RÉPUBLIQUE FRANÇAISE
Liberté Égalité Fraternité

LABORATOIRE NATIONAL DE MÉTROLOGIE ET D'ESSAIS

Impact of (spiked) real matrices on the calibration of UV-visible probe for the in situ determination of nitrate and organic carbon in surface waters

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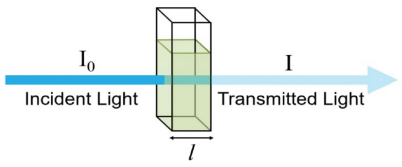
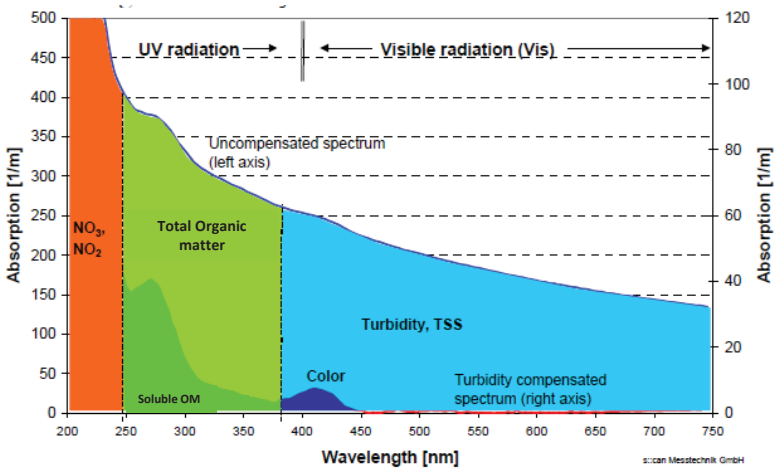
INTRODUCTION

UV-Vis spectroscopy (without reagents) has been investigated since the 80s for monitoring water quality

It is based on the fact that some (pollutant) molecules in water can absorb UV-Vis light at specific wavelengths, following Beer Lambert Law



$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon c l$$



FROM LABORATORY TO FIELD

Laboratory spectrophotometer

Portable device

In situ probes

IN SITU PROBES

DIFFERENT TYPES OF MEASUREMENTS

- Using 1or 2 specific wavelengths

  Nitrates: 220 nm

  Organic matter: 254 nm

- Using part of or entire spectrum

  200 nm – 360 nm

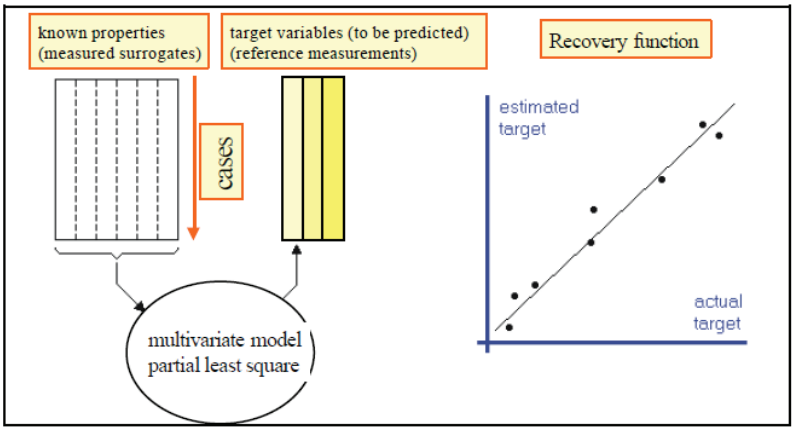
  200 nm – 700 nm

⇒ Calibration using complex mathematical methods to build a predictive model

- **Partial Least Square Regression (PLSR)**
- **Multiple Linear Regression (MLR)**
- **Principal Components Regression (PCR)**
- **Deconvolution: linear combinaison of individual spectrum**

CALIBRATION

PARTIAL LEAST SQUARE REGRESSION



Langergraber et al. AutMoNet 2002

Hundreds to thousands of spectra stored

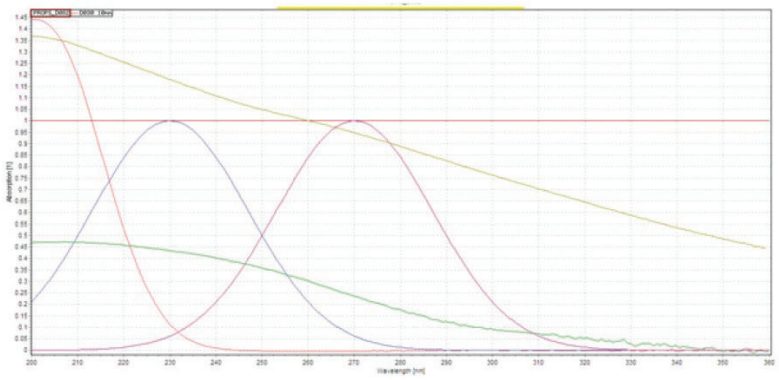
Selection of 5 to 10 (or more) wavelengths that are characteristic of targeted substances and matrix

PLS regression => Factory calibration

CALIBRATION

DECONVOLUTION

- The absorption spectra of the known and expected substances for the respective application are saved on the sensor for calibration.
- A linear combination from the stored absorption spectra is calculated whose result fits best the measured spectra sample
- The sum of all spectral deviations between the absorption spectrum of the medium and the reconstructed absorption spectrum produces the fit error



INSTRUMENTS TESTED

Name	Manufacturer	In situ / portable	Measuring principle	Wavelength (s)	Calibration
Opus	Trios GmbH	In situ	UV-visible absorbance spectra	200-360 nm	deconvolution
Pastel UV	Secoman	portable	UV-visible absorbance spectra	200-350 nm	deconvolution
ISA	GO-systemEletronik GmbH	In situ	UV-visible absorbance spectra	220-700 nm	PLS regression
EXO2 - fDOM	YSI Inc.	In situ	fluorescence	Excitation: 365 nm Emission: 480 nm	Quinine sulfate
EXO2 - NitraLed	YSI Inc.	In situ	UV absorbance	235 nm with organic matter compensation at 275 nm	Linear calibration

INDIVIDUAL SOURCES

ORGANIC MATTER

River monitoring

- Tea leaves => leaching from tree leaves
- Humic substances => leaching from humus in soil
- Protein-like (beef stock and degased beer) => wastewater

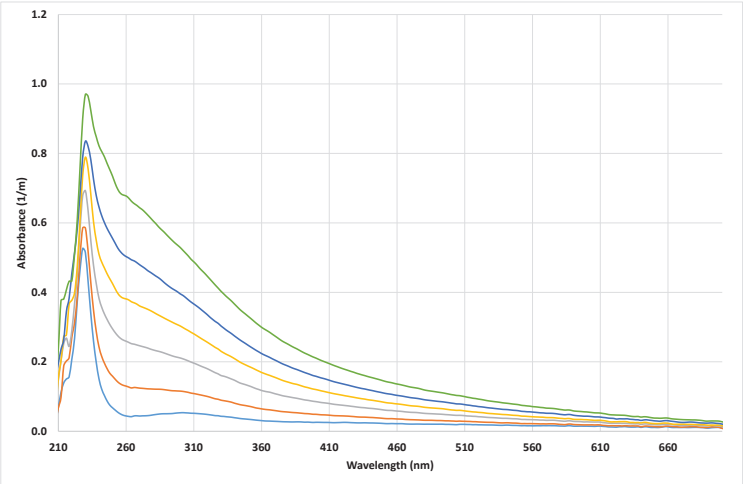
TURBIDITY

- SDVB (styrene divinyl benzene copolymer)
- River suspended matter
- Kaolin (white nanoclay)

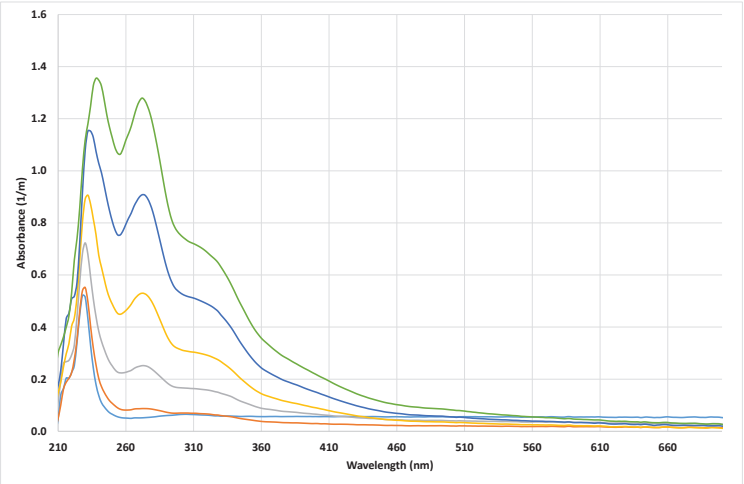
interferences

INDIVIDUAL SOURCES

Humic substances

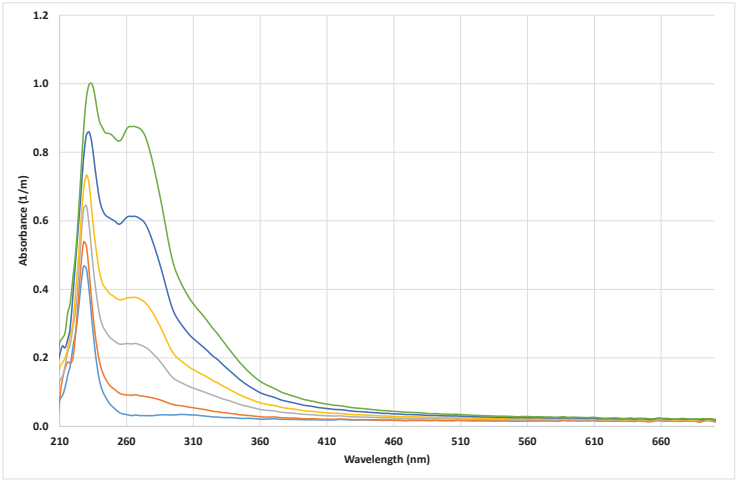


Tea (green + black)

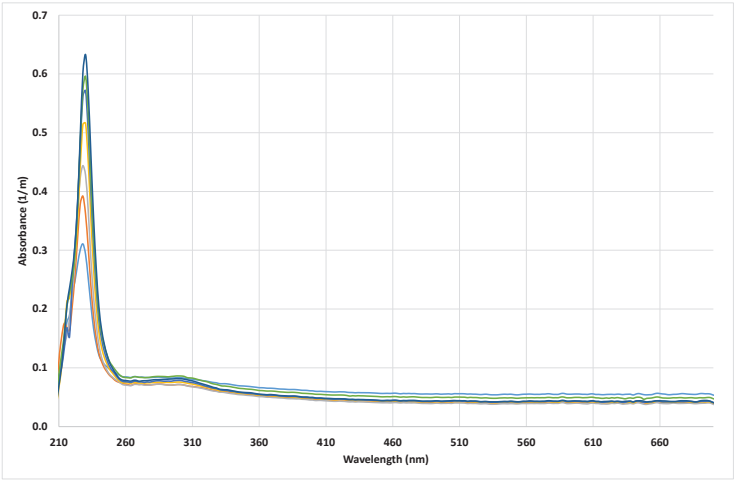


INDIVIDUAL SOURCES

Degased beer



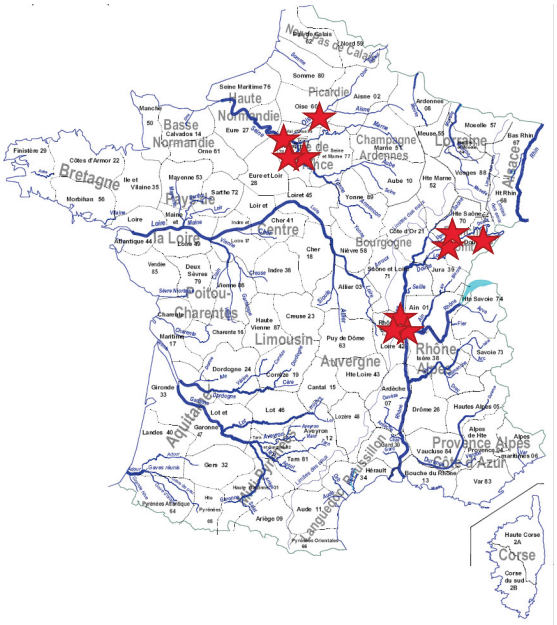
Nitrate



NATURAL WATERS

RIVERS

- Oise (60 km North Paris)
- Seine, Yerres, Orge (South of Paris)
- Rhône, Bourbre, Yzeron (near Lyon)
- Doubs (Baume les Dames, Jura)

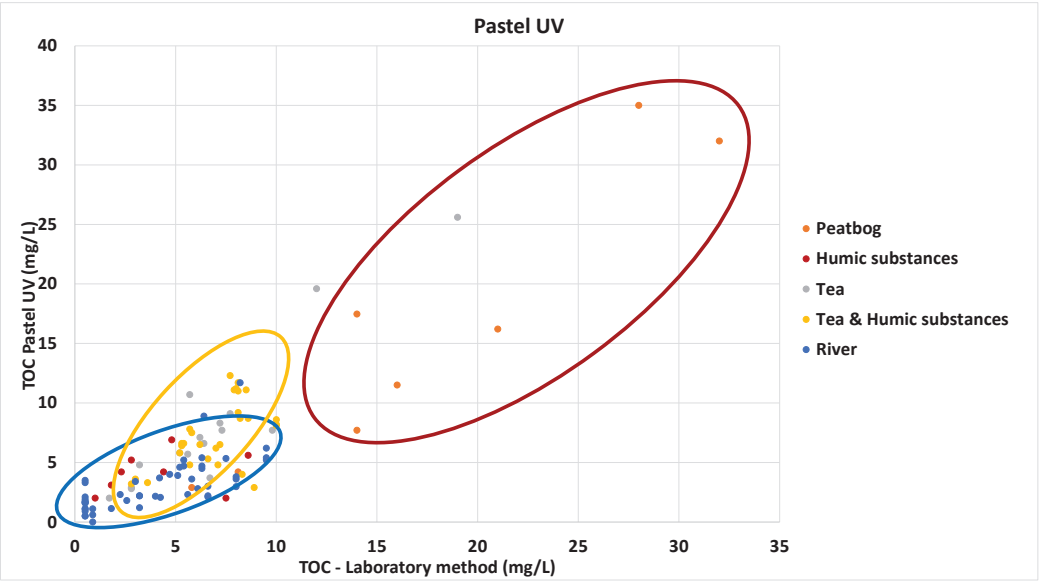


OTHER WATERS

- Tap water (Paris)
- Karst (Baume les Dames, Jura)
- Peatbog (Frasne, Jura)

NATURAL AND SPIKED WATERS

TOC – PASTEL UV



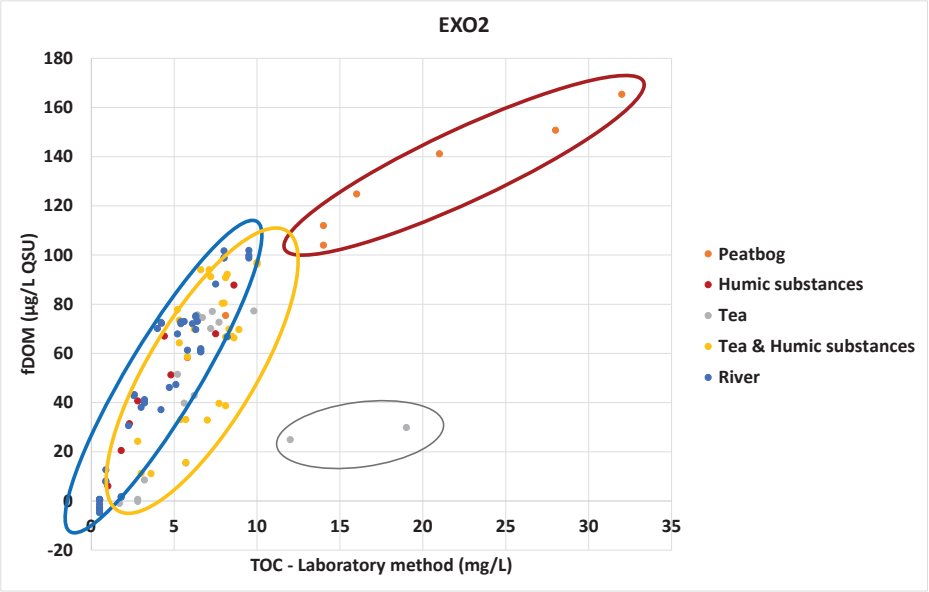
Differences between:

Rivers and spiked samples with Tea and humic substances

Peatbog and all other samples

NATURAL AND SPIKED WATERS

TOC – EXO2



Correction factor:

TOC = fDOM / 11

Except for peatbog

TOC = fDOM / 5

Rivers and spiked samples rather close except for 2 samples (tea)

Peatbogs: upper range

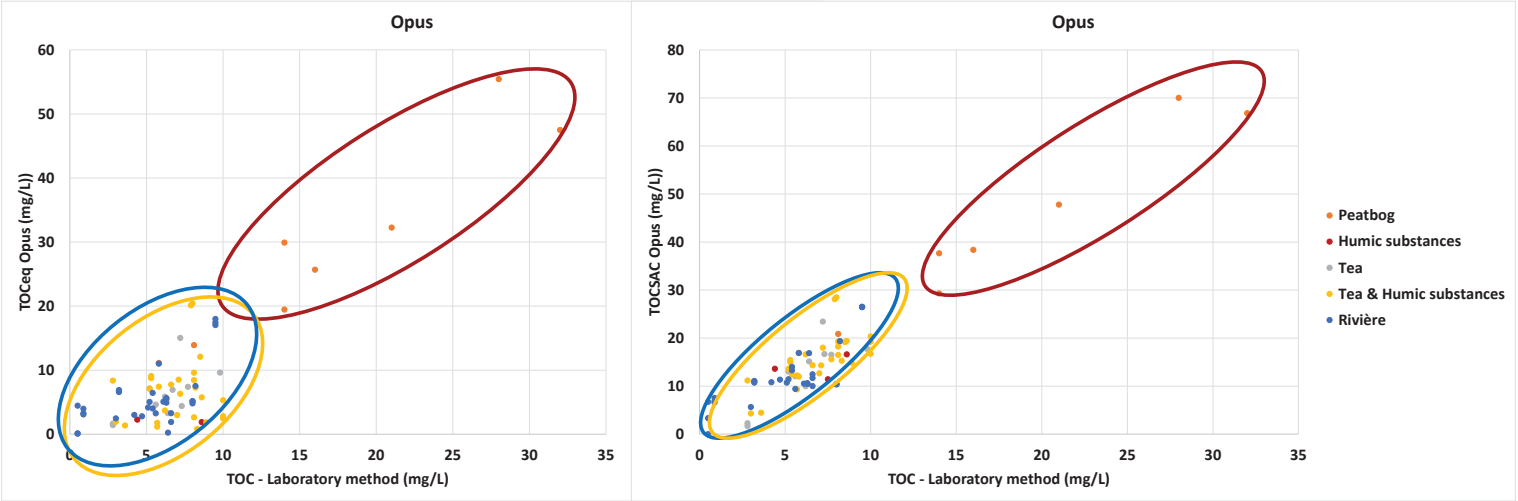
NATURAL AND SPIKED WATERS

TOC - OPUS

- 2 ways of estimating TOC: using deconvolution model or based on absorbance at 254 nm

Correction factor: TOC = TOCeq / 1.7

Correction factor: TOC = TOC_{SAC} / 2.2

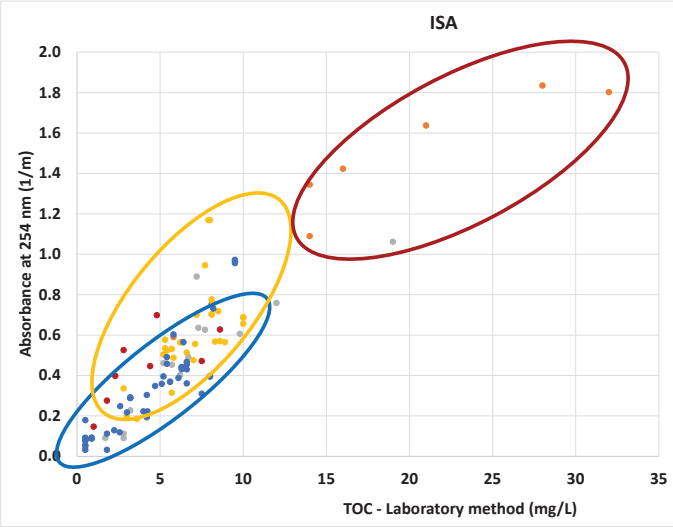


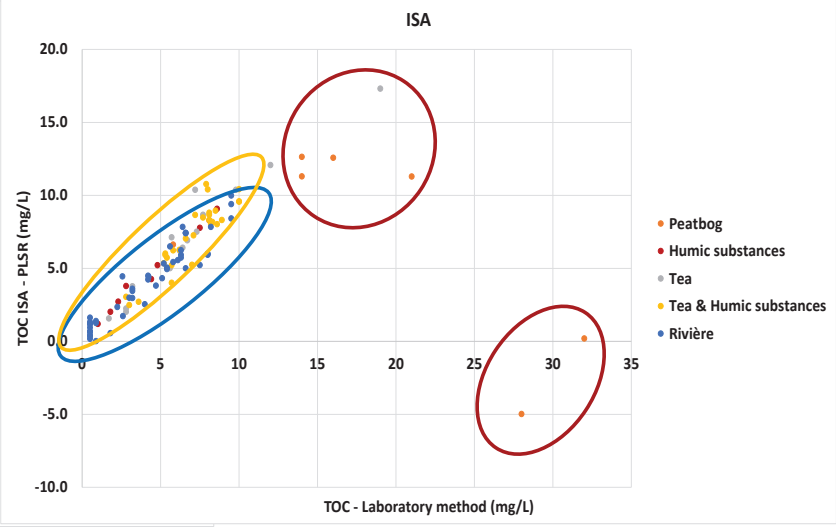
NATURAL AND SPIKED WATERS

TOC - ISA

- 2 ways of estimating TOCusing : the absorbance at 254 nm or a PLSR model

PLSR model without peatbog samples



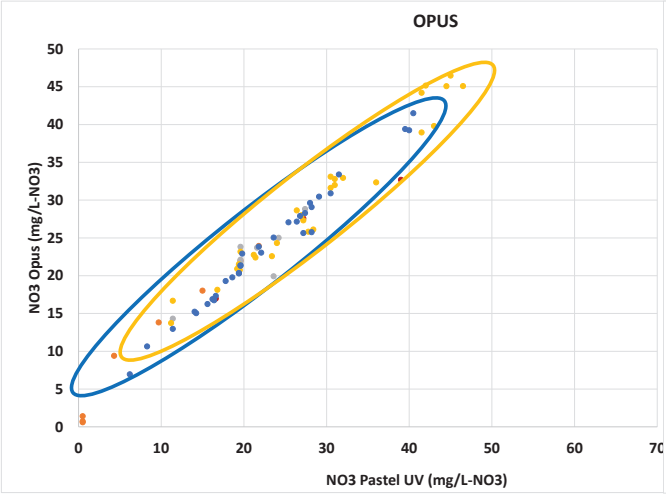


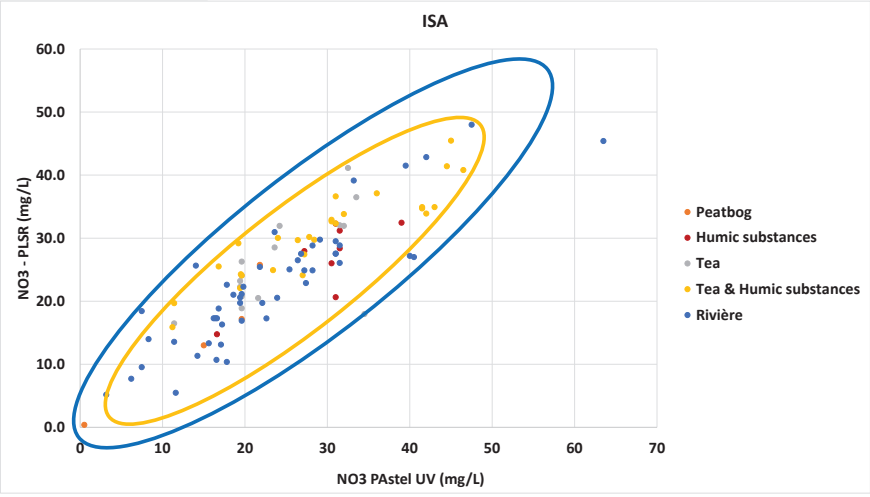
NATURAL AND SPIKED WATERS

NO3 – OPUS & ISA

- Reference for nitrate = Pastel UV (performances assessed according to EN 17075)

PLSR model





RESULTS

TOC

- Centile 90 of the differences (in absolute value) between in situ / portable devices and reference measurement

- Reference measurement:

Lab method EN 1484 (U (k=2) = 9%)

- Range of TOC concentrations:

< 0.5 mg/L to 32 mg/L

Instrument	Centile 90 All samples (n=80-100)	Centile 90 Only rivers (n=14-26)
Pastel UV	63%	63%
fDOM corrected	57%	49%
ISA 284	34%	40%
ISA 285	24%	25%
Opus TOCeq corrected	71%	53%
Opus TOC $_{SAC}$ corrected	46%	38%

PLSR method

Deconvolution method

RESULTS

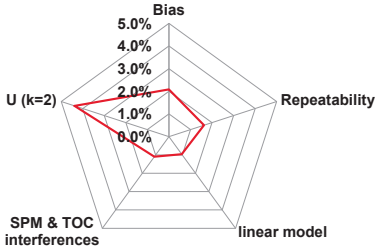
NO3

- Centile 90 of the differences (in absolute value) between in situ / portable devices and reference measurement

- Reference measurement: Pastel UV (U(k=2) = 4.4%). Performances assessed according to EN 17075

- Range of nitrate concentrations:

< 0.5 mg/L-NO3 to 63 mg/L-NO3



Instrument	Centile 90 All samples (n=80-100)	Centile 90 Only rivers (n=14-26)
NitraLed	40%	41%
ISA 284	45%	45%
ISA 285	23%	23%
Opus	15%	15%

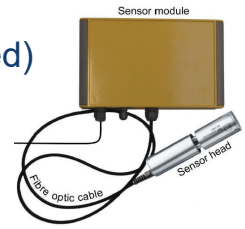
PLSR method

Deconvolution method

CONCLUSION

NITRATE

- Instruments are less affected by matrix and interfences
- Better results with deconvolution method
- ISA probes: quality of fiber optic cable is important (spectrometer is deported)



ORGANIC MATTER (TOC)

- ISA with PLSR show no matrix dependance (except for peatbog)
- Opus needs a local calibration & TOC based on UV254 is less dependant on the matrix
- Pastel UV and EXO2 are matrix dependant

PERSPECTIVES

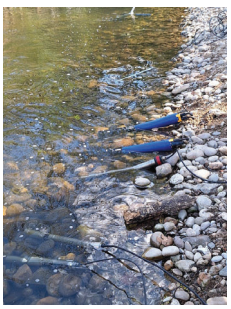
AQUAREF ON SITE INTERCOMPARAISON

- On going
- Under real conditions
- More instruments tested (some identical)
- with factory or homemade calibrations & local calibrations

AQUAREF
Consortium scientifique et technique
BRGM, IFREMER, Ineris, INRAE et LNE

French Reference Laboratory for aquatic monitoring





THANK YOU FOR YOUR ATTENTION

Further information : nathalie.guigues@lne.fr