



A combining mixing model for high-frequency concentration-discharge relationships

TUNQUI NEIRA J.M^{1,2}, Tallec G.¹, Andréassian V.¹, Mouchel JM.²

(1) UP Saclay, INRAE, HYCAR Research Unit, Antony, France

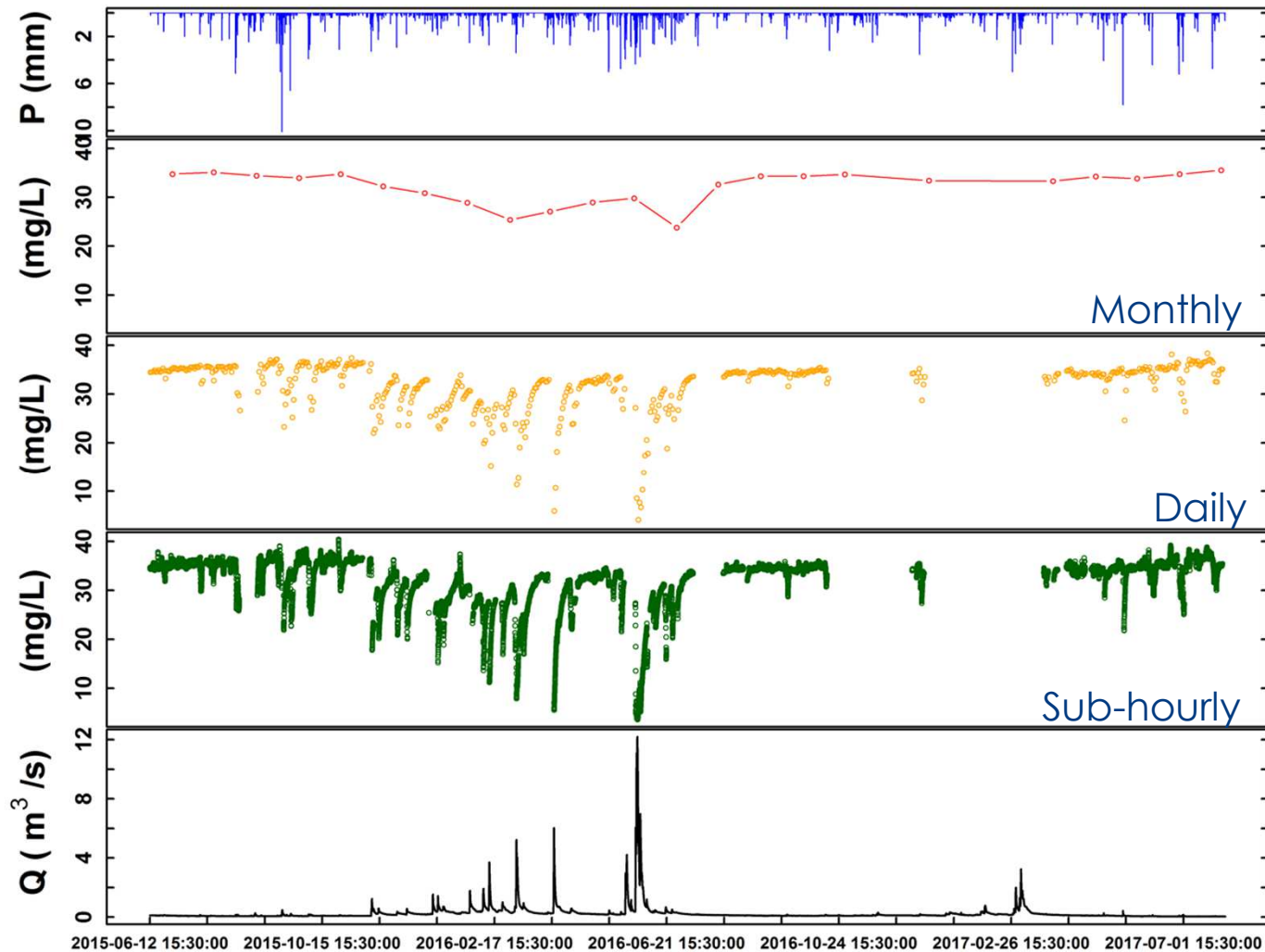
(2) Sorbonne Université, CNRS, EPHE, UMR METIS 7619, Paris, France

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High-frequency measurement

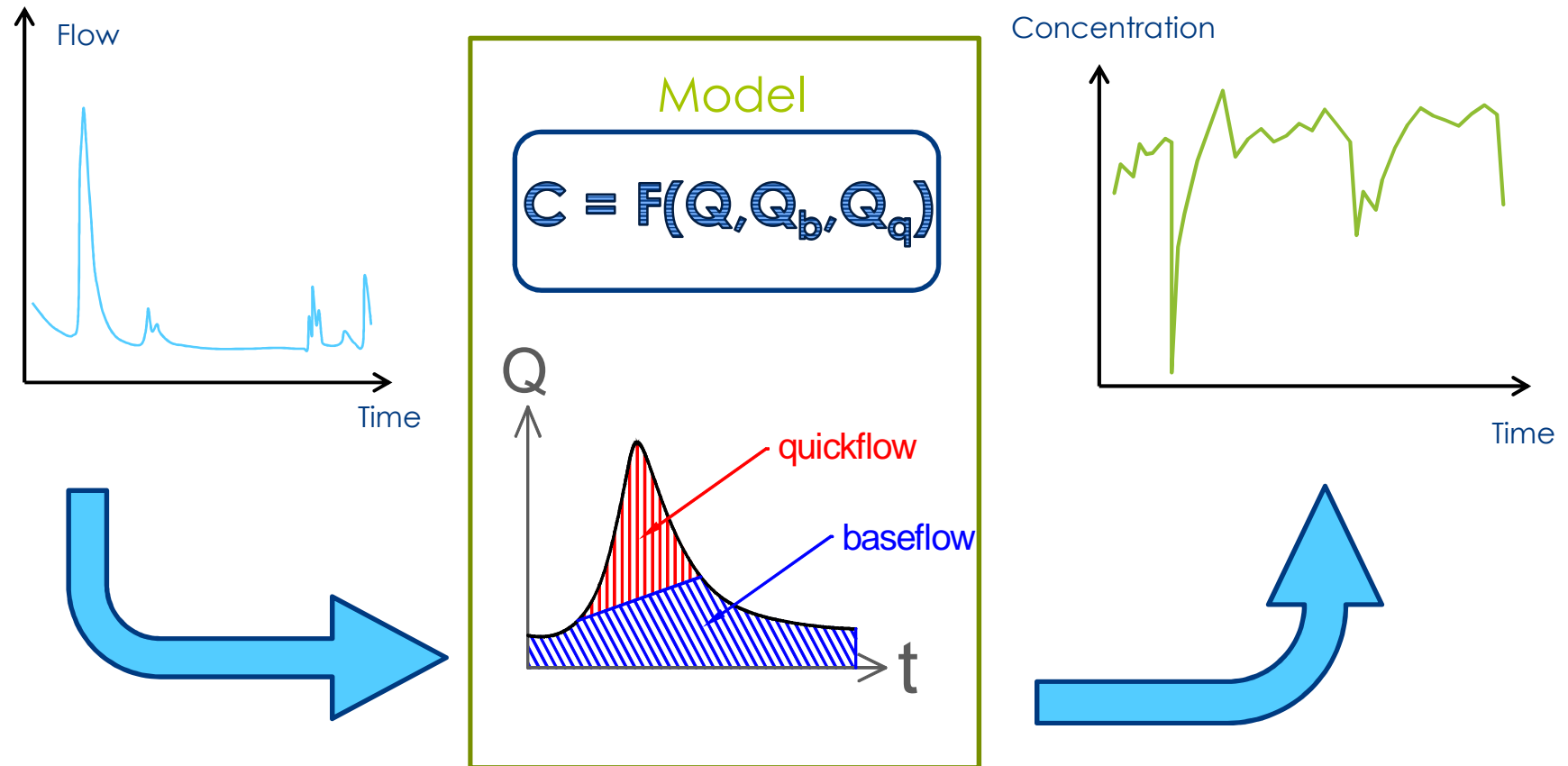
Avenelles Catchment - Chloride



➤ How to use this valuable information?

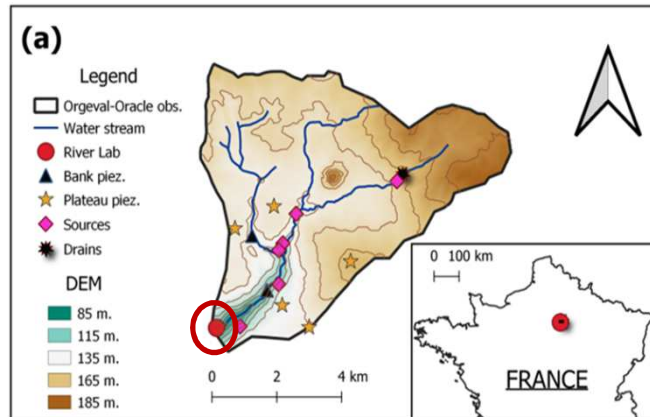
Aims of this study

Can the observed stream HF chemical concentrations be described by the dynamics of several sources related to flow?

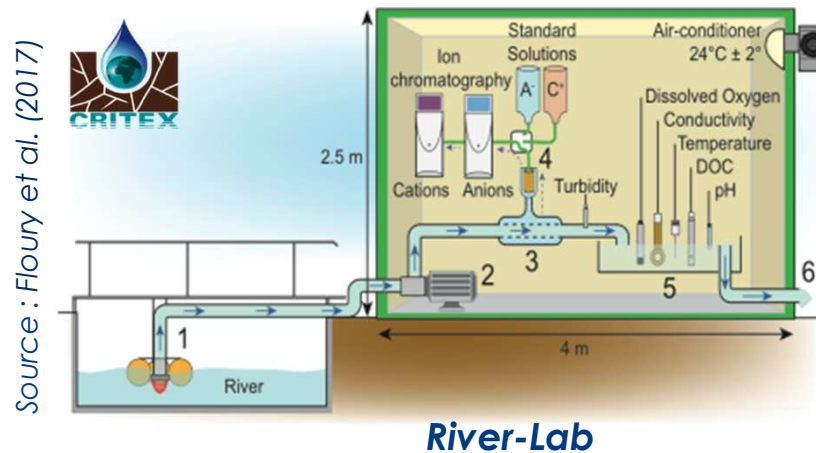


Study site

ORACLE – Orgeval Obs. (1962 -) : Avenelles Sub-catchment



- High-frequency measurements (approx. 30 min.)
- June 2015 - August 2017 (17000 measurements/parameter)
- More than thirty hydrological events



item	Unit	River-Lab station (Avenelles outlet)			Rainfall
		Mean	Min	Max	
sulfate	S-mg.L ⁻¹	19	2	32	0.38
nitrate	N-mg.L ⁻¹	12	3	18	0.75
chloride	Mg.L ⁻¹	30	4	40	1.6
EC	μS.cm ⁻¹	704	267	1015	NA

A combination of methods

$$Q_b = Q - Q_q$$

Hydrograph Separation(RDF
Lyne and Hollick, 1979)

$$C = F(Q)$$

$$C^{1/n} = a + bQ^{1/n}$$

Box-Cox Transformation
(Tunqui Neira et al., 2020)

$$C = F(Q_b, Q_q)$$

$$C = C_b \frac{Q_b}{Q} + C_q \frac{Q_q}{Q}$$

Mixing equation
(Pinder & Jones, 1969)

$$C = F(Q, Q_b, Q_q)$$

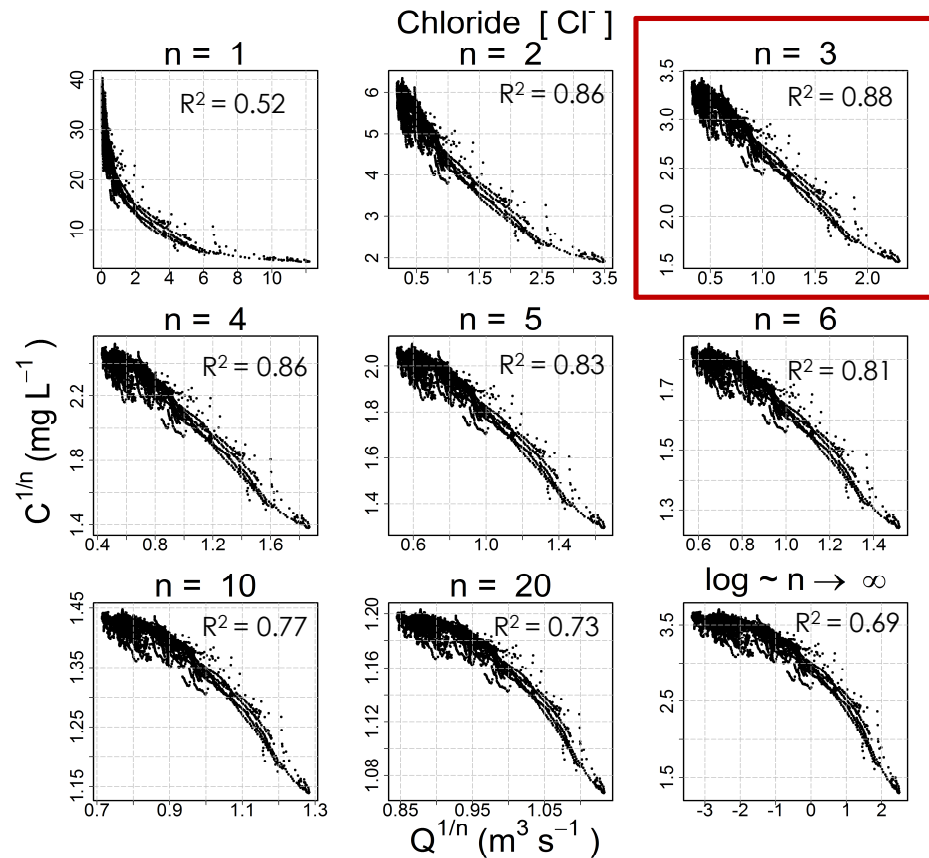
$$C = \underbrace{\left(a_b + b_b Q^{\frac{1}{n}}\right)^n}_{C_b} \frac{Q_b}{Q} + \underbrace{\left(a_q + b_q Q^{\frac{1}{n}}\right)^n}_{C_q} \frac{Q_q}{Q}$$

Combined model

A new HF methodology

- Logarithmic transformation : $\ln(C) = \ln(a) + b \ln(Q)$
- Box – Cox transformation : $C^{1/n} = a + bQ^{1/n}$

Source: Tunqui Neira et al. (2020)



Ion	n
Sulfate	5
Nitrates	5
Chloride	3
EC	5

➤ New transformation, with only 1 additional parameter improves fit

Combined model

$$C = \underbrace{\left(a_b + b_b Q^{\frac{1}{n}}\right)}_{C_b} \frac{Q_b}{Q} + \underbrace{\left(a_q + b_q Q^{\frac{1}{n}}\right)}_{C_q} \frac{Q_q}{Q}$$

→ **Cas 1:** $a_b = a_q = 0$; C_b et C_q constants

$$C = F(Q_b, Q_q)$$

→ **Cas 2:** $a_b = a_q$ et $b_b = b_q$; $C_b = C_q = (a_b + b_b Q^{1/n})^n$

$$C = F(Q)$$

→ **Cas 3:** a et b variable ; C_b et C_q variables

$$C = F(Q, Q_b, Q_q)$$

➤ To compare the performances of the 3 models we use the sRMSE and the Bias

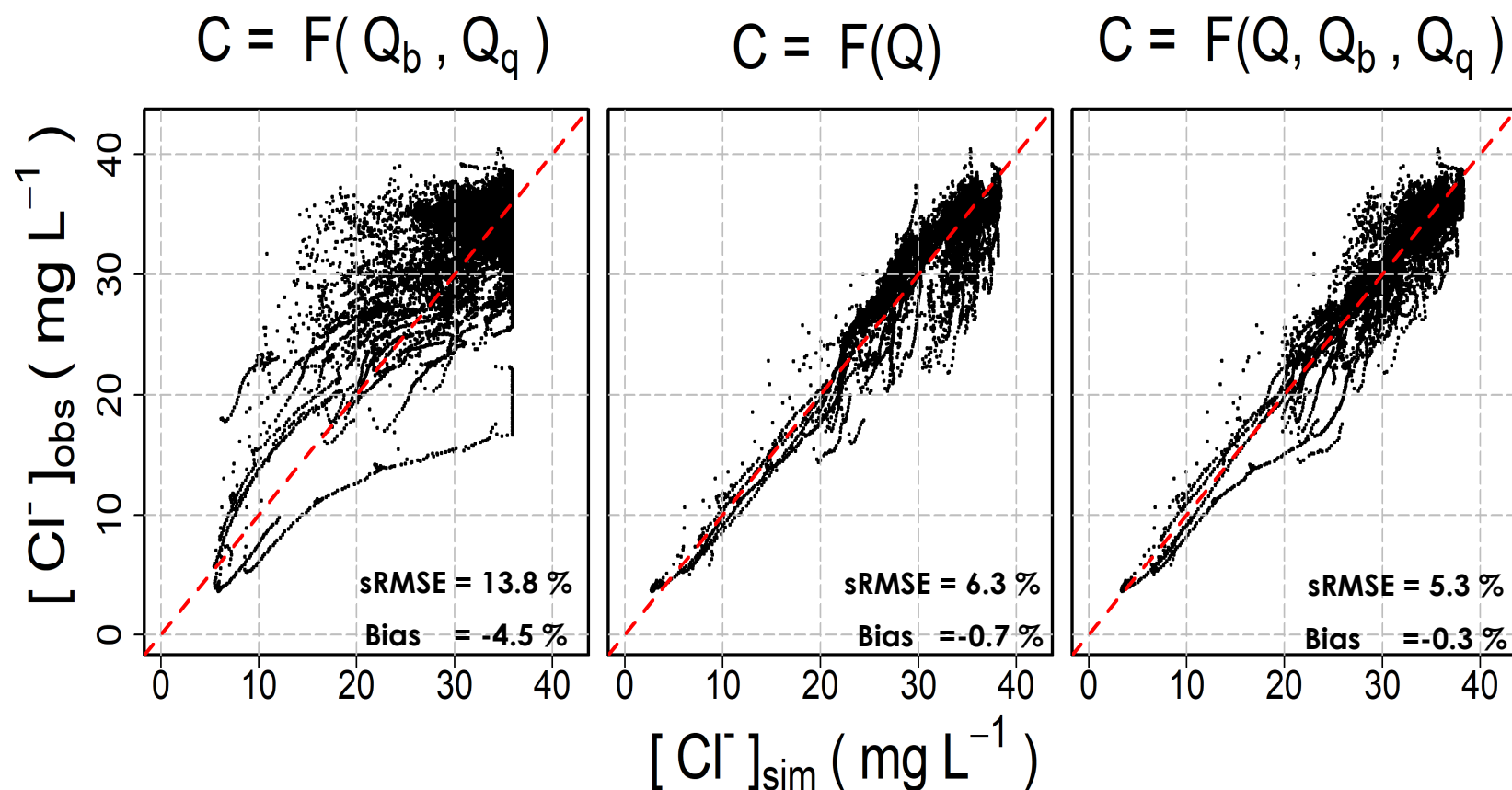
Combining HF methods

Solute	Case	<i>sRMSE</i> %	Bias %
Sulfate	1	18.3	7.3
	2	11.5	3.8
	3	11.3	0.4
Nitrate	1	48.9	46.7
	2	31.8	30.4
	3	27.6	-11.2
Chloride	1	13.8	-4.5
	2	6.3	-0.7
	3	5.3	-0.3
EC	1	10.3	1.5
	2	6.0	2.4
	3	5.2	-0.5

➤ Case 3 better than cases 1 and 2

Combining HF methods

□ Case of Chlorure



➤ Case 3 better than cases 1 and 2

Outcomes and Perspectives

Can hydrograph separation help describe concentration-discharge relationships ?

Yes, a hydrograph separation $C = F(Q, Q_b, Q_q)$ can be used, but only if source variability is introduced as a function of flow.

$$C = \underbrace{\left(a_b + b_b Q^{\frac{1}{n}}\right)}_{C_b} \frac{Q_b}{Q} + \underbrace{\left(a_q + b_q Q^{\frac{1}{n}}\right)}_{C_q} \frac{Q_q}{Q}$$

Should be applied :

- at other catchments and at different time scales
- with hydrograph separation calibration (Q_b, Q_q)

Analyzing model parameters with catchment functioning

Further readings

- Flourey, P., Gaillardet, J., Gayer, E., Bouchez, J., Tallec, G., Ansart, P., Koch, F., Gorge, C., Blanchouin, A., and Roubaty, J. L.: The potamochemical symphony: new progress in the high-frequency acquisition of stream chemical data, *Hydrol. Earth Syst. Sci.*, 21, 6153-6165, 2017.
- Tunqui Neira, J. M., Andréassian, V., Tallec, G., and Mouchel, J. M.: Technical note: A two-sided affine power scaling relationship to represent the concentration–discharge relationship, *Hydrol. Earth Syst. Sci.*, 24, 1823-1830, 10.5194/hess-24-1823-2020, 2020.
- Lyne, V., and Hollick, M.: Stochastic time-variable rainfall-runoff modelling, Institute of Engineers Australia National Conference, 1979, 89-93,
- Pinder, G. F., and Jones, J. F.: Determination of the ground-water component of peak discharge from the chemistry of total runoff, *Water Resources Research*, 5, 438-445, 1969.



What do you think?

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