RÉPUBLIQUE FRANÇAISE
Liberté
Égalité
Fraternité

LABORATOIRE NATIONAL DE MÉTROLOGIE ET D'ESSAIS

NEED FOR THE VALIDATION OF ON-SITE TEST KITS, PORTABLE DEVICES AND CONTINUOUS MEASURING DEVICES FOR WATER QUALITY MONITORING

NATHALIE GUIGUES

Eurachem workshop – 22nd – 23rd May 2023

CONTEXT

Wastewater treatment plant (WWTP) operation

Identification more rapidly of any dysfunction at a WWTP using alternative biochemical Oxygen demand (BOD) test kits with a 2 days response time

→ Urban Wastewater Directive (UWWD) under revision

Accidental or deliberate contamination of drinking water & possible contamination of raw water

Development & implementation of early warning systems, based on continuous monitoring of targeted or untargeted substances.

On-line monitoring of desinfection & turbidity for Water Treatment Plants providing more than 10000 m^3 of water (New Drinking Water Directive – 2020)

Complementary approach to existing quality monitoring systems

Affordable cost, reliable devices producing comparable data between times and locations.

→ Water Framework Directive (WFD) is under revision

CONTEXT

Advantages :

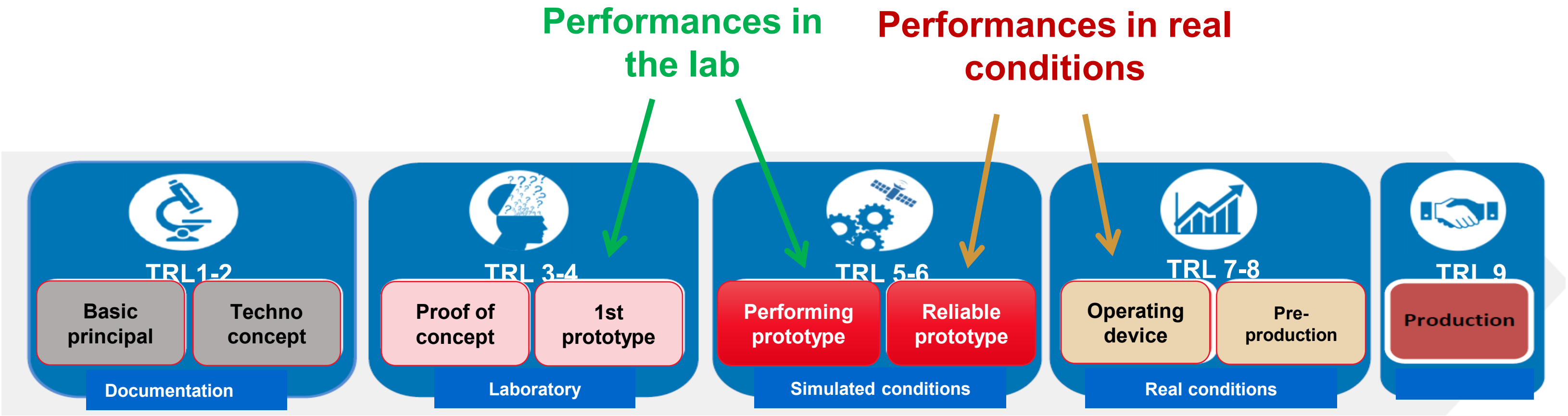
- Fast response / real time
- Easy to perform on site or in the lab
- Fully or partially automated
- Lower cost

However they are:

- Usually not validated
- Perceived as less reliable than conventional methods
- Lacking in information on how to use them and/or how to interpret results

Why is there a need to evaluate the performances of measuring devices for water quality monitoring ?

- For the manufacturer :
  - To optimise and improve the sensor / device
  - To check that the sensor / device is fit for purpose for its intended application
  - to promote devices with claimed performances that have been verified



- For an end user :
  - To have confidence in the performances stated by the developper
  - To select the most appropriate sensor / device with regard to the monitoring objective

VALIDATION PROCEDURE

Need for a **metrological infrastructure** for the **validation** of on-site and on-line devices for water quality monitoring, in order to gain in **comparability and reliability of measurements** and thus **improve the quality of data** obtained

Proposed validation procedure

0. Justification of need and adequacy with intended application
1. Description of the innovative tool
2. Assessment of intra-laboratory performances
3. Transfer to other labs
4. Inter-laboratory Comparisons
5. Demonstration of the equivalence of results

STEP 2 – INTRA LABORATORY PERFORMANCES

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

→ **Portable devices for on-site measurements**
Continuous measuring devices

Assessing the performances under controlled conditions (in the lab)

↓

- Estimation of each individual performance
- Combination of the performances
- Expressing the combined performance as an expanded uncertainty

Assessing the performances under real condition (field trial)

↓

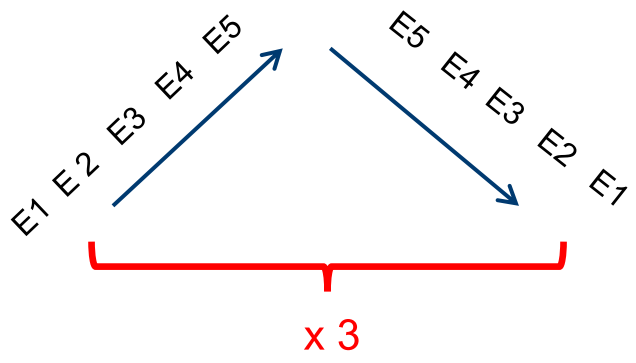
- Demonstrate that the performance (assessed in controlled conditions) is maintained under representative operational conditions

STEP 2 – INTRA LABORATORY PERFORMANCES

Performance under controlled conditions

Metrological performances:

- Repeatability
- Bias
- Deviation from linear model
- Limit of quantification



Use of 5 standard solutions

Intrinsec performaces:

- Physical, biological or chemical interferences
- Response time

Other performances of interest:

- Sample temperature, flowrate
- Drift (continuous device)
- Warm up time (portable device)
- Variation in supply voltage
- Output impedance

➡ **Measurement uncertainty**

STEP 2 – INTRA LABORATORY PERFORMANCES

Example: Turbidity sensor (EXO2 probe) for drinking water monitoring

- Drinking Water Directive thresholds : 1FNU – max 2 FNU
- Technical specification for EXO2 turbidity sensor: accuracy of 0.3 FNU or ±2% of reading from 0 to 999 FNU
- Performances assessed using different strategies:

1-Formazin standard (StablCal®) ➡ Used for calibration and establishing manufacturer's specifications

2-Drinking water spiked with SDVB* ➡ Non toxic and stable microspheres: alternative to formazin US EPA approved

3-Drinking water spiked SPM from river ➡ End-user application

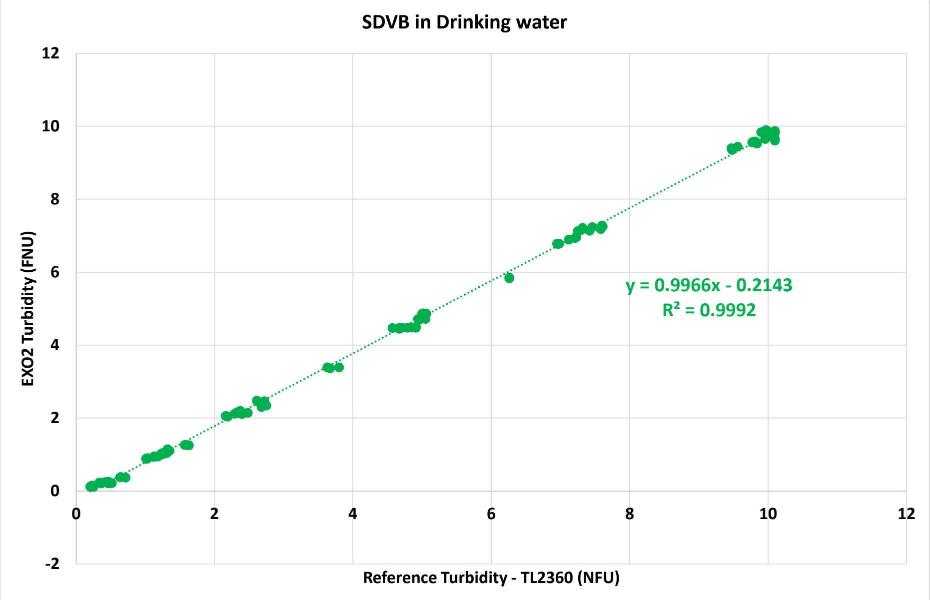
HACH TL 2360 used to establish turbidity value of spiked DW

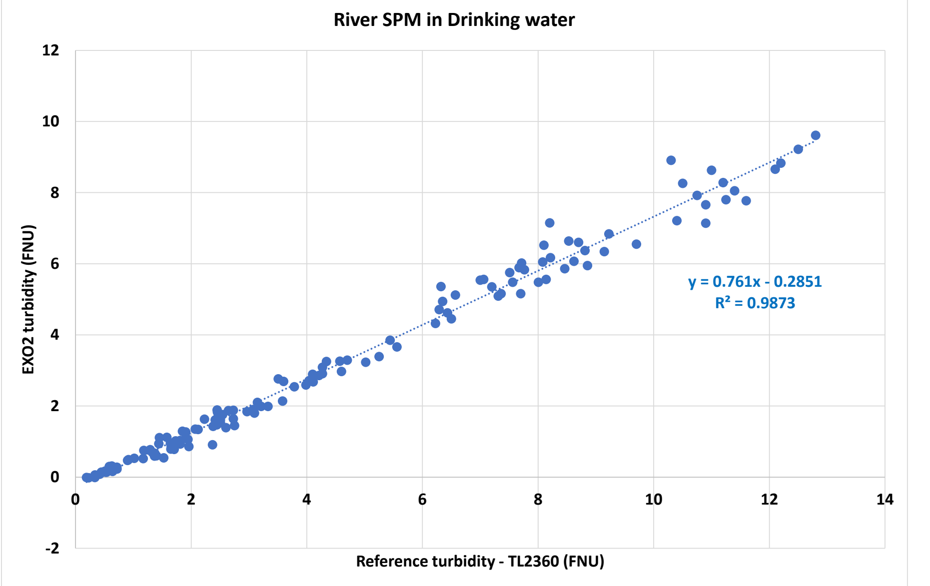
*SDVB (copolymer of styrene divinylbenzene), recommended by US EPA

STEP 2 – INTRA LABORATORY PERFORMANCES

Performance estimations:

	Formazin	SDVB	River SPM
Matrix	Pure water	DW	DW
Range	10 – 1000 FNU	0.5 – 10 FNU	
Bias	1.8%	9.4%	34%
Repeatability	2.5%	2.5%	5.2%
Deviation from lineraity	3,0%	0.4%	2.5%
Uncertainty (k=2)	5.8%	12%	41%





*SDVB (copolymer of styrene divinylbenzene), recommended by US EPA

STEP 3&4 – INTER LABORATORY COMPARISON

PORTABLE DEVICES AND KITS

- Should be performed in real conditions: on site
  - **1 day**
  - **2-4 sites characterised with different level of concentrations**
  - **Ideally 8-10 teams**
- Example: in situ measurements of pH, conductivity, dissolved oxygen and turbidity
  - **Since 2018, twice a year**
  - **2 Accredited PT providers (ISO 17043)**
  - **River waters, bathing waters, wastewaters**

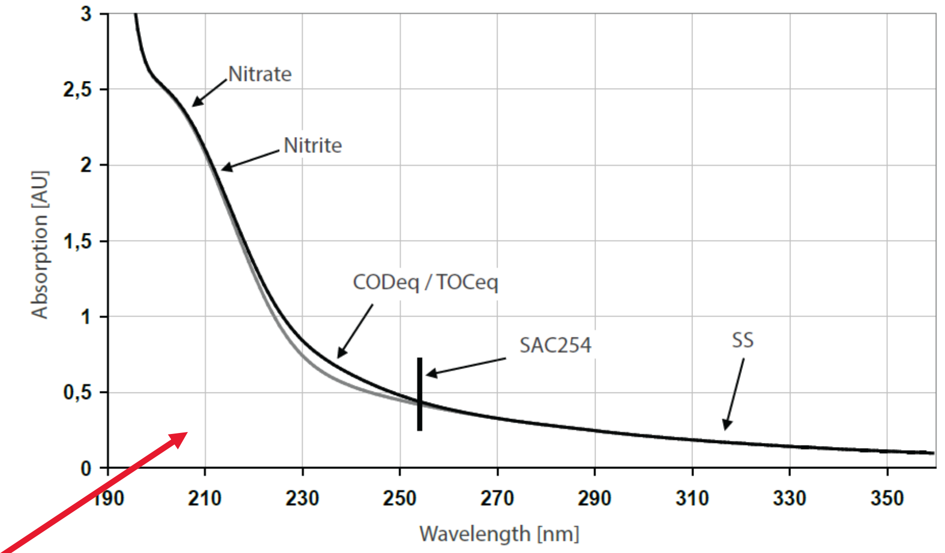
AGLAE BIPEA

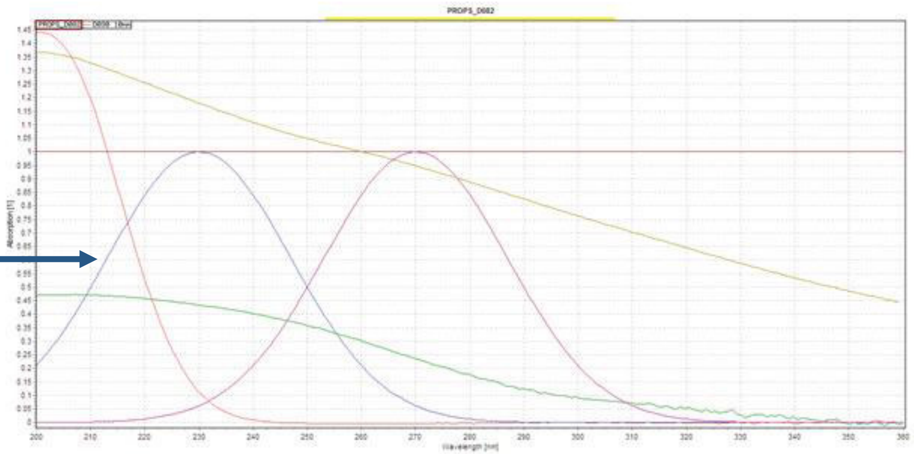
- Other compounds
  - **Selection of 2-4 sites with concentrations above the limit of quantification**
  - **OK for nutrients, organic matter, turbidity**
  - **More difficult for metals and organic compounds**

STEP 3&4 – INTER LABORATORY COMPARISON

CONTINUOUS MEASURING DEVICES

- Should be performed in real condition: on site
  - **Several days to deploy continuous measuring devices**
  - **Installation for 2h to more than 24 h => secure sites**
  - **2-4 sites characterised with different level of concentrations**
  - **Ideally 8-10 teams**
- Examples for UV-visible probes: various calibration methods to be included
  - **Partial Least Squares Regression (PLSR) with 3 to 4 wavelengths and based on several representative spectra**
  - **Combination from the stored absorption spectra whose result fits best with the respective measured absorption spectrum of the medium**
  - **Local calibration to adjust for matrix effect**





➡ On-going ILC for Uv-visible probes within Aquaref – French Reference Laboratory for aquatic monitoring

STEP 5 – EQUIVALENCE OF RESULTS

Case of parameters defined by their method

➡ Different methods = different measurands

- Guidance documents and standards:
  - **ISO/TS 16489:2006** “Water quality – Guidance for establishing the equivalency of results”
  - **EN ISO 17994:2014** “Water quality — Requirements for the comparison of the relative recovery of microorganisms by two quantitative methods”
  - **US EPA 821-B-16-001** “Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA’s Alternate Test Procedure Program”

⇒ Give recommendations to address the demonstration of equivalence of results by two methods

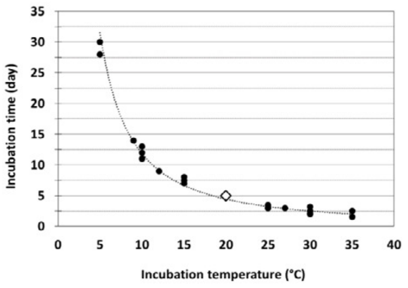
⇒ Different methodologies and statistical tests used.

⇒ Adaptation of these standards is needed to include both portable and continuous measuring devices

STEP 5 – EQUIVALENCE OF RESULTS

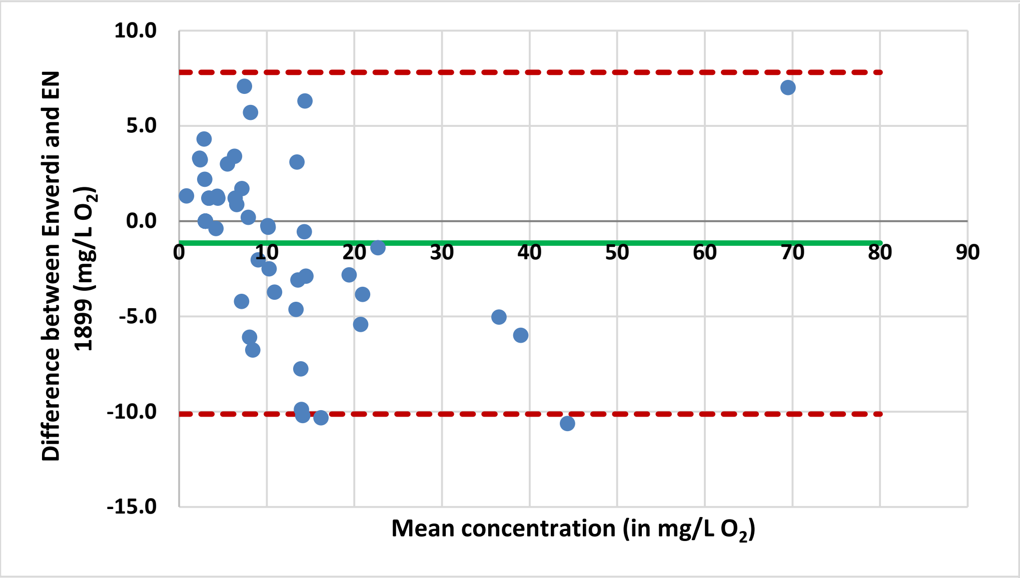
EXAMPLE: BOD ALTERNATIVE METHOD

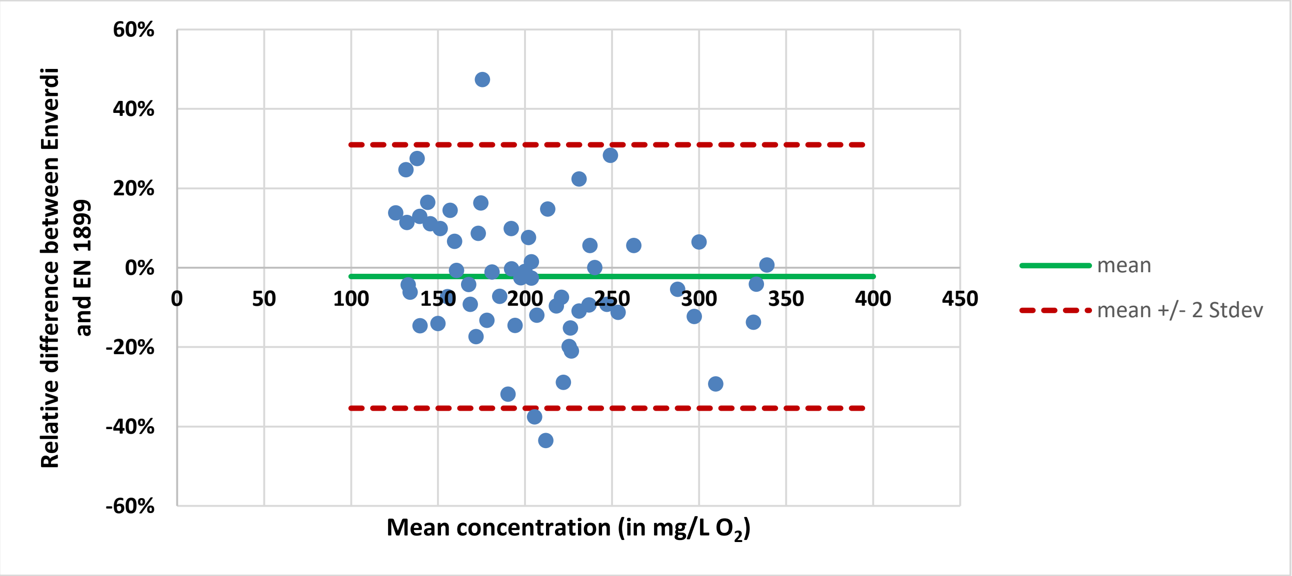
- **Enverdi® kit for wastewaters based on fluorimetric respirometry**



Incubation at 30°C, measurement after 48h

Reference method - EN 1899 – incubation at 20°C, measurement after 5 days, respirometry





CONCLUSION

NEED TO INVESTIGATE AND/ OR CONDUCT:

- Metrological performances assessment, including measurement uncertainty of on-site kits, on site and on-line devices, considering both manufacturers and end-users needs

  e.g. using pure standard solutions versus real matrix samples

- Interlaboratory Comparisons in the field to assess performances in real conditions

- Comparability to a reference method (standardized or recognized/accepted) by demonstrating the equivalence if results for parameters defined by their method

  e.g. organic matter, turbidity

- The design of test benches for laboratory and field conditions

THANK YOU FOR YOUR ATTENTION

Further information : nathalie.guigues@lne.fr