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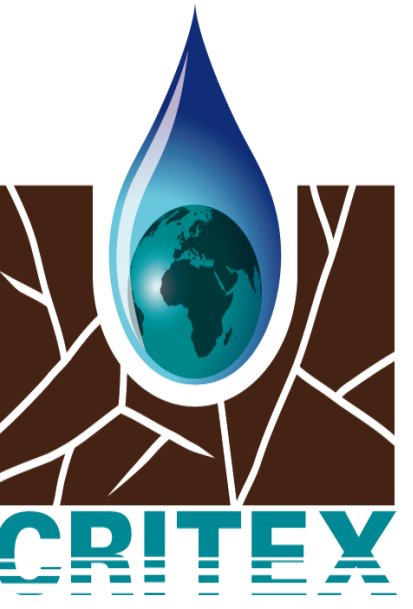
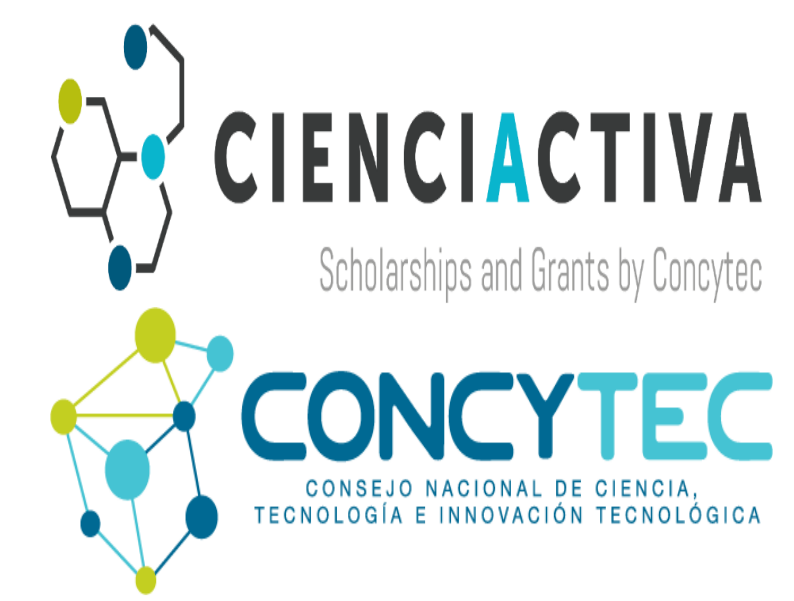
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Quantification the mixing chemical of sources in a stream from downstream chemical data

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1. Objective and Context

- ✓ Determining the various sources that mix to produce the composition of a stream from a chemical data set is not an easy task
- ✓ To answer this question and compute the parameters of the mixing model, namely the composition of the sources, our initial hypotheses are:

- H1 : the observed concentrations in the stream come from a mixture of n sources. In our study we consider $n = 3$, with 2 components used as tracers that we assume conservative in the stream
- H2 : the n sources are characterized by a stable concentration of each tracer

- ✓ But these hypotheses are not enough to provide an unique solution defining the composition of the sources and a complementary criteria must be added. Any set of sufficiently distant sources, in terms of concentrations, would always produce a perfect decomposition of all data. An additional criteria must force the sources to be not too much distant from each other

- ✓ We have therefore set the following objective function for optimization :

$$F = A * \sum_{i,j} \left(C_{ij} - \sum_k \alpha_{ik} S_{kj} \right)^2 + B * \sum_{k,j} \left(S_{kj} - G_j \right)^2 \quad (1)$$

Where the first term : $\sum_{i,j} (C_{ij} - \sum_k \alpha_{ik} S_{kj})^2$ is the residual inertia of the concentrations, C_{ij} (the observed concentration) are a partition of the n sources $\alpha_{ik} S_{kj}$ (α_{ik} the partition et S_{kj} is the concentration of the source) Additional constraints are: $\sum_k \alpha_{ik} = 1$; $0 \leq \alpha_{ik} \leq 1$; $S_{kj} > 0$ (2)

Where the second term $\sum_{k,j} (S_{kj} - G_j)^2$ represents the inertia of the n sources

- ✓ Since we do not *a priori* information on the best weights (A and B) for the two terms in F, we shall study their effect

- This study aims at defining the right A/B ratio to "best" quantify the sources $\alpha_{ik} S_{kj}$

3. Results

3.1 Selection of an « optimal » (A/B) ratio

- Very clear relation between VR and the A/B ratio is observed .The fit curve obtained is a exponential curve
- As an example, we chose an acceptable VR ratio of 0.05 as roughly estimated of the chemical measures errors, which corresponds to a (A/B): **1.23**

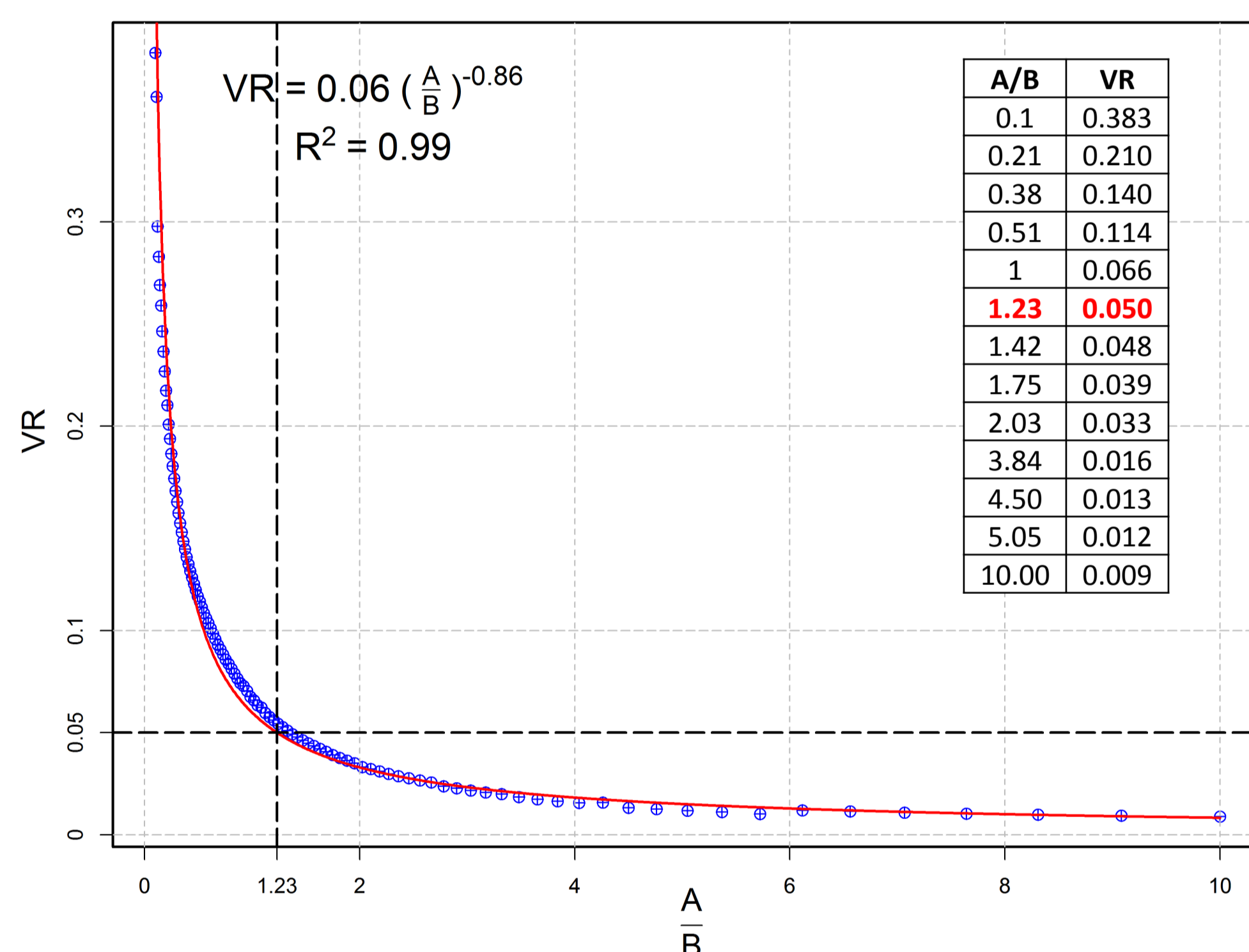


Figure 3 : Fit curve from the scatterplot between (A/B) and VR

3.2 Quantification of mixing sources S_{kj}

- Our analysis makes it possible to define the sources with respect to the expected VR

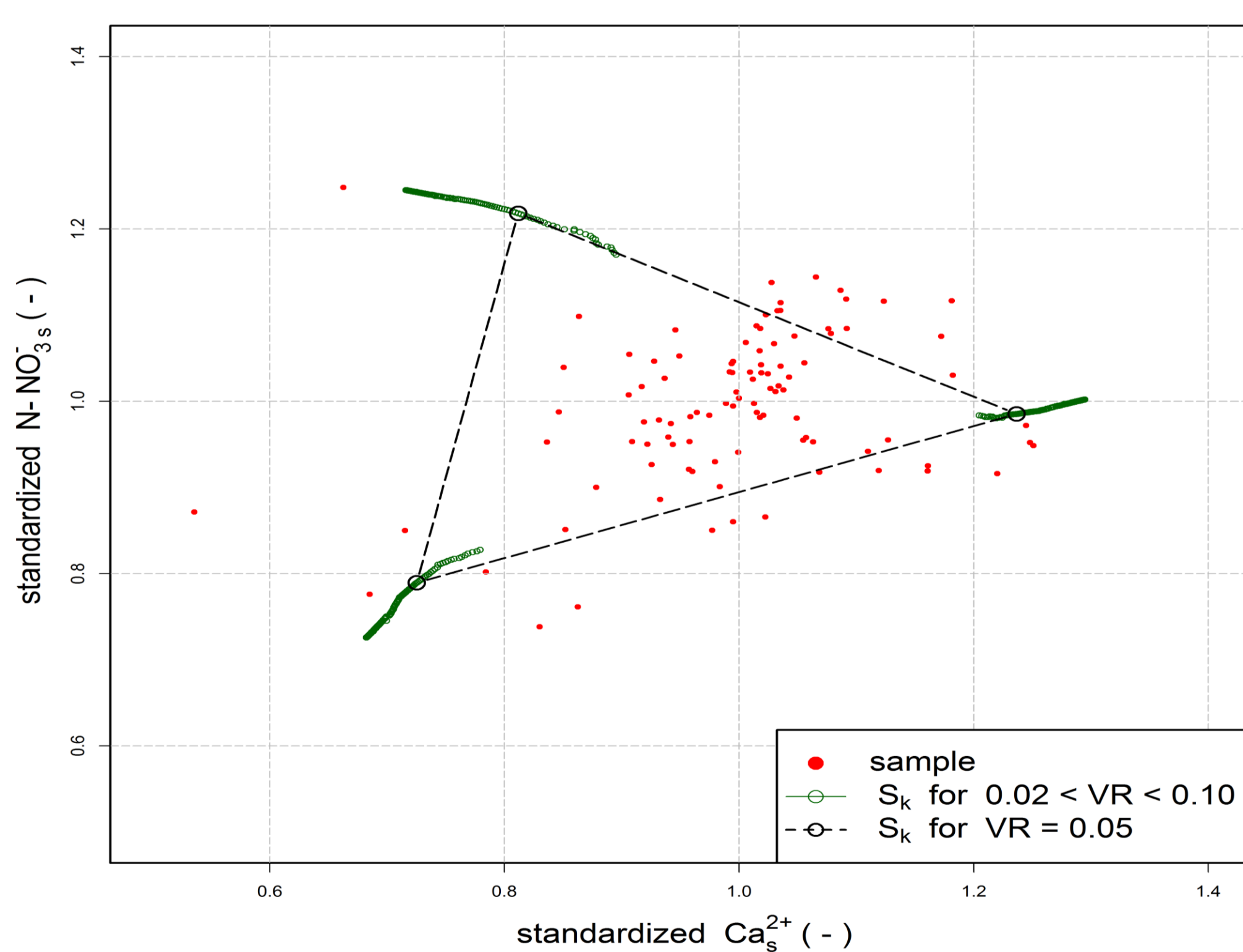


Figure 4 : tracing of the different source compositions S_{kj} (green lines) calculated for $0.02 < VR < 0.10$. The black line represents the source composition for $VR = 0.05$ and $(A/B) = 1.23$

- ✓ The 3 different green lines show the evolution of the composition of sources for VR varying between $0.02 < VR < 0.10$
- ✓ The black triangle show the concentration of the sources obtained for $VR = 0.05$

Table 2: Source composition obtained for $(A/B = 1.23$ and $VR = 0.05$)

Source Composition for $(A/B = 1.23$ and $VR = 0.05)$		
S_{kj}	Ca^{2+} (mgL ⁻¹)	$N-NO_3^-$ (mgL ⁻¹)
S_1	89.18	9.55
S_2	99.89	14.74
S_3	152.03	11.92

4. Conclusions

- Our model allows to quantify mixing chemical sources in a stream at the cost of an additional constraint regarding the non-explained variance of the concentrations in the stream

5. Perspectives

- For the moment, the physical origin of these sources (rain, aquifer, soil, etc.) has not been determined, but the obtained composition of the sources will be compared to what is known about the composition of various potential sources in the catchment.
- Several random extraction in the data set will make it possible to observe the variability of the obtained composition of sources.
- Interesting information on the hydrological behavior of the catchment can be obtained by apply the methodology to the entire record through a sliding window.

2. Material & Methods

2.1 Material

- We use high frequency data from Avenelles catchment (ORACLE/Orgeval Observatory) and especially the calcium and nitrate concentrations

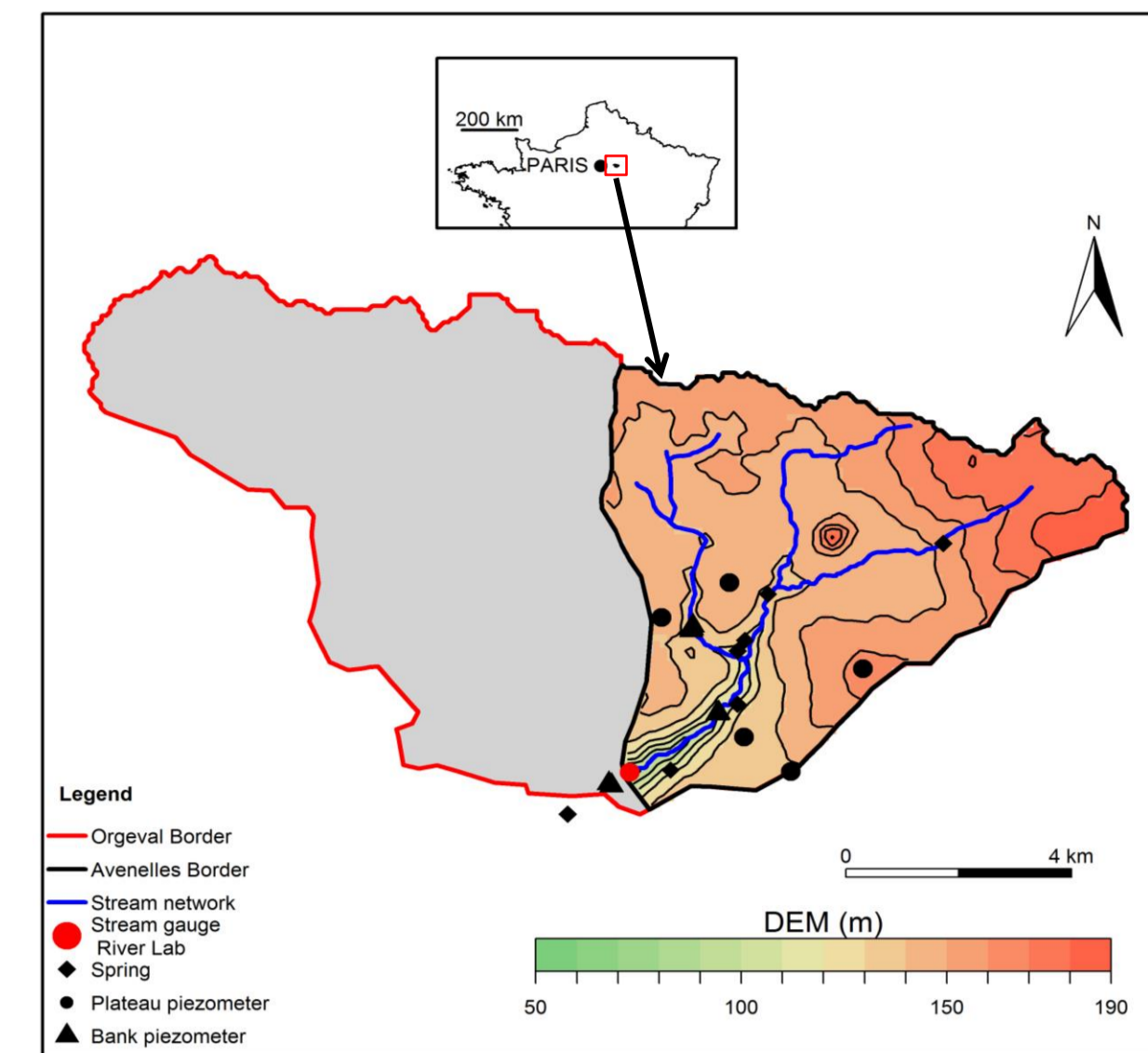


Figure 1 : ORACLE observatory

- ✓ Avenelles catchment (46 km²)
- ✓ High-frequency measurements from River Lab [2] (approximately every 30 minutes) from June 2015 to July 2017
- ✓ Seven chemical elements measured (Table 1)

Table 1: Summary of the mean values, min and max of the chemical elements studied from the high frequency measurements

item	Unit	Avenelles Catchment		
		Mean	Min	Max
chloride	mgL ⁻¹	30	4	40
sulfate	SmgL ⁻¹	19	2	32
magnesium	mgL ⁻¹	9	3	15
sodium	mgL ⁻¹	13	2	17
nitrate	NmgL ⁻¹	12	3	18
calcium	mgL ⁻¹	124	37	202
EC	μSm ⁻¹	704	267	1015

- For computational reasons, we only use a sample of 100 random points from the data series (over 16000 points) (Figure 2, red dots)

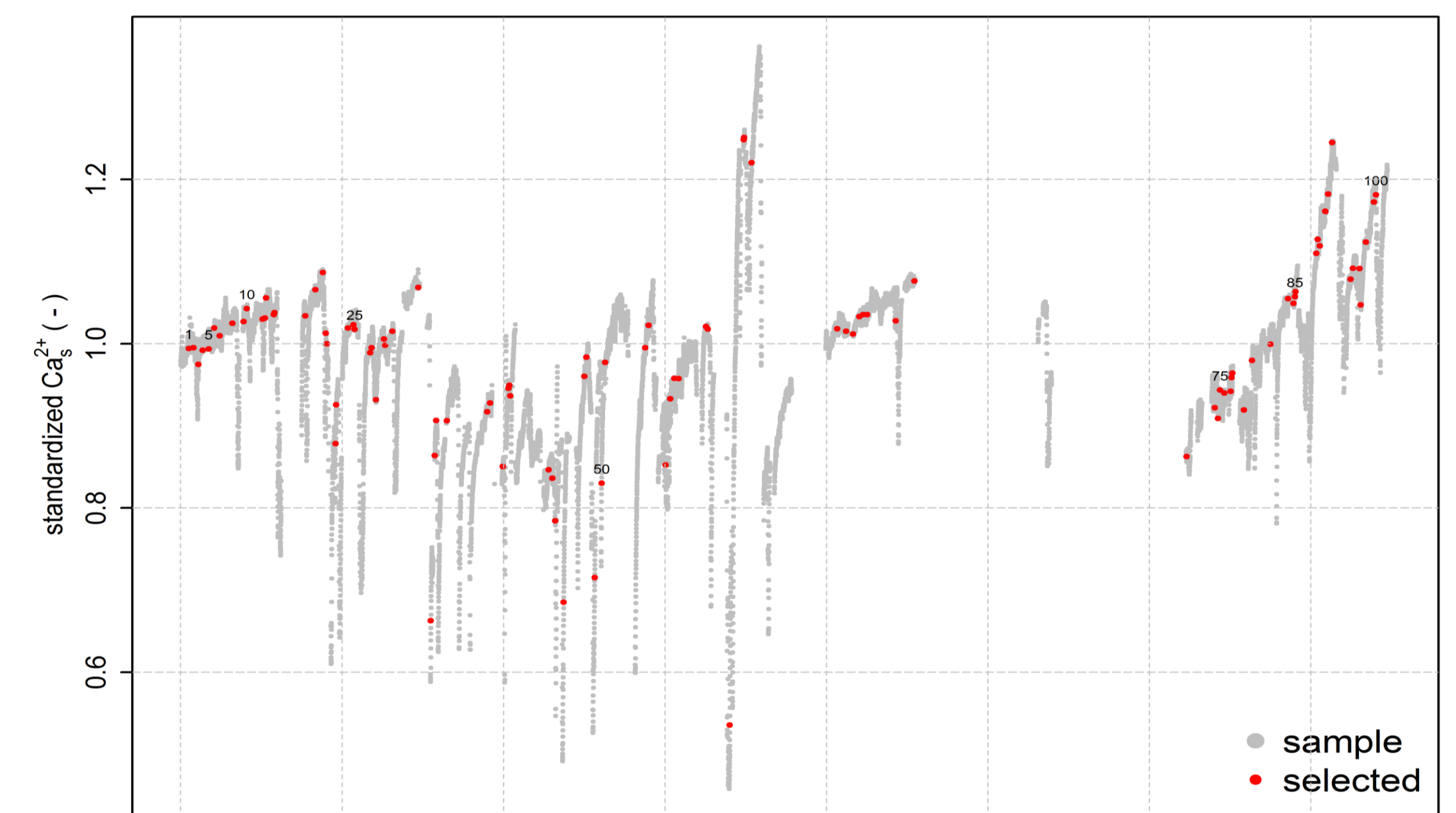


Figure 2 : Points selected (in red) for our sample, taken from our HF data set (gray dots)

- ✓ These 100 points contain most of the different phenomena captured in the high frequency data set
- ✓ Calcium and nitrate concentrations were standardized. i.e. the measured concentrations were divided by their median:

$$c_s = \frac{C_j}{\hat{C}_j}$$

c_s : standardized concentration(-)

C_j : streamflow concentration (mg.L⁻¹)

\hat{C}_j : Median of the stream concentration(mg.L⁻¹)

2.2 Methods

- We applied 100 different A/B ratio ranging from 0 to 10.
- We evaluate the quality of the estimation by the ratio of the residual variances to initial variance of the data set:

$$VR = \frac{\sum_{i,j} (C_{ij} - \sum_k \alpha_{ik} S_{kj})^2}{\sum_{i,j} (C_{ij} - G'_j)^2} \quad (3)$$

Where G'_j is the center of gravity of the scatterplot of points C_{ij}

- To solve α_{ik} and S_{kj} : we used the "solnp" function of the RSOLNP package on R (<https://cran.r-project.org/web/packages/Rsolnp/Rsolnp.pdf>). The "solnp" algorithm is based on the non-linear optimization of the parameters using the augmented Lagrangian method [2]. It makes it relatively easy to deal with both inequality and equality constraints simultaneously (Eq.2).

6. References

- [1] Floury et al. (2017) The potamochemical symphony: new progress in the high-frequency acquisition of stream chemical data. Hydrol. Earth Syst. Sci. 21 (2017) 6153-6165.
- [2] Ye, Y., 1988. Interior algorithms for linear, quadratic, and linearly constrained convex programming, Stanford University, 120 pp.

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