


Estimation of the measurement uncertainty, including the contribution arising from sampling, of water quality parameters in surface water of the Loire River Basin, France

Nathalie Guigues & Bénédicte Lepot

AQUAREF - French National Reference Laboratory in support of aquatic monitoring

- Created in 2007
- Consortium of 5 Institutes : BRGM, IFREMER, INERIS, IRSTEa and LNE
- Objectives are to:
 - | Optimise and transfer methodologies to improve water quality monitoring
 - **Sampling**  Aquaref conducts studies on contamination during sampling, **uncertainty estimation including sampling**, technical support for PT on sampling etc.
 - Analysis
 - QA/QC
 - | Propose and validate new approaches/ tools for water quality monitoring

Loire River Basin study:

Design a validation study in order to :

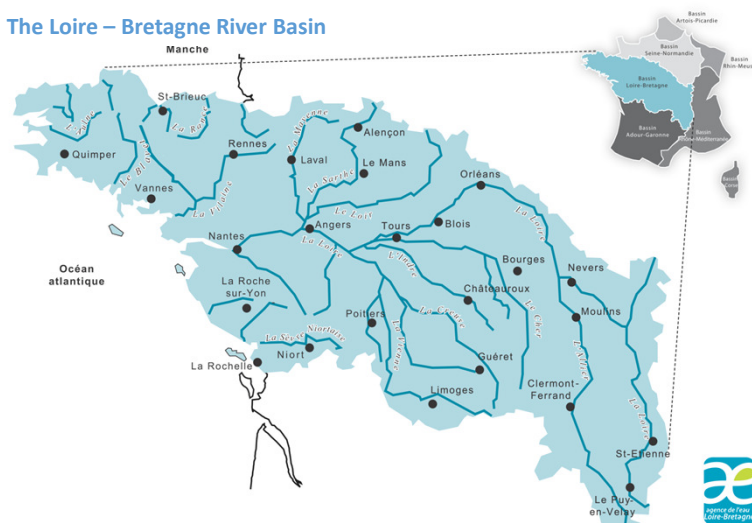
- Estimate the measurement uncertainty of water quality parameters including sampling, preservation, transport and analysis
- Check that the measurement variance does not impair the monitoring of the environmental variability

Loire River :

- 1010 km
- From the Massif Central to Nantes
- Geological diversity (basalt and granitic rocks with carbonated sedimentary areas)
- Anthropogenic inputs : mainly agricultural

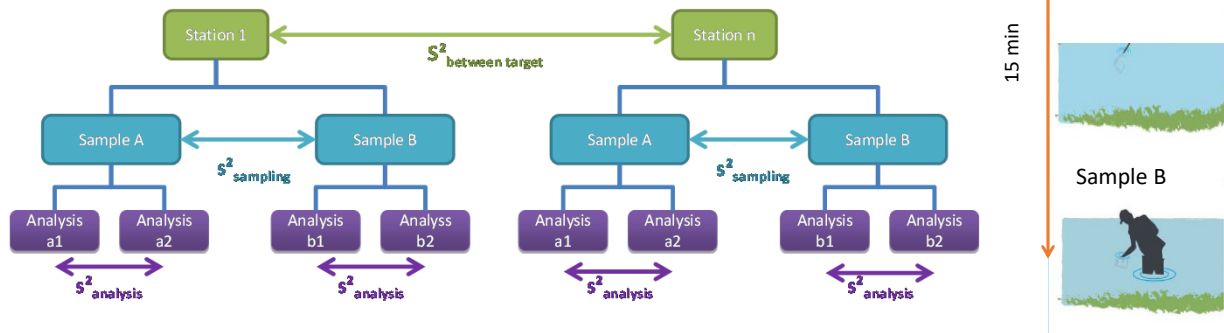
Loire Bretagne River Basin : 1/5th of France

The Loire – Bretagne River Basin



Methodology

Duplicate method



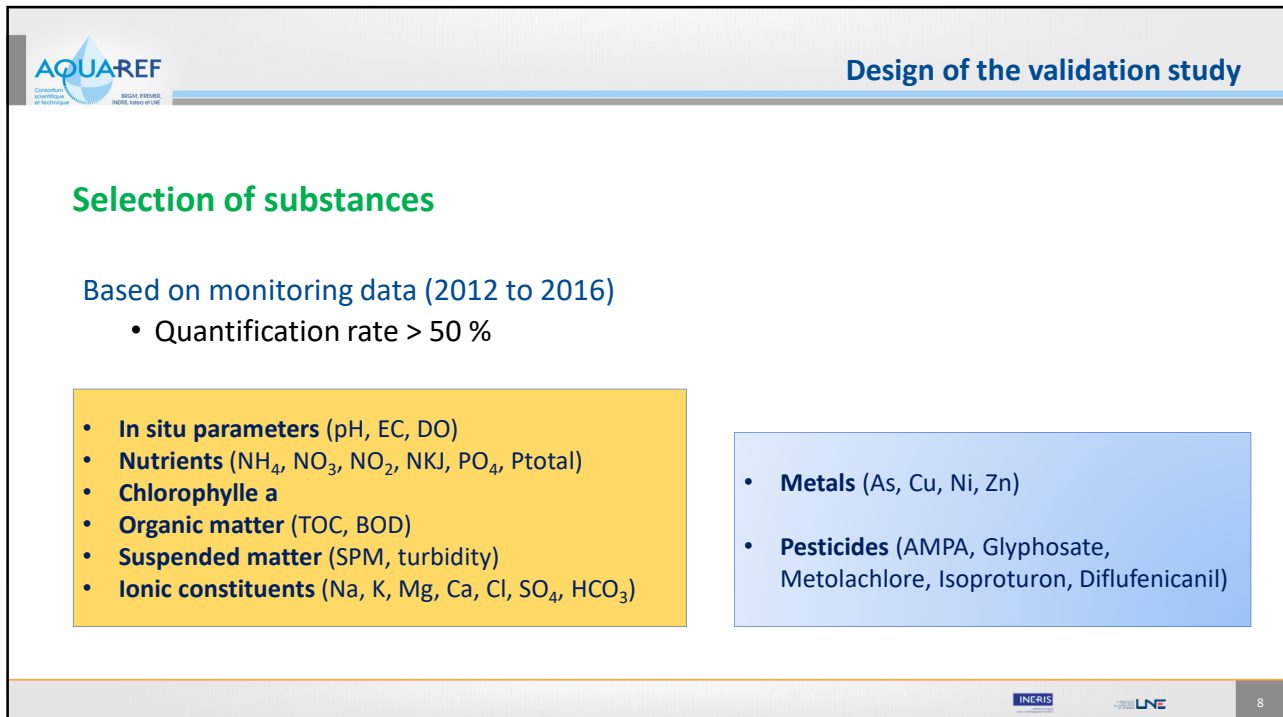
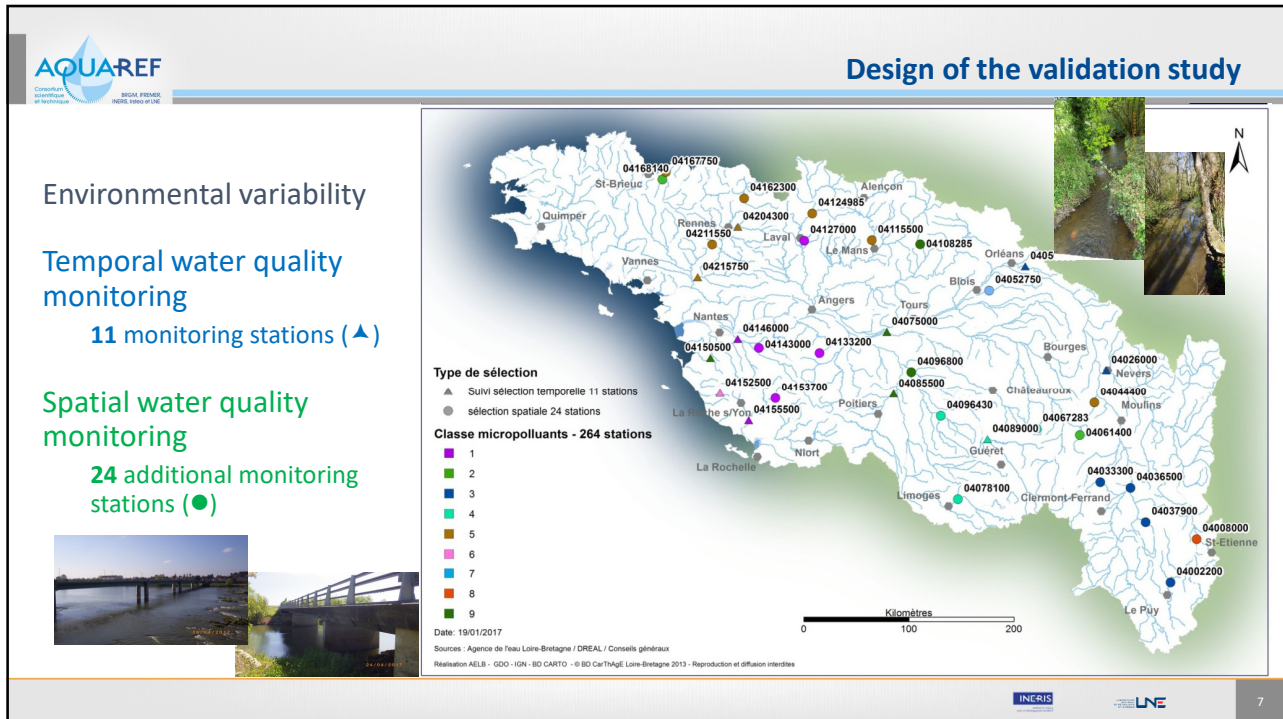
Selection of monitoring stations


420 WFD monitoring stations in the Loire-Bretagne River Basin

- 35 selected monitoring stations (8%)

Use of multivariate statistics to group the stations according to their chemical composition similarities (e.g. HCA)

- 9 clusters were identified
- Selection of small streams to large rivers





AQUAREF
Conseils
environnement
et technique

Design of the validation study

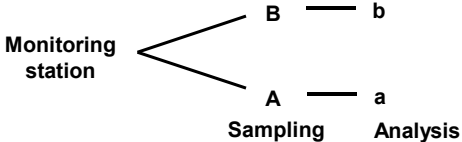
Outline

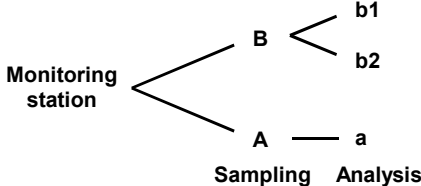
Spatial variability



- 11 + 24 monitoring stations
- 1 field campaign (October 2017)
- All water quality parameters except « metals » and « pesticides »


Temporal variability

- 11 monitoring stations
- 7 field campaigns (April – December 2017)
- All water quality parameters except « ionic constituents »








9




AQUAREF
Conseils
environnement
et technique

Design of the validation study

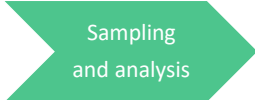
Who did what ?



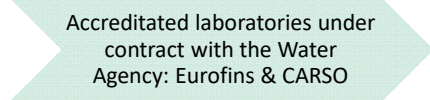
Design



Aquaref and Loire-Bretagne Water Agency




Sampling and analysis

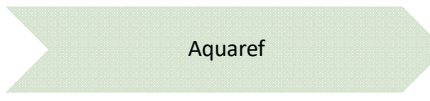


Accredited laboratories under contract with the Water Agency: Eurofins & CARSO

Analysis were performed under intermediate precision






Data calculation & interpretation



Aquaref

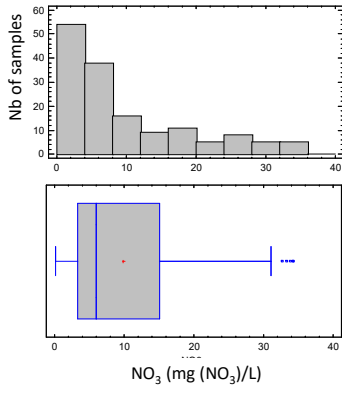
RANOVA2 software



10


Results

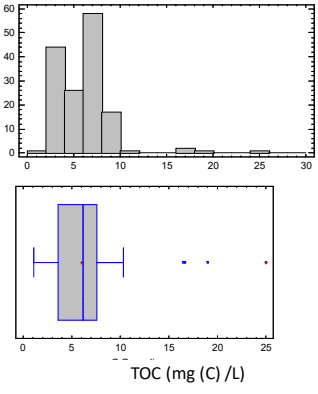
Looking at the data ...

Nitrates



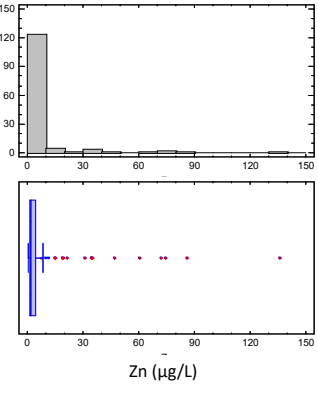
NO₃ (mg (NO₃)/L)

Total Organic Carbon





TOC (mg (C) /L)


Zinc



Zn (µg/L)

➔ **A priori, no need to log transform the data**
Robust ANOVA appears to be appropriate to take into account extreme data



11

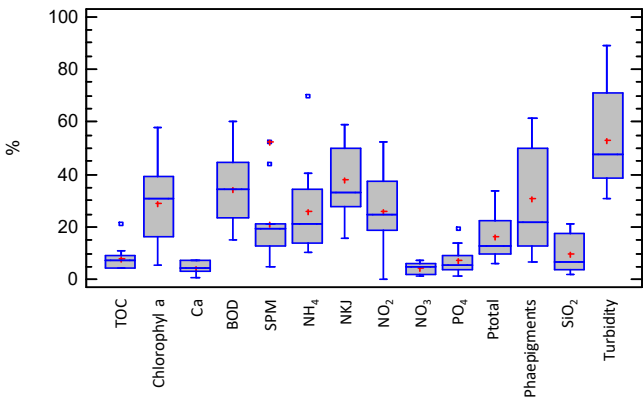

Results



Measurement uncertainty $U_{meas} (k=2)$

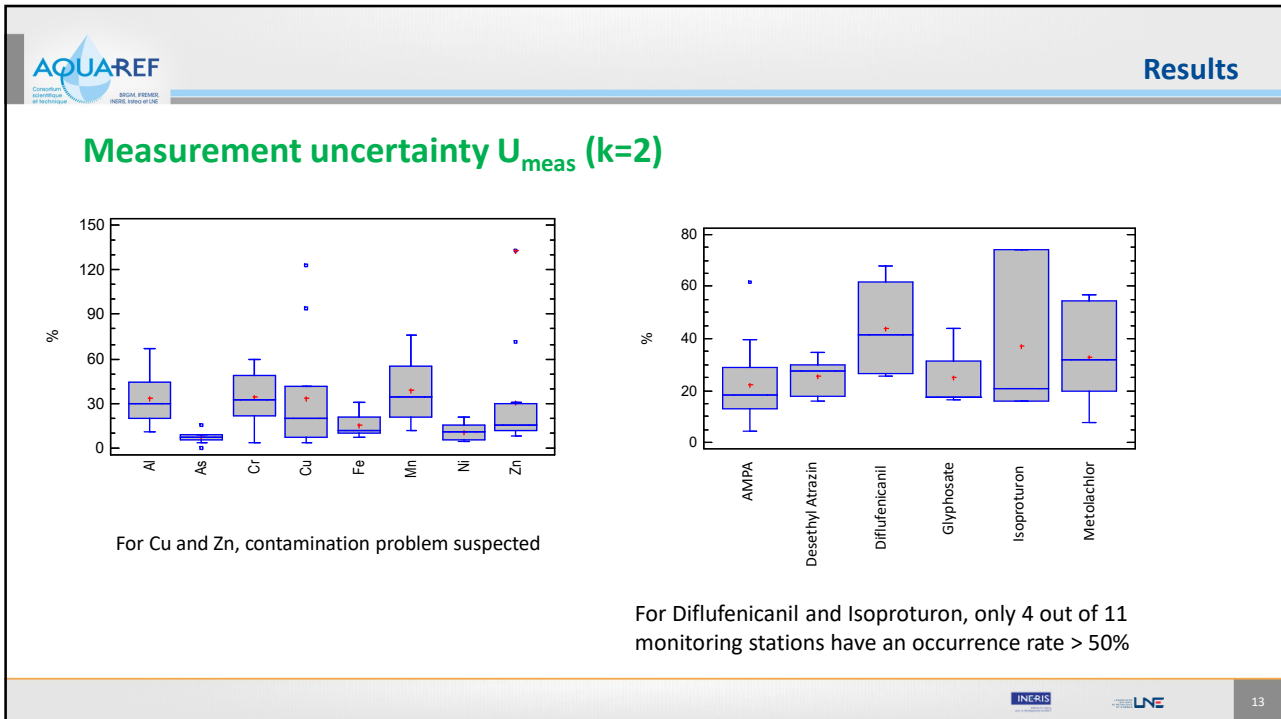
Estimation of the measurement uncertainty ($k=2$) at each of the 11 « temporal » monitoring stations

↓

For Turbidity, NKJ, BOD and phaeopigments: low level of concentration measured





12

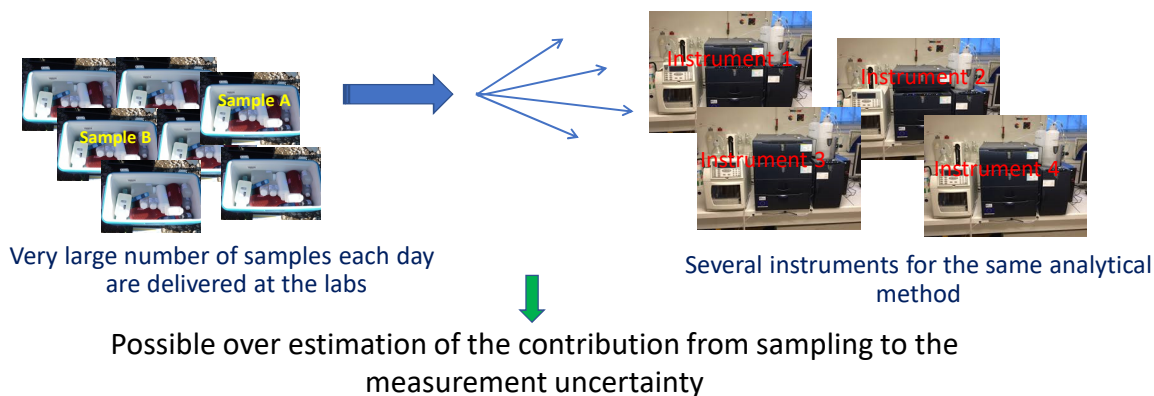


At the Loire-Bretagne River Basin Scale

$U_{meas} < 5\%$	$5\% \leq U_{meas} < 10\%$	$10\% \leq U_{meas} < 20\%$	$20\% \leq U_{meas} < 50\%$	$U_{meas} \geq 50\%$
Na, K, Mg, Ca, Cl, SO ₄ , HCO ₃ , NO ₃	TOC, PO ₄ , SiO ₂	Ptotal, SPM	NH ₄ , NO ₂ , NKJ, BOD, Turbidity, Chlorophyl a, phaeopig.,	
	As, Ni	Fe, Zn	Al, Cu, Cr, Mn	
		AMPA, Benzotriaz, MetolCL OXA, MetolCL ESA	Glyphosate, Metolachlore, Atrazine, DEA, Bentazone, mecoprop, propiconazole, boscalid, Diflufenic, Isoproturon, 2,4 MCPA, 24D, CGA 369873, Dimethamid, Diuron, DmetamiESA, HHCB, Imidaclopr, MetazCIESA, MetazCLOXA,, Terbutryne	AlaCIESA, DmetamiOXA, NOA 413173

Measurement uncertainty arising from sampling

Analysis performed under intermediate precision and not under repeatability conditions



Comparing measurement uncertainties from:

- This study (U_{meas})
- Analytical uncertainties provided by the accredited laboratories (U_{ana})

$$U_{\text{meas}} \ll U_{\text{ana}}$$

TOC, Ca, NO₃, PO₄, Ptotal
As
AMPA

$$U_{\text{meas}} \cong U_{\text{ana}}$$

All other substances

Over estimation of the analytical uncertainty ?  Should we investigated how it is estimated ?

- The Water Agencies are kin to conduct such a validation study to get a better knowledge of the measurement uncertainty at their River Basin scale
- Improvement of the methodology is however needed
 - | How can the accredited laboratory practises be taken into account to estimate the contribution of sampling ?
 - | When the concentration range is important, can data be aggregated ?

