative variability.

109

110 most influential solutes as together they provide more than 60% of EC. Although f_{Cl} and
 111 f_{Na} display some variability (especially after day 200), they are the weights with the lowest
 112 relative variability. Other ions have lower contributions, around 10% or less, except for H^+
 113 which has remarkably high and variable contributions related to acidic stream conditions
 114 during high flows.²⁵ Regardless of the particular dynamics, all solutes show potential for
 115 pattern exploration, including the dependence on stream discharge and the interdependence
 116 with other solutes. Because the weights f_i represent the EC contribution of each solute
 117 compared to that of the whole solution, the variability in f_i follows from contrasting solute
 118 behavior. This is most visible in the second part of the dataset, where most f_i are charac-
 119 terized by sharp depressions that correspond to H^+ peaks during high flows. Computations
 120 also showed (Figure S3) that the coefficients a_i only have minor variations in time (max
 121 $\pm 1\%$), so they could be effectively considered as a solute property.

122 **Retrieving high-frequency solute dynamics**

123 For solutes whose weights can be reliably predicted, one can use equation 4 to obtain solute
124 concentration estimates at the same frequency as EC. This can be especially useful to com-
125 plement long-term water quality surveys that are often conducted by environmental agencies.
126 Indeed, in the absence of higher-frequency information, low-frequency solute concentrations
127 are typically interpolated over the sampling interval to, e.g., estimate solute loads. The
128 second goal of the analysis is then to assess whether the use of continuous EC signal to
129 integrate low-frequency solute measurements is able to provide an approximation of solute
130 behavior which is significantly better than the simple interpolation of low-frequency concen-
131 tration measurements. This is not a trivial hypothesis as by using EC one could induce an
132 unrealistic behavior to the solute and ultimately get a worse approximation. To address this
133 problem, we used again the UHF dataset and selected the two ions with the highest contri-
134 butions to EC, i.e., chloride and sodium. For both solutes, we first extracted low-frequency
135 (e.g., weekly) “grab” subsamples of the dataset, which may represent the low-frequency grab
136 samples available from a water quality campaign. Then, instead of using the grab samples
137 to interpolate their solute concentration, we used them to interpolate their ion contributions
138 to EC and obtain high-frequency estimates of $f_i(t)$ and $a_i(t)$. Such estimates were finally
139 coupled to the measured EC signal (equation (4)) to obtain high-frequency estimates of so-
140 lute concentration. This procedure was implemented for grab sample frequencies from 14
141 hours to 31 days. As predictions are influenced by the choice of the first extracted sample, a
142 different prediction was generated for each possible choice of the initial sample. To evaluate
143 the quality of the EC-aided method, we computed a prediction error as the mean absolute
144 difference between the measured and estimated high-frequency concentrations (excluding the
145 data points corresponding to the grab samples, as their error is null by definition). For com-
146 parison, we computed the prediction error originating from the simple interpolation of the
147 grab samples’ concentrations. Results are shown in Figure 2, where the errors are plotted as a
148 function of the sampling frequency. All curves start from an error of about 2% corresponding

149 to the highest extractable frequency (14-hour). For increasing sampling intervals the errors
 150 grow, but the curves featuring the EC-aided methodology remain substantially lower than
 151 the ones corresponding to the linear interpolation, with approximately 40% error reduction.
 152 Figure 2 also shows that the error of the EC methodology with 14-day frequency is the same
 153 as the one from a linear interpolation at 3-day frequency. For additional comparison, we also
 154 computed the error of a least-square linear regression between solute concentration and EC
 155 (Section S5.1). The error of the regression behaves as an asymptote for the EC-aided esti-
 156 mate, suggesting that these two methods approximately converge for very large (>1 month)
 157 sampling intervals. This is not surprising as by progressively increasing the sampling interval
 158 one tends to a single, mean solute contribution to EC, which in turn tends to the slope of
 159 the linear regression when the intercept is close to 0 (Section S5.2).

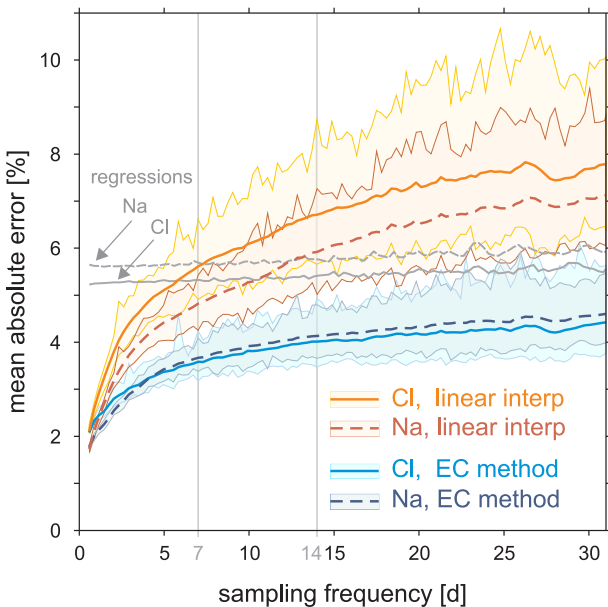


Figure 2: Solute concentration prediction error plotted against the sampling frequency of the grab samples. As for each frequency several predictions are available (depending on the choice of the initial grab sample), bands indicate the 90% confidence interval of the error distribution and lines indicate the mean error across all the possible predictions. Blue colors refer to the error of the EC method, red colors refer to the simple linear interpolation of the grab samples. Gray lines indicate the mean error of a linear regression between EC and solute concentration (Section S5).

160 An example of chloride estimation using biweekly samples is further shown in Figure 3.

161 The plot shows that, compared to a linear interpolation, the estimated chloride concentra-
 162 tion is able to reproduce most of the high-frequency fluctuations of the real signal. Indeed,
 163 the empirical distribution of the predicted concentration is very similar to that of measured
 164 chloride (Figure 3, inset). Figure 3 also shows that the use of a linear regression to estimate
 165 chloride concentration can accurately reproduce the high-frequency fluctuations, but it can-
 166 not reproduce some seasonal trends like those between days 80-200, hence the mean error of
 the performance (as shown in Figure 2) remains relatively high.

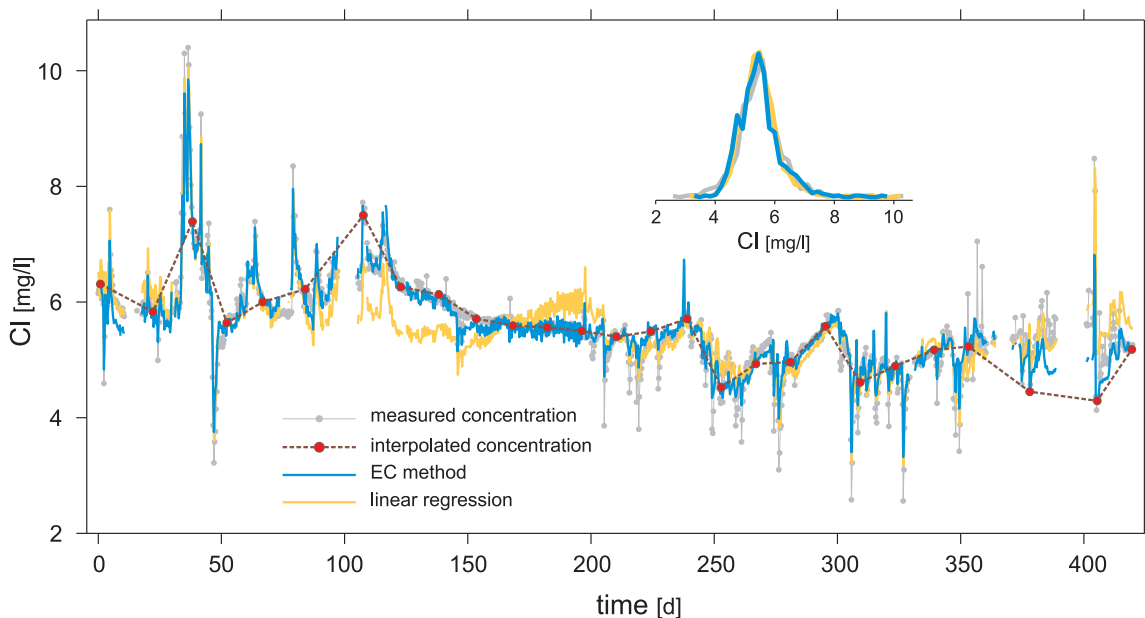


Figure 3: Example of chloride prediction based on biweekly grab samples. The inset reports the empirical distributions of the measured and estimated chloride signals. The interpolated concentration gives an incomplete picture of chloride behavior, while the regression with EC misses the seasonal chloride dynamics. The EC-aided methodology captures all main solute dynamics.

167

168 Discussion

169 The core and novelty of the approach is the interpretation of EC as a bulk signal of hy-
 170 drochemistry to be decrypted. Regardless of the “decoding” technique, the opportunity to
 171 decompose the EC signal to trace the presence of different ions in the flowing water (as

172 shown in Figure 1) is a new avenue which calls for additional research. One strength of the
173 methodology is its mechanistic foundation which allows understanding the complex dynam-
174 ics of the EC signal. Indeed, EC is not just *correlated* to Cl and Na, rather it is *caused* by
175 those solutes.

176 The proof-of-concept application to UHF provides some preliminary guidelines as to
177 where the approach is expected to work. Solutes with low contributions to EC are more dif-
178 ficult to isolate in the EC decomposition and are prone to high relative errors on the weights
179 f_i estimation (Figure S5). This directly translates into higher errors in the concentration
180 estimate (Section S4.3). The variability in the weights f_i (Figure 1) arises when solutes
181 have contrasting behaviors and it represents the major challenge to the EC decomposition
182 (Section S4.3). Simplified techniques like the linear interpolation of low-frequency f_i values
183 are sufficient to show the potential of the approach and can provide valid approximations
184 for the highly-contributing solutes (like Cl and Na at UHF, Figure 2), but better algorithms
185 are required to approximate the weights f_i for poorly-contributing solutes (like Ca and NO₃
186 at UHF). Further developments of the approach, hence, point to improved algorithms that
187 explicitly take into account the integrated solute dynamics and incorporate hydrochemical
188 knowledge available for the site. Moreover, other variables may be embedded like water flow,
189 temperature and pH, that typically have an influence on solute concentration²⁶ and are often
190 available at the same frequency as EC.

191 The UHF stream is a natural environment where EC is low and mostly controlled by
192 two solutes, but it is also characterized by acidic conditions at high flows that cause sharp
193 variations in the contributions f_i . Different systems are expected to have very different con-
194 tributions to EC depending on their particular hydrochemistry, but the approach is general
195 and can be explored in various ways, e.g., starting from the computation of the contributions
196 to EC for the existing water quality datasets. The approach is also obviously related to the
197 ability to accurately measure EC (which requires maintenance of the sensor) and can be
198 influenced by several undesired factors, like road salting during snow seasons.²⁷

199 Long-term water quality campaigns are being conducted in many sites worldwide by
200 research groups and water-quality agencies. By installing EC probes in such sites (if not
201 already present), the methodology can be immediately applied at almost zero cost. For
202 example, results suggest that continuous EC measurements at Plynlimon could be coupled
203 to long-term chloride measurements²⁸ to aid the estimation of high-frequency chloride con-
204 centration. There is indeed enormous potential for deploying cheap networks of EC probes
205 in streamflow (as also for precipitation or groundwaters) and identify multiple signatures
206 of hydrologic transport. This is not currently done because EC is traditionally treated as
207 a qualitative indicator¹⁸ of total dissolved solids, but the key result of this research is that
208 there is much more information that can be recovered from the EC signal.

209 Finally, results introduce a potential for using the EC signal in solute transport modeling.
210 State-of-the-art models^{6,29} can provide outputs at high temporal resolutions and are often
211 limited by data availability. Given the high information potential contained in EC and
212 addressed in this paper, we envision the opportunity in the future to use information from
213 continuous EC signal to support the calibration of transport models.

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221 **Supporting Information Available**

222 The following file is available free of charge.

- 223 • Supporting Information: details on methods and results

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324 **Graphical TOC Entry**

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