1. Point-by-point response to Referee #1

Dear Colleague,

Thank you for your review, which will help us improve our technical note. Please find below a detailed response to the points you raised:

It would gain in scientific merit if the ranges of applicability of the new parameterisation and its predictive uncertainty were discussed. The number of parameters is increased by one (from two to three), which might not seem to be much but it must introduce more uncertainty to the results. We have computed the predictive confidence interval, as it is common in case of linear regression (Jonnston, 1972 pp. 154-155; see also the discussion in Andréassian et al., 2007) and present the results in Figure 1 below. The figure speaks for itself: the predictive interval (blue surface for a 50 % predictive confidence interval, red for 95%) is much narrower for the 2S-APS relationship. This means that predictive uncertainty is more impacted by the error than by the number of parameters. We will add this graph in the final version of the paper.



Figure 1: Predictive confidence interval computed for the 2S-APS relationship and the power-law for the 3 ions and the EC relationship. In blue the 50 % and in red the 95 % predictive confidence

Specific comments

1. Table 1: The authors use "sulfate" instead of sulphate throughout the whole paper. It is an American spelling and personally I would prefer the classic spelling.

We will change it in the revised manuscript

2. Page 8 line 138... (a,b) pairs from eq. 3...

We will change it in the revised manuscript

References:

Andréassian, V., Lerat, J., Loumagne, C., Mathevet, T., Michel, C., Oudin, L., and Perrin, C.: What is really undermining hydrologic science today?, Hydrological Processes, 21, 2819-2822, 10.1002/hyp.6854, 2007.

Jonnston, J.: Econometric Methods, McGraw - Hill Book Company, USA, 437 pp., 1972.

2. Point-by-point response to Referee #2

Dear Colleague,

Thank you for your review, which will help us improve our technical note. Please find below a detailed response to the points you raised:

Specific comments

Line 50, Table 1: use mg S L-1 instead of Smg L-1, more over the coefficient of variation could be added to give a simple measure for the variation within the data set, although the less often used $(q90-q10)/\mu$) statistic is already presented but without mentioning it in the manuscript anymore.

With respect to the nomenclature of the sulphate ion, we will make the corresponding changes in the final manuscript.

We will replace $(q90-q10)/\mu$) with the Coefficient of Variation (CV) in the final manuscript, and also add a few explanatory lines on this criterion.

Line 143 ff: the use of the NSEB criteria reduces the sensitivity of this objective function compared to the original NSE. If the concertation variability is small compared to the discharge variability solute loads are highly controlled by discharge. Therefor combining concentration with load objective function will further reduce the sensitivity of these criteria in those cases. To provide a most transparent evaluation I suggest to provide all five given criteria separately not only in the calibration mode but also in the validation mode

Line 187, Table 6: here all five introduced evaluation criteria should be given to allow an assessment of the new approach in more detail, e.g. distinguish between concentration and load calculations.

We will add the four remaining criteria (NSE and NSEB of concentration and load) in the final version of the manuscript.

Line 169, Table 5: I would suggest to provide the mean concentration of the solutes in the table although they have been provided already in table 1 making the assessment of the RMSE easier

We will add the mean concentration of solutes in Table 5 in the final version of the manuscript.

Line 187: It seems that the new approach has especially advantages if the variability of concentration and probably also discharge is large. If this is the case this would allow for a more detailed discussion of the advantages and possibly also limitations of the new approach.

We wanted to keep the discussion short because this is a technical note, however in the final manuscript we will add a short section showing the advantages and limitations of this new approach.

3. List of all relevant changes made in the manuscript

Lines and page	Changes made			
Ln 47 to 53 page 3	Modification of table 1 at the request of reference #2: use of the coefficient of variation (CV) and a brief explanation of this criterion applied in our data			
Ln 158 to 160 page 9	Introduction of Appendix 2 in the main text			
Ln 166 to 170 pages 9 & 10	Addition of table 5 with the 5 NSE criteria obtained for the two relationships studied during the calibration period at the request of referee #2			
Ln 178 page 10	modification of table 6 at the request of referee #2: addition of mean concentrations of solutes to make the assessment of the RMSE easier			
Ln 190 to 195 page 12	Addition of table 7 with the 5 NSE criteria obtained for the two relationships studied during the validation period at the request of referee #2			
Ln 202 page 12	modification of table 6 at the request of referee #2: addition of mean concentrations of solutes to make the assessment of the RMSE easier			
Ln 214 to 215 page 13	Addition of a remark concerning the limitations of this study			
Ln 295 to 308 pages 16 & 17	Appendix 2 containing the calculation of the predictive confidence interval (PI) to respond to the remark made by referee #1			

4. Marked-up manuscript version

1 **Technical Note:**

2 A two-sided affine power scaling relationship to represent the

3 concentration-discharge relationship

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7 Abstract

8 This technical note deals with the mathematical representation of concentration-discharge 9 relationships. We propose a two-sided affine power scaling relationship (2S-APS) as an alternative to 10 the classic one-sided power scaling relationship (commonly known as "power law"). We also discuss 11 the identification of the parameters of the proposed relationship, using an appropriate numerical 12 criterion. The application of 2S-APS to the high-frequency chemical time series of the Orgeval-Oracle 13 observatory is presented (in calibration and validation mode): It yields better results for several solutes 14 and for electrical conductivity in comparison with the power law relationship.

15 Keywords

16 Concentration–discharge relationships; log–log space; power law, high-frequency chemical data

17 **1. Introduction**

The relationship between solute concentrations and river discharge (from now on "C-Q relationship") is an age-old topic in hydrology (see among others Durum, 1953;Hem, 1948;Lenz and Sawyer, 1944). It would be impossible to list here all the articles that have addressed this subject, and we refer our readers to the most recent reviews (e.g. Bieroza et al., 2018;Botter et al., 2019;Moatar et al., 2017) for an updated view of the ongoing research on C-Q relationships.

23 Many complex models have been proposed to represent C-Q relationships, from the tracer mass 24 balance (e.g. Minaudo et al., 2019) to the multiple regression methods (e.g. Hirsch et al., 2010). 25 Nonetheless, for the past 50 years the simple mathematical formalism known as "power law" has 26 enjoyed lasting popularity among hydrologists and hydrochemists (see e.g. Edwards, 1973;Gunnerson, 27 1967;Hall, 1970, 1971). Over the years, however, some shortcomings of this relationship have become 28 apparent: Recently, Minaudo et al. (2019) mentioned that, "fitting a single linear regression on C-Q 29 plots is sometimes questionable due to large dispersion in C-Q plots (even log transformed)". Also, Moatar et al. (2017) present an extensive typology of shapes (in log–log space) for the French national water quality database, which shows that the power law must be modified to represent the C-Q relationship for dissolved components as well as for particulate-bound elements.

This technical note presents a two-sided affine power scaling relationship (named "2S-APS") that can be seen as a generalization of the power law. And although we do not wish to claim that it can be universally applicable, we argue here that it allows for a better description and modeling of the C-Q relationship of some solutes as a natural extension of the power law.

37 **2. Test dataset**

We used the half-hourly (every 30 min) hydrochemical dataset collected by the in situ *River Lab* laboratory at the Oracle-Orgeval observatory (Floury et al., 2017;Tallec et al., 2015). A short description of the study site is given in Appendix 1. We used dissolved concentrations of three ions – sodium [Na⁺], sulphate [S-SO₄²⁻], and chloride [Cl⁻] – as well as electrical conductivity (EC). This dataset was collected from June 2015 to March 2018, averaging 20,700 measurement points.

As our main objective in this note is to compare the performance of two relationships (the new 2S-APS
and the classic power law), we divided our dataset into two parts to perform a split-sample test
(Klemeš, 1986): We used June 2015 to July 2017 for calibration (of both relationships), and August
2017 to March 2018 for validation. Table 1 presents the main characteristics of both periods.

- 47 Table 1: Summary of high-frequency dissolved concentrations and electrical conductivity (EC;
- 48 average, minimum, maximum values and coefficient of variation) from the River Lab at the Oracle-
- 49 Orgeval observatory, divided into two groups: June 2015 to July 2017 (calibration period) and August
- 50 **2017 to March 2018 (validation period).**

Soluto	Unit	Calibration period (June 2015 to July 2017)						
Solute		<mark>Mean (μ)</mark>	<mark>Min</mark>	<mark>Max</mark>	<mark>CV</mark>			
<mark>Sodium</mark>	<mark>mg.L⁻¹</mark>	<mark>13</mark>	<mark>2</mark>	<mark>17</mark>	<mark>0.12</mark>			
<mark>Sulphate</mark>	<mark>mgS.L⁻¹</mark>	<mark>19</mark>	<mark>2</mark>	<mark>32</mark>	<mark>0.19</mark>			
<mark>Chloride</mark>	<mark>mg.L⁻¹</mark>	<mark>30</mark>	<mark>4</mark>	<mark>40</mark>	<mark>0.15</mark>			
<mark>EC</mark>	<mark>µS.cm⁻¹</mark>	<mark>704</mark>	<mark>267</mark>	<mark>1015</mark>	<mark>0.11</mark>			
		Validation	period (Au	gust 2017 to N	larch 2018)			
<mark>Sodium</mark>	mg.L ⁻¹	<mark>13</mark>	3		<mark>0.24</mark>			
<mark>Sulphate</mark>	<mark>mgS.L⁻¹</mark>	<mark>18</mark>	<mark>3</mark>	<mark>26</mark>	<mark>0.27</mark>			
<mark>Chloride</mark>	<mark>mg.L⁻¹</mark>	<mark>29</mark>	<mark>4</mark>	<mark>40</mark>	<mark>0.29</mark>			
FC	uS cm ⁻¹	<mark>576</mark>	171	<mark>813</mark>	0.25			

51 Table 1 shows a slight difference in the coefficient of variation (CV), which represents the dispersion

52 of data with respect to their average value between the calibration and the validation period: this is

53 due to the number of data used, which much larger in the case of the calibration period.

3. Mathematical formulations

55 **3.1 Classic one-sided power scaling relationship (power law)**

56 Since at least 50 years ago, a one-sided power scaling relationship (commonly known as power law) 57 has been used to represent and model the relationship between solute concentration (C) and 58 discharge (Q) (Eq. (1)).

$$C = aQ^b$$
 Eq. (1)

From a numerical point of view, the relationship presented in Eq. (1) is generally adjusted by first
transforming the dependent (*C*) and independent (*Q*) variables using a logarithmic transformation,
and then adjusting a linear model (Eq. (2)).

- $\ln(C) = \ln(a) + b.\ln(Q)$ Eq. (2)
- Graphically, this is equivalent to plotting concentration and discharge in a log-log space, where
 parameters *a* and *b* can be identified either graphically or numerically, under the assumptions of linear
 regression.

65 3.2 Limits of the power law

In many cases, the power law appears visually adequate (and conceptually simple), which explains its 66 67 lasting popularity. With the advent of high-frequency measuring devices in recent years, the size of the 68 datasets has exploded, and the C-Q relationship can now be analyzed on a wider span (Kirchner et al., 69 2004). Figure 1 shows an example from our own high-frequency dataset: the 17,500 data points (which 70 correspond to the calibration period of Table 1) represent half-hourly measurements collected over a 71 2-year period, during which the catchment was exposed to a variety of high- and low-flow events, thus 72 providing a great opportunity for exploring the shape of the C-Q relationship. This being said, we do 73 not wish to imply that a similar behavior could not been identified in medium- and low-frequency 74 datasets, which remain essential tools with which to analyze and understand long-term hydrochemical 75 processes (e.g. Godsey et al., 2009; Moatar et al., 2017).





77 78

Figure 1: Concentration-discharge relationship observed at the Oracle-Orgeval observatory 79 (measurements from the River Lab) for chloride ions [Cl⁻]: (a) standard axes, (b) logarithmic axes. 80

Figure 1 illustrates the inadequateness of the power law for this dataset: The C-Q relationship evolves from a well-defined concave shape on the left to a slightly convex shape on the right in the log–log space. From the point of view of a modeler wishing to adjust a linear model, one has gone beyond the straight shape that was aimed at. Note that this is true for our dataset, and that it does not need to always be the case: The log–log space can be well adapted in some situations (see examples in the paper by Moatar et al., 2017).

87 88

3.3 A two-sided affine power scaling relationship as a progressive alternative to the power law

As a progressive alternative to the one-sided power scaling relationship (power law), we propose to use a two-sided affine power scaling (2S-APS) relationship as shown in Eq. (3) (Box and Cox, 1964;Howarth and Earle, 1979).

$$C^{\frac{1}{n}} = a + bQ^{\frac{1}{n}}$$
 Eq. (3)

From a numerical point of view, the relationship presented in Eq. (3) is equivalent to first transforming the dependent (*C*) and independent (*Q*) variables using a so-called Box–Cox transformation (Box and Cox, 1964), and then adjusting a linear model. In comparison with the logarithmic transformation, the additional degree of freedom offered by *n* allows for a range of transformations, from the untransformed variable (*n* = 1) to the logarithmic transformation ($n \rightarrow \infty$). This "progressive" property was underlined long ago by Box and Cox (1964): When *n* takes high values, Eq. (3) converges toward the one-sided power scaling relationship (power law) (Eq. (1)). The reason is simple:

$$C^{\frac{1}{n}} = e^{\frac{1}{n}lnC} \approx 1 + \frac{1}{n}lnC$$
 when *n* is large.

99 Thus, for large values of *n*, Eq. (3) can be written as:

$$1 + \frac{1}{n}\ln C \approx a + b + \frac{b}{n}\ln Q$$

100 That is equivalent to:

 $\ln C \approx A + b \cdot \ln Q$ (with A = n(a + b - 1))

101 The progressive behavior and the convergence toward the log–log space are clearly evident in Figure

102

2.

103



104



3.4 Choosing an appropriate transformation for different ion species
 (calibration mode)

Because the hydro-biogeochemical processes that control the transport and reaction of ions are different, different ionic species may have a C-Q relationship of distinct shape (Moatar et al., 2017). In Figure 3, we show the behavior of three ions and the EC from the same catchment and the same dataset (all four from the Oracle-Orgeval observatory) with different transformations (n = 1, 3, 5 and logarithmic transformation). The optimal shape was chosen numerically: We transformed our data series of *C* and *Q* using different values of *n* (i.e., $C^* = C^{1/n}$ and $Q^* = Q^{1/n}$) and logarithmic transformation (i.e., $C^{**} = \log(C)$ and $Q^{**} = \log(Q)$). With these transformed values, we performed

- a linear regression and computed parameter a and b and the coefficient of determination (R^2) (see Table 2). The n considered as optimal has the highest R^2 value (see Table 2). However, we could also have followed the advice of Box et al. (2016, p. 331) and done it visually (Figure 3).



121

Figure 3: C-Q behavior of three different chemical species and the electrical conductivity with different 2S-APS transformations (n =1, 3, 5, and log). The optimal power parameter (black dots) was chosen based on the R^2 criterion. Note that we have removed the scale on the axes to focus only on the change in shape in the C-Q relationship.

- 129 Table 2: Coefficient of determination (R^2) calculated for n = 1 (no transformation), n = optimal value
- for two-sided affine power scaling relationship (Figure 3) and $n \rightarrow \infty$ (log-log space) for each ion and

131	for electrical conductivit	v (EC). Note that the R ² is com	puted from transformed values
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Solute	n	R ²
	n = 1 (no transformation)	0.53
Sodium	<i>n</i> = 3 (optimal)	0.73
	$n \rightarrow \infty$ (log–log)	0.53
	<pre>n = 1 (no transformation)</pre>	0.32
Sulphate	<i>n</i> = 5 (optimal)	0.81
	$n \rightarrow \infty$ (log–log)	0.77
	n = 1 (no transformation)	0.52
Chloride	<i>n</i> = 3 (optimal)	0.88
	$n \rightarrow \infty$ (log–log)	0.69
	n = 1 (no transformation)	0.38
EC	<i>n</i> = 5 (optimal)	0.79
	$n \rightarrow \infty$ (log–log)	0.74

132

133 The results given in Table 2 show the better quality of the fit obtained with the optimal value of *n*.

4. Numerical identification of the parameters for the 2S-APS relationship

The extremely large number of values in this high-frequency dataset may cause problems for a robust identification over the full range of discharges using a simple linear regression. Indeed, the largest discharge values are in small numbers (in our dataset only 1% of discharges are in the range [2.6 m³s⁻¹] 139 ¹, 12.2 m³s⁻¹], and they correspond to the lowest concentrations (see Figure 1)).

140 To address this question, we successively tested a large number of (a,b) pairs from Eq. (3) (n remaining fixed at the optimal value given in Table 2). Each pair yields a series of simulated concentrations (C_{sim}) 141 142 that can be compared with the observed concentrations (C_{obs}). Among the many numerical criteria 143 that could be used, we chose the bounded version of the Nash and Sutcliffe (1970) efficiency criterion 144 NSEB (Mathevet et al., 2006), which is commonly used in hydrological modeling. NSEB can be computed on concentrations or on discharge-weighted concentrations (which corresponds to the 145 146 load). We chose the average of both, because we found that it allows more weight to be given to the 147 extremely low concentrations and thus to avoid the issue of under-representation of highdischarge/low-concentration measurement points. Table 3 presents the formula for these numerical 148 149 criteria.

We retained as optimal the pair of (a,b) that yielded the highest $NSEB_{comb}$ value (we explored in a systematic fashion the range [1–5] for a and [-1.2–1.2] for b). Table 3: Numerical criteria used for optimization (C_{obs} – observed concentration, C_{sim} – simulated concentration, Q – observed discharge). The Nash and Sutcliffe (1970) efficiency (NSE) criterion is well known and widely used in the field of hydrology. The rescaling proposed by Mathevet et al. (2006) transforms NSE into NSEB, which varies between -1 and 1 (its optimal value). The advantage of this rescaled version is to avoid the occurrence of large negative values (the original NSE criterion varies in the range [- ∞ , 1]).

$NSE_{conc} = 1 - \frac{\sum_{t} (C_{obs}^{t} - C_{sim}^{t})^{2}}{\sum_{t} (C_{obs}^{t} - \overline{C_{obs}})^{2}}$	Eq. (4)
$NSEB_{conc} = \frac{NSE_{conc}}{2 - NSE_{conc}}$	Eq. (5)
$NSE_{load} = 1 - \frac{\sum_{t} \left(Q^{t} C_{obs}^{t} - Q^{t} C_{sim}^{t}\right)^{2}}{\sum_{t} \left(Q^{t} C_{obs}^{t} - \overline{QC_{obs}}\right)^{2}}$	Eq. (6)
$NSEB_{load} = \frac{NSE_{load}}{2 - NSE_{load}}$	Eq. (7)
$NSEB_{comb} = \frac{1}{2}(NSEB_{conc} + NSEB_{load})$	Eq. (8)

158 In Appendix 2, we show that our proposed methodology for the identification of parameters a, b and 159 n, based on the $NSEB_{comb}$ criterion, is effective also from the point of view of the predictive

160 confidence interval.

161 **5. Results**

162 **5.1 Results in calibration mode**

163 The optimal values of *a* and *b* corresponding to the simulation of each ion and EC with the highest

164 *NSEB_{comb}* criterion and the *n* value identified in Figure 3 and Table 2 are presented in Table 4.

165 **Table 4: Summary of values** *a*, *b*, and *n* used to obtain the optimal *NSEB*_{comb} criterion.

lon	n	а	b	NSEB _{comb}
Sodium	3	2.70	-0.60	0.68
Sulphate	5	2.20	-0.55	0.69
Chloride	3	3.70	-1.00	0.83
EC	5	4.20	-0.70	0.77

166 The five NSE criteria (defined in Table 3) used to identify the parameters of the 2S-APS relationship

167 have also been computed for the power-law relationship. The results are given in Table 5: the values

168 obtained for the 2S-APS relationship are always higher than those calculated for the power-law

169 relationship.

Caluta			<mark>2S-APS</mark>					Power-la	<mark>w</mark>	
Solute -	<mark>NSE_{conc}</mark>	<mark>NSEB_{conc}</mark>	<mark>NSE_{load}</mark>	NSEB _{load}	NSEB _{comb}	<mark>NSE_{conc}</mark>	<mark>NSEB_{conc}</mark>	<mark>NSE_{load}</mark>	NSEB _{load}	NSEB _{comb}
<mark>Sodium</mark>	<mark>0.58</mark>	<mark>0.41</mark>	<mark>0.97</mark>	<mark>0.95</mark>	<mark>0.68</mark>	<mark>0.27</mark>	<mark>0.16</mark>	<mark>0.67</mark>	<mark>0.51</mark>	<mark>0.33</mark>
<mark>Sulfate</mark>	<mark>0.61</mark>	<mark>0.44</mark>	<mark>0.97</mark>	<mark>0.94</mark>	<mark>0.69</mark>	<mark>0.58</mark>	<mark>0.41</mark>	<mark>0.87</mark>	<mark>0.77</mark>	<mark>0.59</mark>
<mark>Chloride</mark>	0.83	<mark>0.71</mark>	<mark>0.97</mark>	<mark>0.95</mark>	<mark>0.83</mark>	<mark>0.68</mark>	<mark>0.52</mark>	<mark>0.60</mark>	<mark>0.43</mark>	<mark>0.47</mark>
<mark>EC</mark>	<mark>0.73</mark>	<mark>0.57</mark>	<mark>0.99</mark>	<mark>0.98</mark>	<mark>0.77</mark>	<mark>0.68</mark>	<mark>0.51</mark>	<mark>0.96</mark>	<mark>0.91</mark>	<mark>0.71</mark>

170 **Table 5: NSE criteria computed for the three ions and EC.**

171

Also for comparing the two relationships, we used the *RMSE* criterion. The results are shown in Table
6; they illustrate (for our catchment) the better performance (i.e., lower *RMSE* value) of the proposed
2S-APS relationship for the three ions (sodium, sulphate, and chloride) over the power law relationship.
For EC, there is a slight advantage over the power law. A test of the equality of variance (*F-test*) was
performed between the *RMSE* obtained for the two relationships: Because of the very large number

177 of points in our dataset, all differences were highly significant (*p*-value <0.001)

Table 6: Summary of values of RMSE criterion calculated for the three ions and EC.

Coluto	Mogn	<mark>2S-APS</mark>	Power law	
Solute	weun	RMSE	<mark>RMSE</mark>	
<mark>Sodium</mark>	<mark>13 mgL⁻¹</mark>	<mark>1.10 mgL⁻¹</mark>	<mark>1.22 mgL⁻¹</mark>	
Sulphate	<mark>19 mgL⁻¹</mark>	<mark>2.17 mgL⁻¹</mark>	<mark>2.22 mgL⁻¹</mark>	
Chloride	<mark>30 mgL⁻¹</mark>	<mark>2.00 mgL⁻¹</mark>	<mark>2.91 mgL⁻¹</mark>	
EC	<mark>704 µS.cm⁻¹</mark>	<mark>41.9 μS.cm⁻¹</mark>	<mark>41.3 μS.cm⁻¹</mark>	

179

Figure 4 illustrates the comparison of the quality of simulation over the entire calibration dataset between the power law and 2S-APS relationships. In general, the two-sided affine power scaling relationship yields better simulated concentrations than the classic power law relationship for the two ions (according to the results of Table 6). This is particularly evident over the low concentrations (see Figure 4). This better performance is more apparent in the case of sodium and chloride ions.





Figure 4: Comparison of simulated concentrations with observed concentrations for: (a) two-sided
 affine power scaling (2S-APS) relationship, (b) power law (calibration mode).

189 **5.2 Results in validation mode**

190 For the validation mode, we applied the above-calibrated relationships to a different time period

191 (August 2017 to March 2018). We used as in Table 5 the five NSE criteria (see Table 3) to compare the

192 performance between the two relationships studied. The results are given in Table 7. As in the

- 193 calibration period, the values obtained for the 2S-APS relationship are higher than those calculated for
- 194 the power law.

Table 7: NSE criteria computed for the three ions and EC.

C 1 1 1			<mark>2S-APS</mark>					Power-la	<mark>w</mark>	
Solute	<mark>NSE_{conc}</mark>	NSEB _{conc}	<mark>NSE_{load}</mark>	NSEB _{load}	NSEB _{comb}	<mark>NSE_{conc}</mark>	NSEB _{conc}	NSE _{load}	NSEB _{load}	NSEB _{comb}
<mark>Sodium</mark>	<mark>0.81</mark>	<mark>0.69</mark>	<mark>0.95</mark>	<mark>0.91</mark>	<mark>0.80</mark>	<mark>0.35</mark>	<mark>0.21</mark>	<mark>0.87</mark>	<mark>0.77</mark>	<mark>0.49</mark>
<mark>Sulfate</mark>	<mark>0.92</mark>	<mark>0.85</mark>	<mark>0.94</mark>	<mark>0.88</mark>	<mark>0.86</mark>	<mark>0.80</mark>	<mark>0.67</mark>	<mark>0.90</mark>	<mark>0.83</mark>	<mark>0.75</mark>
<mark>Chloride</mark>	<mark>. 0.84</mark>	<mark>0.73</mark>	<mark>0.90</mark>	<mark>0.83</mark>	<mark>0.79</mark>	<mark>0.66</mark>	<mark>0.50</mark>	<mark>0.85</mark>	<mark>0.73</mark>	<mark>0.62</mark>
<mark>EC</mark>	<mark>0.68</mark>	<mark>0.52</mark>	<mark>0.91</mark>	<mark>0.84</mark>	<mark>0.68</mark>	<mark>0.12</mark>	<mark>0.06</mark>	<mark>0.81</mark>	<mark>0.67</mark>	<mark>0.37</mark>

196

Also, as in the calibration mode, we computed the RMSE criterion. The results are shown in Table 8. The RMSE criterion illustrates (for our catchment) the better performance of the proposed 2S-APS relationship over the power law relationship for all the solutes. Unlike the calibration case, the quality of the simulation of EC using the 2S-APS relationship has a much better performance than the one simulated by the power law relationship.

Table 8: Summary of values of RMSE criterion calculated for the three ions and EC with the validation dataset.

Coluto	Mean	<mark>2S-APS</mark>	<mark>Power law</mark>
Solute		<mark>RMSE</mark>	<mark>RMSE</mark>
<mark>Sodium</mark>	<mark>13 mgL⁻¹</mark>	<mark>1.48 mgL⁻¹</mark>	<mark>1.90 mgL⁻¹</mark>
<mark>Sulphate</mark>	<mark>18 mgL⁻¹</mark>	<mark>1.65 mgL⁻¹</mark>	<mark>2.33 mgL⁻¹</mark>
Chloride	<mark>29 mgL⁻¹</mark>	<mark>3.69 mgL⁻¹</mark>	<mark>4.34 mgL⁻¹</mark>
<mark>EC</mark>	<mark>576 μS.cm⁻¹</mark>	<mark>62.3 μS.cm⁻¹</mark>	<mark>78.8 µS.cm⁻¹</mark>

204

205 **6. Conclusion**

206 In this technical note, we tested and validated a three-parameter relationship (2S-APS) as an 207 alternative to the classic two-parameter one-sided power scaling relationship (commonly known as 208 "power law"), to represent the concentration–discharge relationship. We also proposed a way to 209 calibrate the 2S-APS relationship.

- 210 Our results (in calibration and validation mode) show that the 2S-APS relationship can be a valid
- alternative to the power law: In our dataset, the concentrations simulated for sodium, sulphate, and
- chloride as well as the EC are significantly better in validation mode, with a reduction in RMSE ranging
- 213 between 15 and 26%.
- 214 Naturally, because the data used for this study come from a single catchment, wider tests will be
- 215 necessary to judge of the generality of our results.
- 216 *Data availability*. Data will be available in a dedicated database website after a contract accepted on
- 217 behalf of all institutes.
- 218 *Competing interests*. The authors declare that they have no conflict of interest.
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280 8. Appendix 1 – Description of the River Lab

281 In June 2015, the "River Lab" was deployed on the bank of the Avenelles River (within the limits of the 282 Oracle-Orgeval observatory, see Figure 5) to measure the concentration of all major dissolved species at high frequency (Floury et al., 2017). The River Lab's concept is to "permanently" install a series of 283 laboratory instruments in the field in a confined bungalow next to the river. River Lab performs a 284 285 complete analysis every 30 min using two Dionex® ICS-2100 ionic chromatography (IC) systems by 286 continuous sampling and filtration of stream water. River Lab measures the concentration of all major dissolved species ([Mg²⁺], [K⁺], [Ca²⁺], [Na⁺], [Sr²⁺], [F⁻], [SO₄²⁻] [NO₃⁻], [Cl⁻], [PO₄³⁻]). In addition, a set of 287 288 physico-chemical probes is deployed to measure pH, conductivity, dissolved O₂, dissolved organic 289 carbon (DOC), turbidity, and temperature. The discharge is measured continuously via a gauging 290 station located at the River Lab site.

All the technical qualities, calibration of the equipment, comparison with laboratory measurements,

degree of accuracy, etc. have been well described in a publication by Floury et al. (2017).



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Figure 5: Location of the River Lab (red dot) on the Avenelles River, Oracle-Orgeval observatory.

9. Appendix 2 – Predictive confidence interval (PI)

We have computed the predictive confidence interval, a well-known methodology used in linear 296 297 regression (Jonnston, 1972 pp. 154-155 ; see also the discussion in Andréassian et al., 2007) to verify 298 whether the 2S-APS relationship and the associated parameter identification methodology increase or 299 decrease the uncertainty with respect to the power-law relationship (linear regression with log <mark>transformation). We show two intervals: 50% and 95%. The results are given in Figure 6</mark>: clearly, <mark>the</mark> 300 predictive interval (blue surface for a 50 % predictive confidence interval, red for 95%) is much 301 302 narrower for the 2S-APS relationship than for the power-law relationship. This can only reinforce our 303 preference for the 2S-APS relationship.

304





Figure 6: Predictive confidence interval computed for the 2S-APS relationship and the power-law for
 the 3 ions and the EC relationship. In blue the 50 % and in red the 95 % predictive confidence
 intervals.