

Sensors & water quality parameters

Temperature, electrical conductivity, pH, dissolved oxygen, turbidity, nitrates, organic matter (fDOM & DOC), chlorophyll a, PAHs



Performances in controlled conditions (2011)

3 sets of probes

6 different days over a 3 week time period

Each day :

- 3 temperatures (5, 15 et 25 °C)
- 3 standard solutions or reference materials
- 3 repetitions per standard solution



Performances in real conditions (2011)

3 months trial at one monitoring station

5 sets of probes

- 1) Verification of performances :
 - 3 standard solutions or reference materials
 - 7 field campaigns over 3 months
- 2) Comparaison with a reference method twice a week: in situ measurement / or sampling & analysis



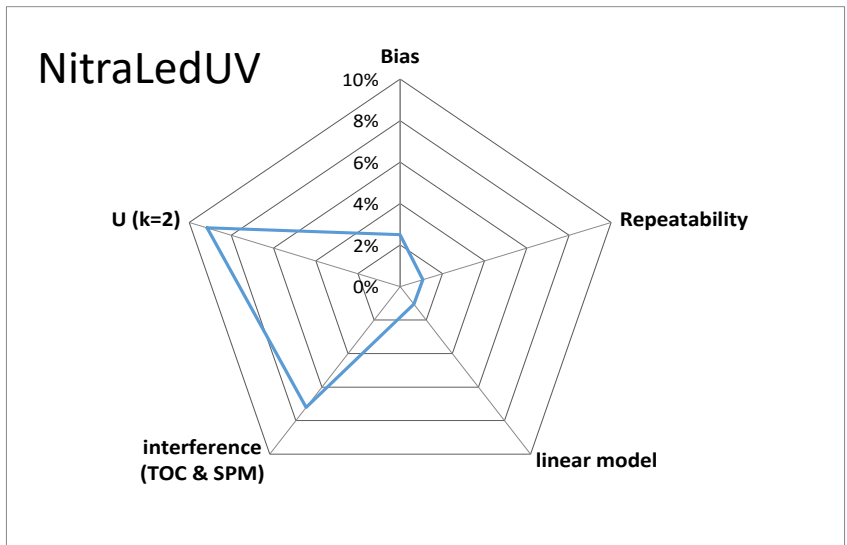
Measurement uncertainty (2011)

- A. Using Laboratory data
- B. Using field verification data
- C. Using « in situ » continuous data
 - Dispersion of the 5 probes => **precision**
 - Comparison with laboratory analysis / on site measurement => **bias**

Performances in controlled conditions (2019-2020)

EN 17075:2018 – Water quality – General requirements and performance test procedures for water monitoring equipment – Continuous measuring devices

- Estimation of each individual performance
 - Bias, repeatability, linear model
 - Limit of quantification
 - Interferences
 - Environmental factors (e.g. water temperature, flow rate)
 - Other performances (e.g. power supply)
- Combination of the performances
- Expressing the combined performance as an expanded uncertainty $U (k=2)$



Nathalie Guigues¹, Maxime Savatier², Béatrice Lalere¹

¹ LNE, 1 rue Gaston boissier, 75015 Paris, France

²ANDRA, Centre de Meuse/Haute-Marne RD 960 - BP 9 - 55290 Bure

contact: nathalie.guigues@lne.fr

Long-term Environmental Program (OPE) and surface water quality monitoring



A long-term environmental programme (OPE) was set up in 2007 by ANDRA (French national radioactive waste management Agency) as a research tool for observing simultaneously various environmental media such as water, air, soil, flora, fauna and human activities within an upstream and rural catchment, in the north-eastern part of France (approx. 250 km from Paris).

The OPE water quality monitoring program was optimised in 2011 in order to better take into account the high variability in time and space of the water quality of the rivers in relation to its karstic hydrological system. **Six monitoring stations** located on the Saulx, Ornain and Orge rivers were instrumented in 2012 to monitor continuously key water quality parameters such as temperature, electrical conductivity, dissolved oxygen, pH and turbidity, by means of multiparameter probes.

New approach for estimating measurement uncertainty of real-time data

- Based on the methodology described in EN 17075 (field trial)
- Using the monthly quality controls implemented since March 2012 at the 6 OPE monitoring stations as well as data from maintenance.
- Estimating the 90 percentile of the difference (in absolute value) between quality controls and in situ measurements
- Comparing the 90 percentile to the uncertainties estimated during the 2011 and 2019- 2020 performances tests

Example: Electrical Conductivity at 25°C

➤ Hydrolab probe (2012-2019)

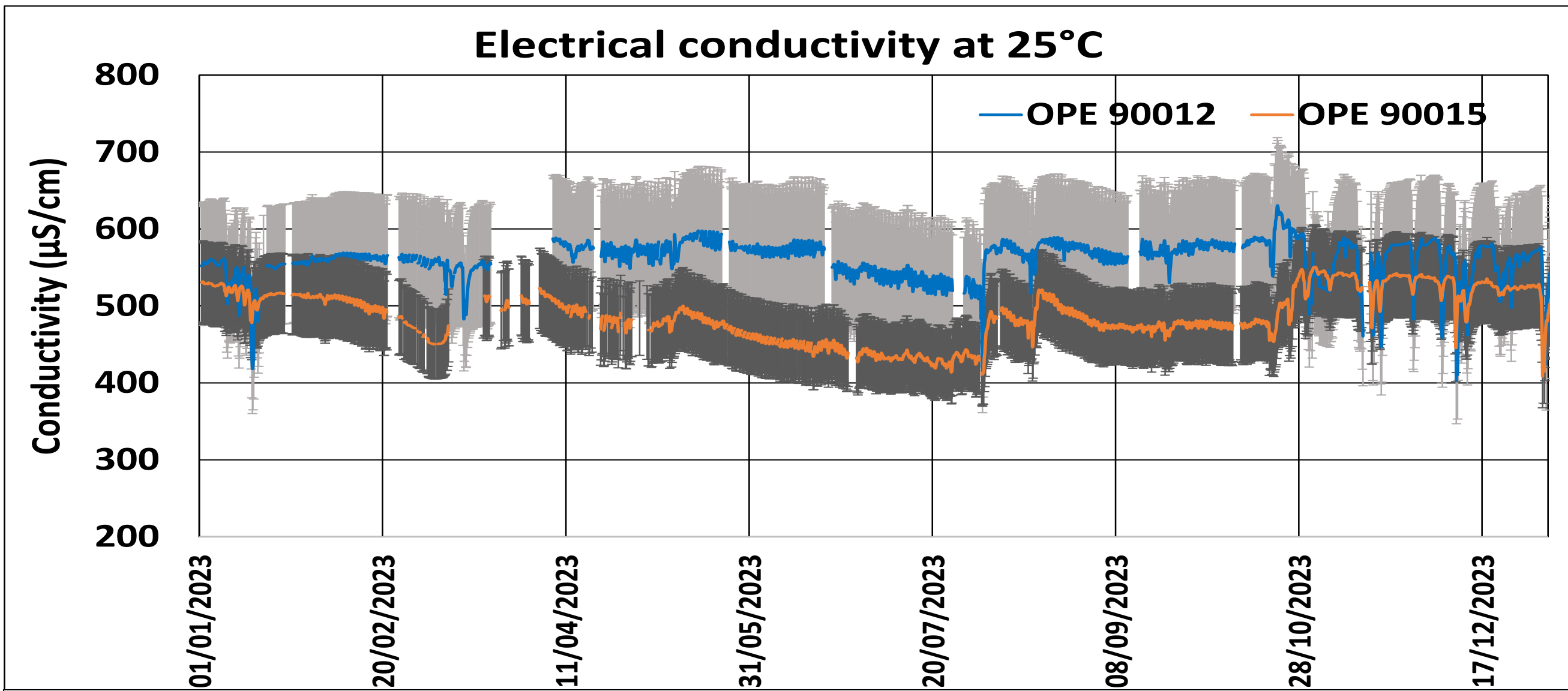
Approach	EST3012	OPE90011	OPE90012	OPE90013	OPE90014	OPE90015
U (k=2) – A. Controlled conditions– 2011			6.4%			
U (k=2) – B. Real conditions– 2011			13%			
U (k=2) – C. In situ - 2011			9.6%			
Percentile 90 – In situ comparaison		9.0%	11%	13%	8.9%	8.0%
Percentile 90 – Maintenance	4.9%	3.1%	5.0%	5.9%	4.8%	4.6%

➤ EXO2 probe (2020-2022)

Approach	EST3012	OPE90011	OPE90012	OPE90013	OPE90014	OPE90015
U (k=2) – Controlled conditions (EN 17075)			2.1%			
Percentile 90 – In situ comparaison	10%	9.4%	13%	14%	10%	11%
Percentile 90 – Maintenance			4.1%			

Retained measurement uncertainty

2012-2019 (Hydrolab probe)	From 2020 (EXO2 probe)
U (k=2) = 9% for EST3012, OPE90011, OPE90014, OPE90015	U (k=2) = 10% for EST3012, OPE90011, OPE90014, OPE90015
U (k=2) = 13% for OPE0012 et OPE90013	U (k=2) = 14% for OPE0012 et OPE90013



⇒ Significant difference between monitoring stations at low flow rate (summer)
⇒ Saulx recieves inputs of water during low flow with higher conductivity than Ornain (seepage, groundwater).
Context: OPE90012 is downstream from springs coming from Barrois limestones while OPE90015 is downstream from Canal de la Marne au Rhin. Mean conductivity in boreholes sampled in the Barrois limestones is 660±90 µS/cm while mean conductivity in Canal de la Marne au Rhin is 490 ±30 µS/cm (where ± is one standard deviation).

Example: pH

As pH tends to drift, quality index have been defined, following USGS recommendations

Quality Index	pH measured – pH corrected	U (k=2)
1 – very good	≤ 0.2	U_0
2 - good	0.2 – 0.5	$1.5 U_0$
3 - average	0.5 – 0.8	$2 U_0$
4- poor	> 0.8	$2.5 U_0$

2012-2019 (Hydrolab probe):

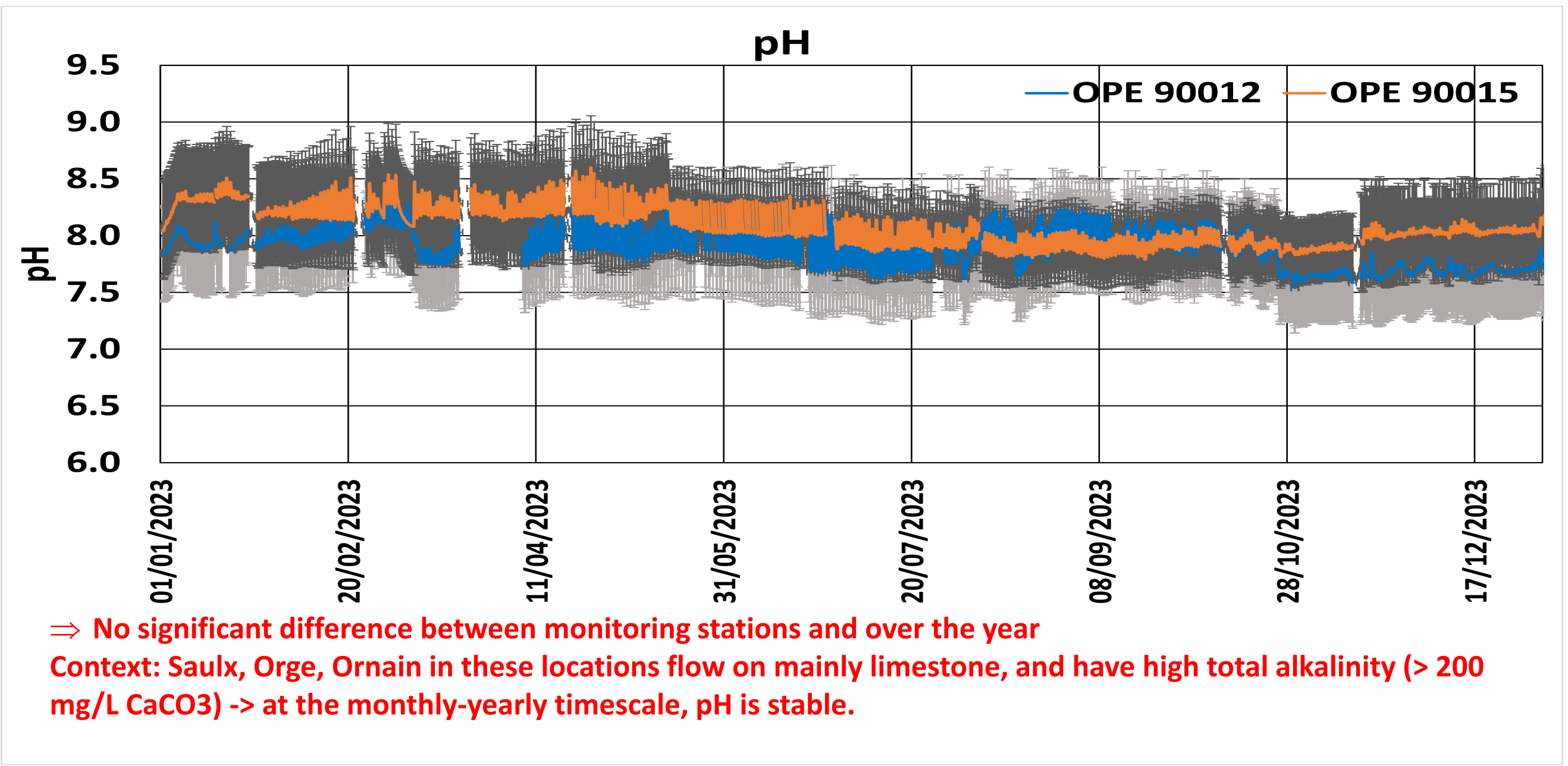
$U_0 (k=2) = 4.0\%$

From 2020 (EXO2 probe):

$U_0 (k=2) = 3.5\%$

➤ EXO2 probe (2020-2022)

Quality index	Data distribution					
	EST3012	OPE90011	OPE90012	OPE90013	OPE90014	OPE90015
1	79%	86%	97%	81%	94%	81%
2	8%	4%	0%	19%	3%	10%
3	5%	0%	3%	0%	3%	6%
4	8%	10%	0%	0%	0%	3%



CONCLUSION

This work allowed us to estimating the measurement uncertainty in real-time. The 90 percentile method using on-going quality controls is more realistic than evaluations carried out under controlled conditions. it takes into account real conditions over a hydrological year (temperature, flow of watercourses, interferences etc.) as well as long-term deployment conditions (biofouling). It is a prerequisite to not over-interpret variations that are within the measurement uncertainty and thus identify significant trends over time which can then be interpreted more confidently using local knowledge on hydrology, geology and geochemistry.