Accuracy of different on-line sensors for the estimation of pollutant concentrations (TSS, COD total and dissolved) in wastewater, stormwater and all water

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Summary

- Context
- Objectives
- Materials & Methods
- Results
- Conclusions

Context

- *On-line* monitoring for pollutants concentrations
- No sensors able to measure directly TSS or COD / Need of sets of samples to calibrate correlation functions
- Many surrogate sensors
- No study to compare them

Objectives

- Compare different surrogate sensors to estimate pollutants concentrations
- Find most accurate sensors for on-line monitoring
- Compare different methods to remove outliers

Materials & Methods

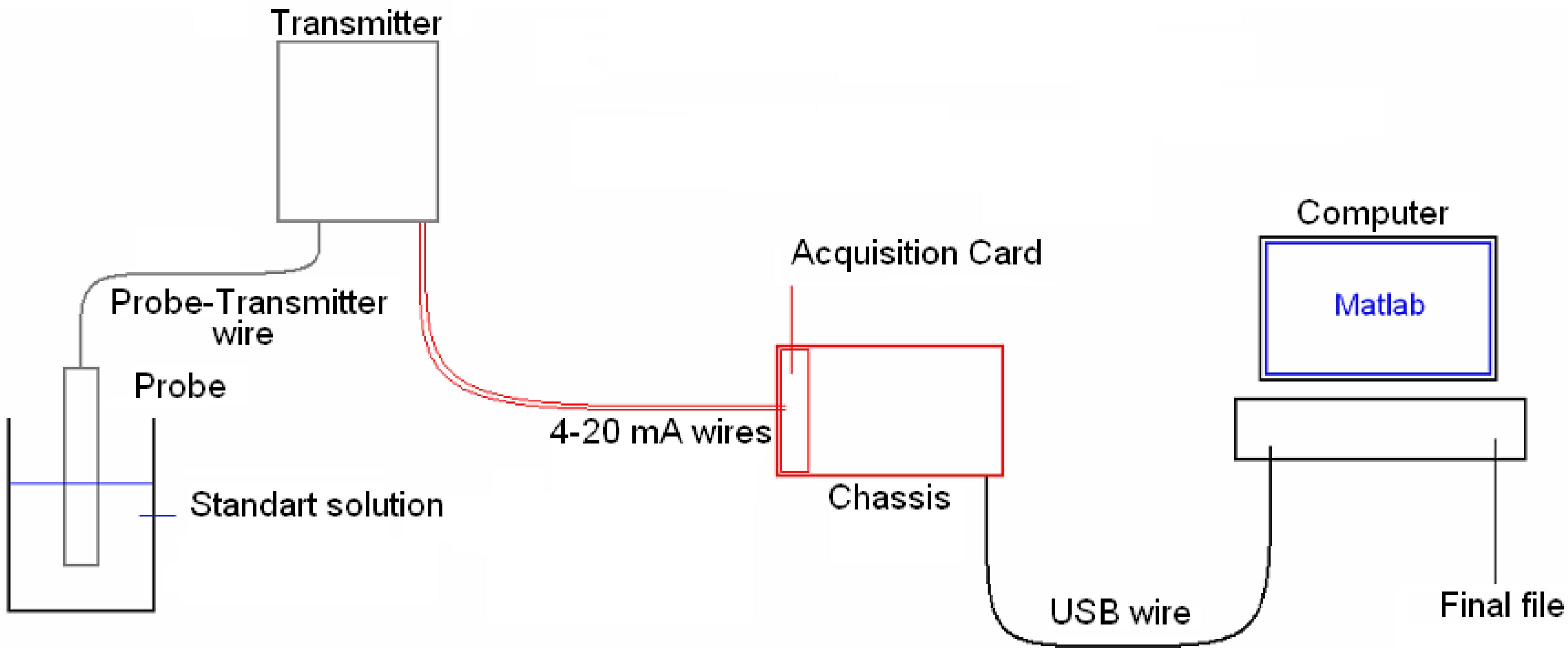
- Materials
  - Grab sampling (inlet of a WWTP – combined sewer)
    - 94 samples collected during dry weather
    - 44 samples collected during wet weather
    - 165 samples for all weather (dry and wet)

Materials & Methods

- Materials
  - 7 sensors
    - Single wavelength (IR: 880 nm) turbidity meters: *Krohne, Endress-Hauser*,
    - Double wavelength (UV: 254 and Vis: 560 nm) turbidity meter: *EFS*,
    - UV/vis spectrometer: *s::can*
    - Microwave sensor: *Metso Automation*
    - pH and conductivity meters: *Yokogawa*

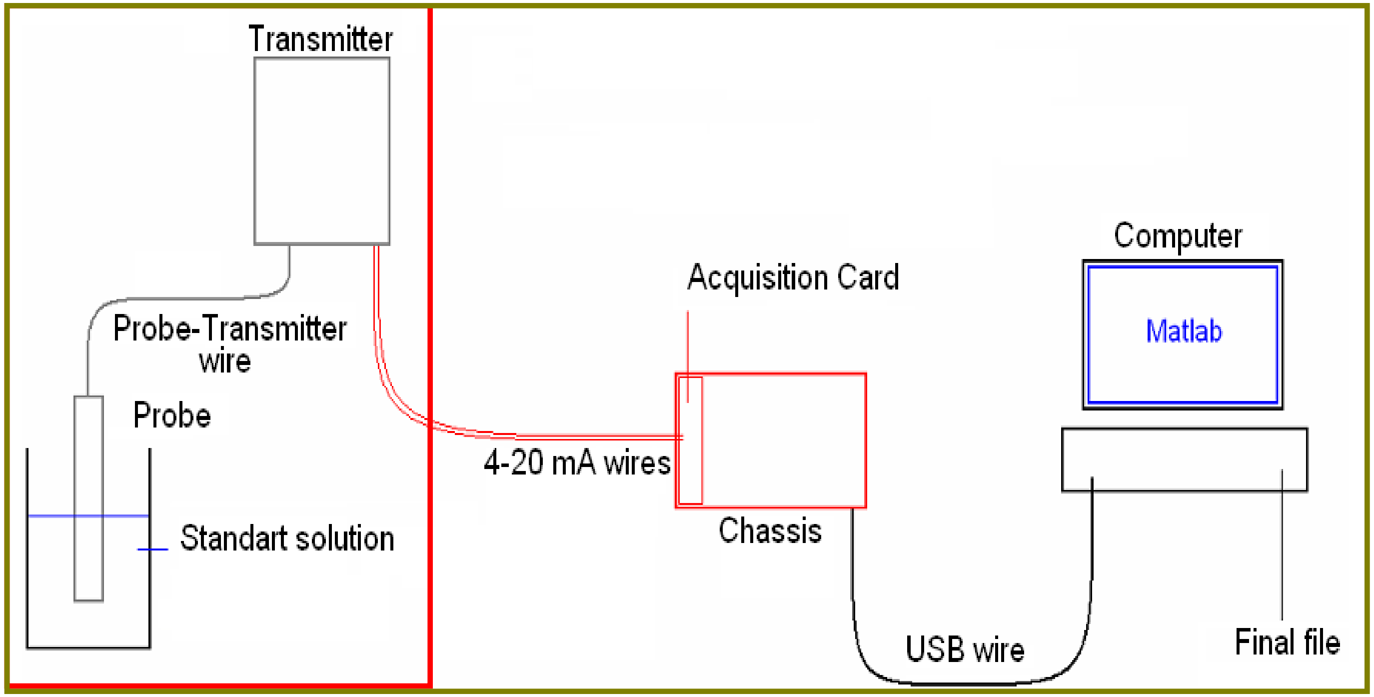
Materials & Methods

- Materials
  - Connexion of sensors



Materials & Methods

- Methods
  - 1. Sensors calibration



Materials & Methods

- Methods
  - 2. Lab analyses and recorded data:
    - Triplicates
    - TSS: NF T90-105-2 (1997)
    - Total and dissolved COD: NF T90-101 (2001)
    - *p* and *u(p)* for each pollutant and each sample
    - 60 values given by sensors (*x* and *u(x)*) or 10-15 spectra for UV-vis

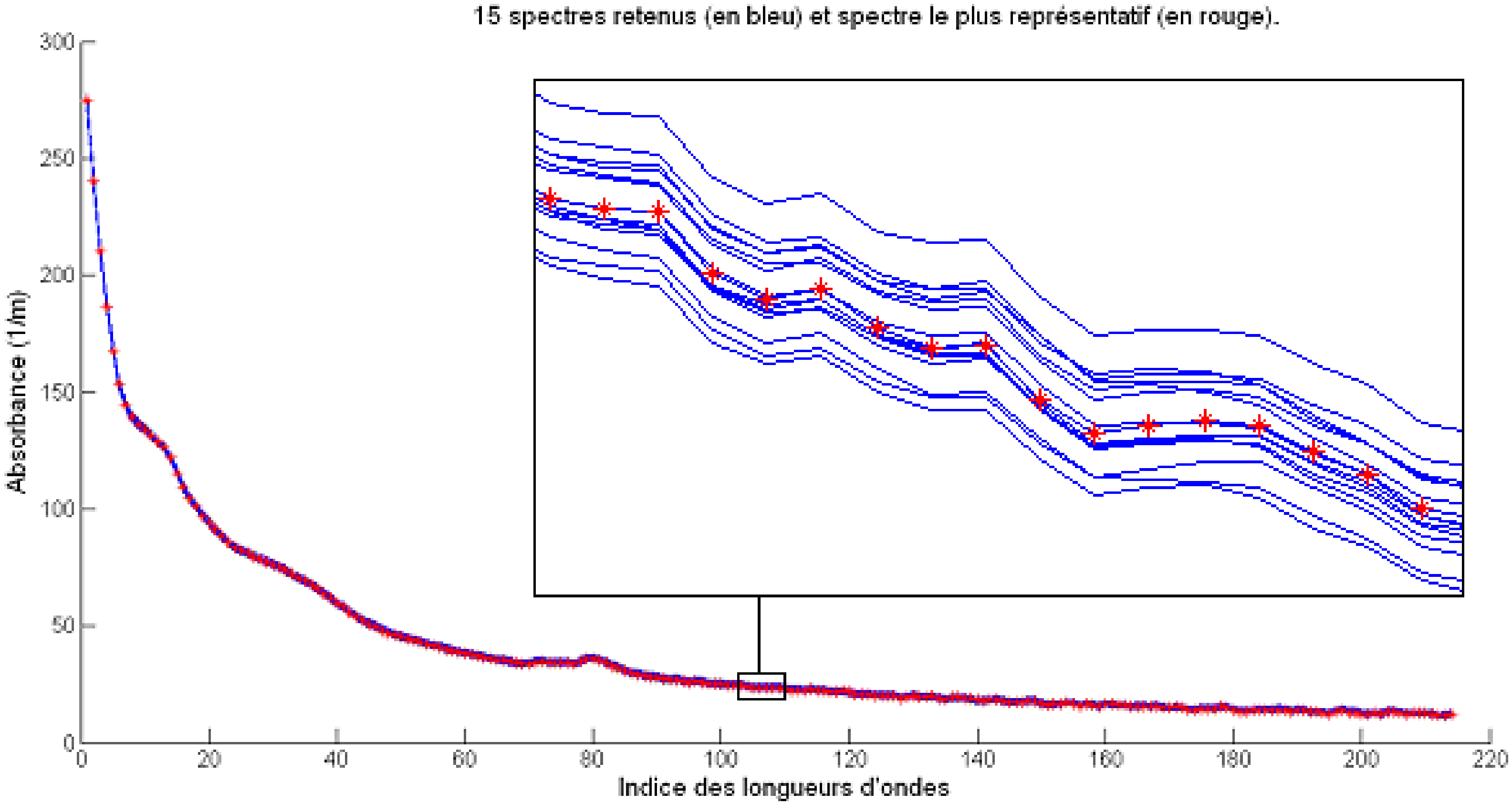
Materials & Methods

- Methods
  - 3. Outliers detection

    3.a. Pretreatment of recorded spectra (for each sample)

    - removal of « most extreme » spectra
    - search of « the most in the middle » one, based of data depth theory (Lopez-Pintado et Romo, 2006)
    - evaluation of standard uncertainty for each wavelength

Materials & Methods



Materials & Methods

- Methods

  3.b. Three steps method (for each dataset, Bertrand Krajewski et al, 2007):

  - outliers in TSS, total and dissolved COD in triplicates
  - too uncertain values (10 % for TSS, 20 % for COD, 5 % for sensors values)
  - abnormal samples:
    - Mahalanobis distance (DM)
    - Euclidean distance (DE), to evaluate if one sample could strongly affect the correlation function

Materials & Methods

- Methods
  - 4. Calculation of correlation functions:
    - For univariate models: Williamson method

$$S = \sum_{i=1}^{M} \left[\frac{1}{u^2(x_i)} \cdot (X_i - x_i)^2 + \frac{1}{u^2(y_i)} \cdot (P_i - p_i)^2 \right]$$

    - For spectral regression: PLS (Torres & Bertrand-Krajewski, 2008)
    - For multivariate models:

$$S_{EXTENDED} = \sum_{i=1}^{M} \left\{ \sum_{j=1}^{N_V} \left[\frac{1}{u^2(x_{j,i})} \cdot (X_{j,i} - x_{j,i})^2 \right] + \frac{1}{u^2(p_i)} \cdot (P_i - p_i)^2 \right\}$$

Materials & Methods

- Methods
  - Evaluation of accuracy
    - RMSEP criterion (Dantas Filho *et al*, 2005)

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{M} \left(P_i - p_i\right)^2}{M}}$$

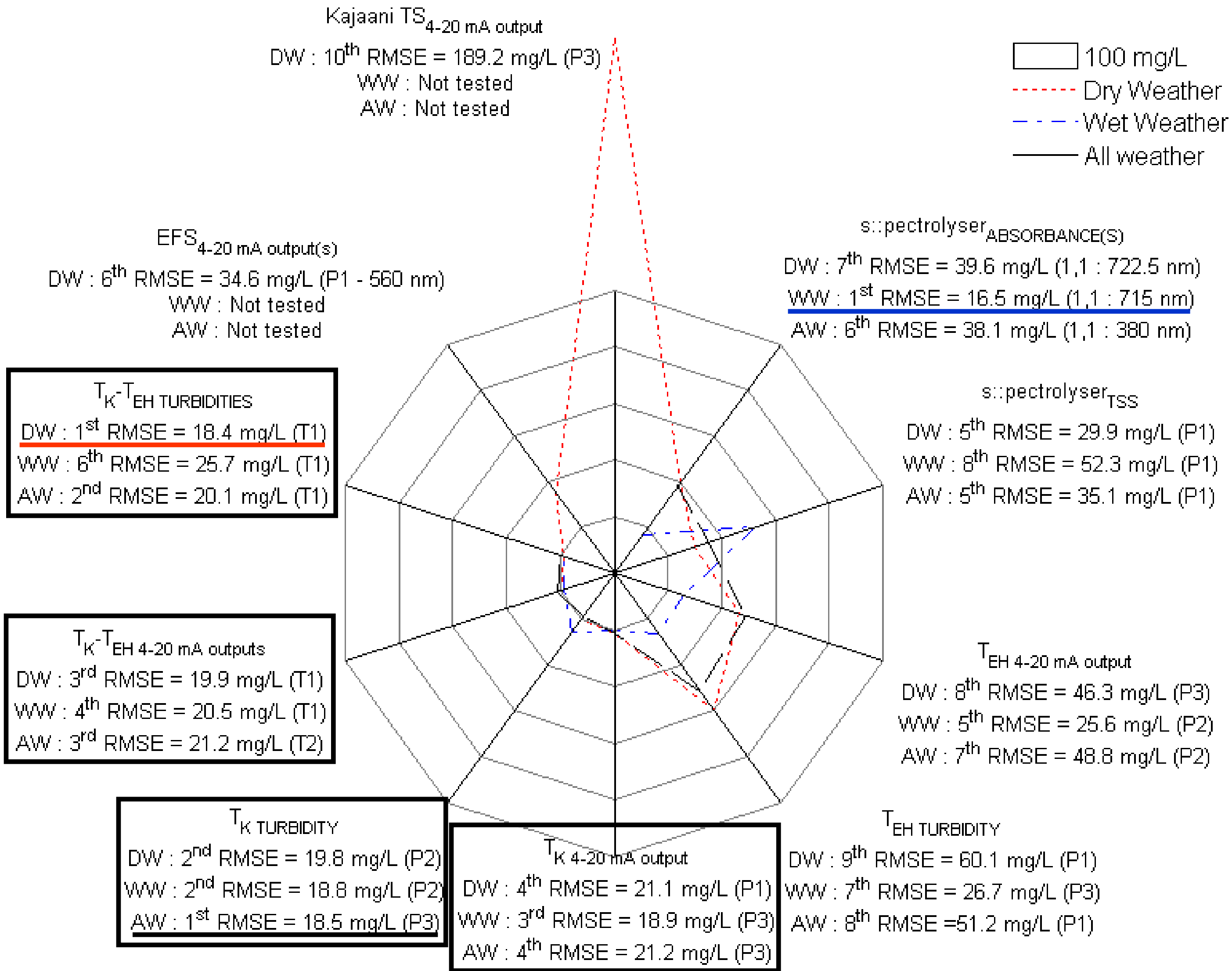
Results

Set	Data	Methods	*n*-tuple (*TSS, total COD, dissolved COD*, …	Initial number	Validated number
Dry	4-20 mA output	*DM*	…, T_{RH} T_K pH, $Cond$)	94	79
Dry	Physical units	*DM*	…, T_{RH} T_K pH, $Cond$)	94	68
Dry	4-20 mA output	*DM*	…, EFS_1, EFS_2)	47	42
Dry	Spectra	*DM*	…, *spectra*)	94	66
Dry	Spectra	*DE*	…, *spectra*)	94	78 - 77 - 79
Wet	4-20 mA output	*DM*	…, T_{RH} T_K pH, $Cond$)	44	40
Wet	Physical units	*DM*	…, T_{RH} T_K pH, $Cond$)	44	30
Wet	Spectra	*DM*	…, *spectra*)	44	34
Wet	Spectra	*DE*	…, *spectra*)	44	34 - 36 - 35
All	4-20 mA output	*DM*	…, T_{RH} T_K pH, $Cond$)	165	144
All	Physical units	*DM*	…, T_{RH} T_K pH, $Cond$)	165	100
All	Spectra	*DM*	…, *spectra*)	165	130
All	Spectra	*DE*	…, *spectra*)	165	136 - 136 - 138

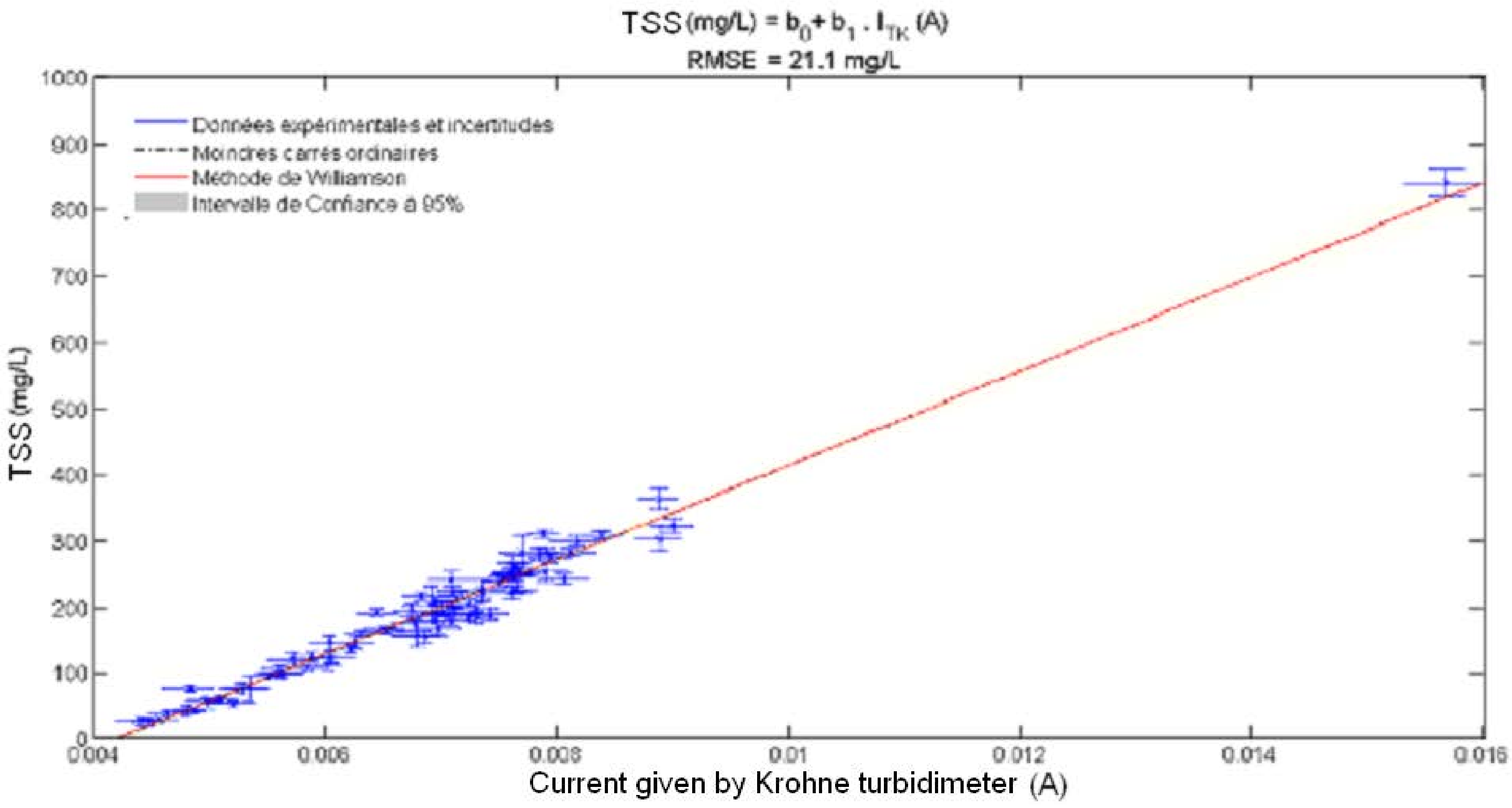
Results

Set	Pollutant	*RMSEP* (mg/L) with DE	*RMSEP* (mg/L) with DM
Dry	TSS, one wavelength	40.0	91.3
Dry	Total COD, one wavelength	61.7	129.1
Dry	Dissolved COD, two wavelengths	28.3	35.3
Dry	Dissolved COD, one wavelength	28.0	30.6
Wet	TSS, one wavelength	16.5	31.6
Wet	Total COD, one wavelength	41.9	41.9
Wet	Dissolved COD, two wavelengths	6.9	8.2
Wet	Dissolved COD, one wavelength	12.1	12.2

Results (for TSS)



Results (for TSS)

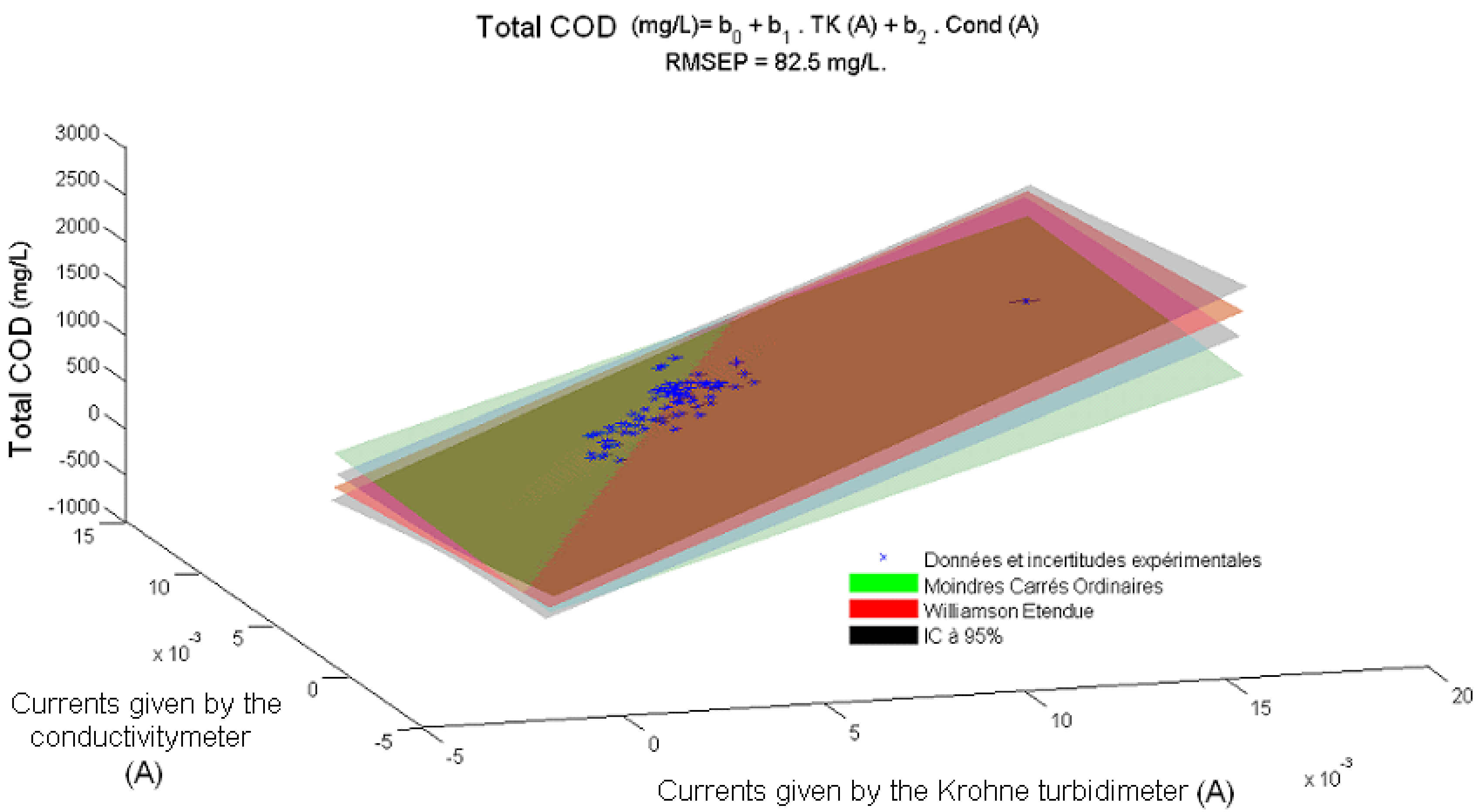


Results (for total COD)

- For each data set
  - DW: 2 wavelengths (EFS)
  - WW: T_{EH}-T_K-Cond
  - AW: T_{EH}-T_K-Cond

- Global conclusions
  - Nephelometric turbidity meter with conductivity meter provides accurate model
  - Spectrometer (local > spectral)

Results


Total COD (mg/L)= b0 + b1 . TK (A) + b2 . Cond (A)
RMSEP = 82.5 mg/L.
Total COD (mg/L)
3000
2500
2000
1500
1000
500
0
-500
-1000
15
10
5
0
-5
x 10-3
Currents given by the conductivitymeter (A)
-5
0
5
10
15
20
x 10-3
Currents given by the Krohne turbidimeter (A)
Données et incertitudes expérimentales
Moindres Carrés Ordinaires
Williamson Etendue
IC à 95%

Results (for dissolved COD)

- Spectral calibration provides always the best models (200 – 230 nm)

Conclusions (Methods)

- DE method give more accurate models than DM method
- A PLS calibration is not always more accurate than a local calibration
- 4-20 mA outputs and physical units provide models with comparable accuracy

Conclusions (Sensors)

- No sensor is the most accurate one for all pollutants and all data sets
- Microwave sensor was not adapted to our range of concentrations
- Use of conductivity seems to improve the accuracy to predict total COD concentrations

Thanks for you attention

Questions ? ...

Models tested

- Polynomials: $[P] = c_0 + \sum_{i=1}^{N_{MAX}} c_i \times X^i$
- Multivariate models:

$$[P] = c_0 + c_1 \times X + c_2 \times Y + c_3 \times Z$$

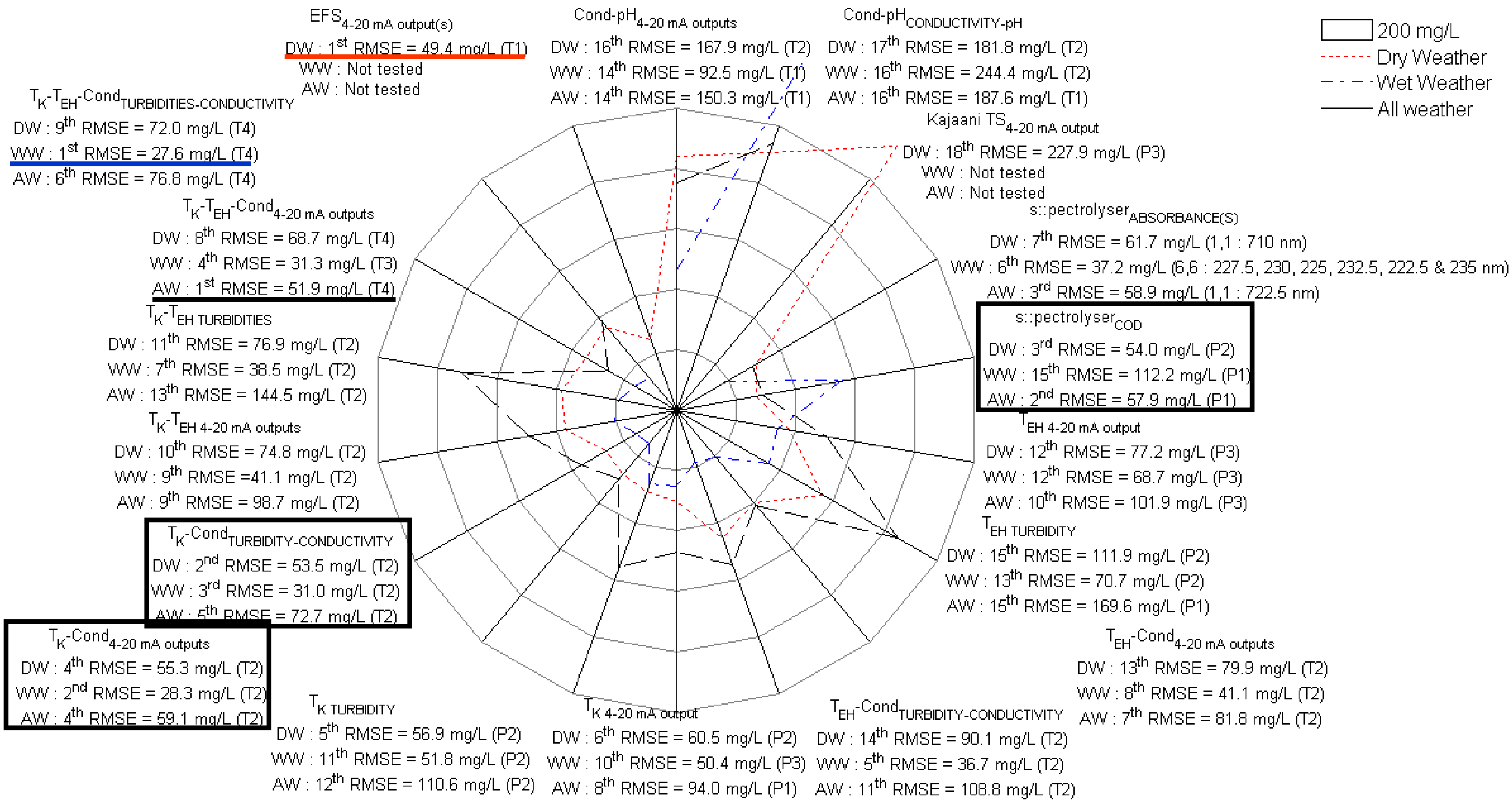
$$[P] = c_0 + c_1 \times X + c_2 \times Y + c_3 \times X^2 + c_4 \times Y^2 + c_5 \times X \times Y$$

$$[P] = c_0 + c_1 \times X + c_2 \times Y$$

$$[P] = c_0 + c_1 \times X + c_2 \times Y + c_3 \times Z + c_4 \times X^2 + c_5 \times Y^2 + c_6 \times Z^2 + c_7 \times X \times Y + c_8 \times X \times Z + c_9 \times Y \times Z$$

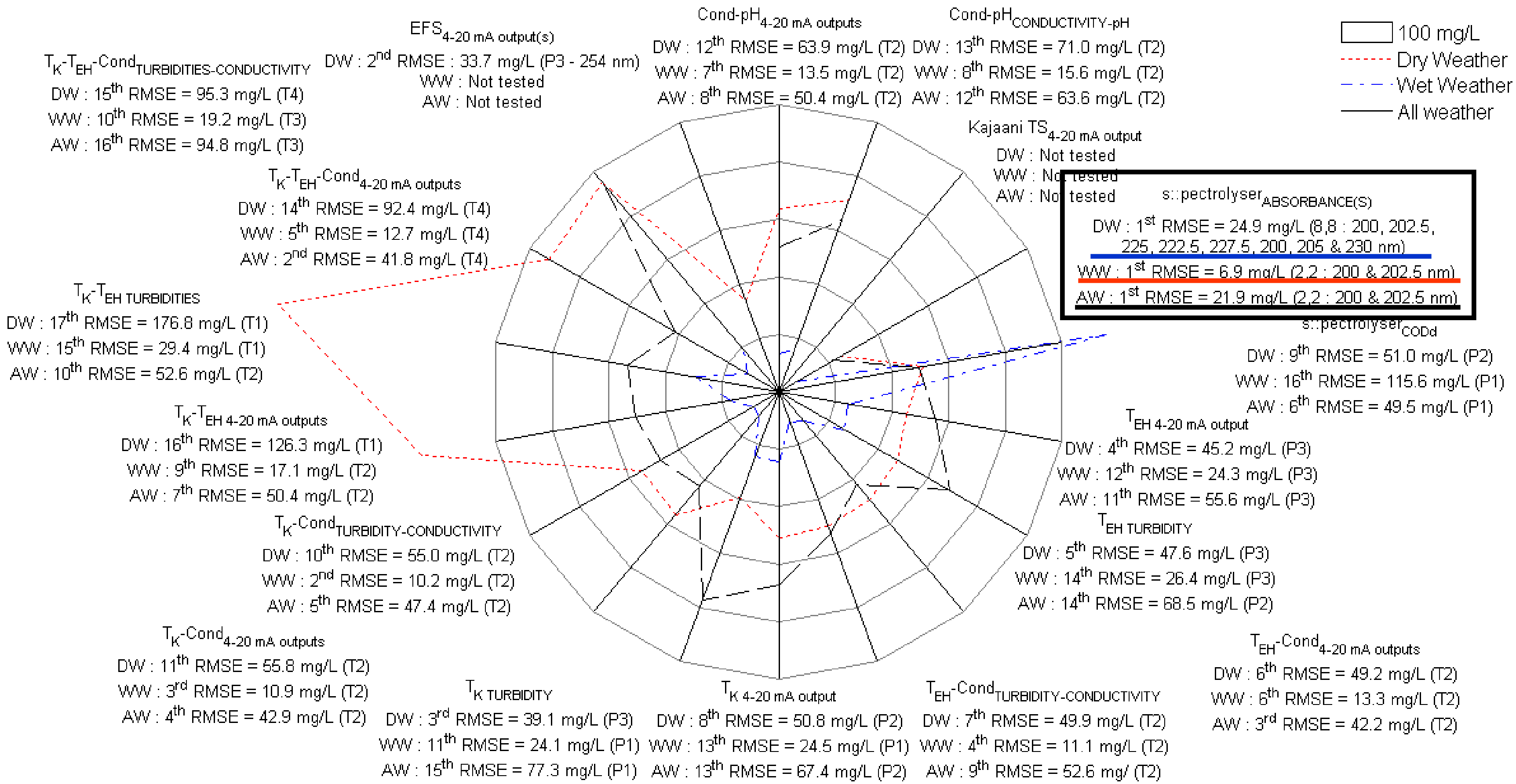
- PLS models: $[P] = c_0 + \sum_{i=1}^{N_{VI}} c_i \times Abs_i$

Results



200 mg/L
Dry Weather
Wet Weather
All weather
EFS4-20 mA output(s)
DW : 1st RMSE = 49.4 mg/L (T1)
WW : Not tested
AW : Not tested
Cond-pH4-20 mA outputs
DW : 16th RMSE = 167.9 mg/L (T2)
WW : 14th RMSE = 92.5 mg/L (T1)
AW : 14th RMSE = 150.3 mg/L (T1)
Cond-pHCONDUCTIVITY-pH
DW : 17th RMSE = 181.8 mg/L (T2)
WW : 16th RMSE = 244.4 mg/L (T2)
AW : 16th RMSE = 187.6 mg/L (T1)
Kajaani TS4-20 mA output
DW : 18th RMSE = 227.9 mg/L (P3)
WW : Not tested
AW : Not tested
s::pectrolyserABSORBANCE(S)
DW : 7th RMSE = 61.7 mg/L (1,1 : 710 nm)
WW : 6th RMSE = 37.2 mg/L (6,6 : 227.5, 230, 225, 232.5, 222.5 & 235 nm)
AW : 3rd RMSE = 58.9 mg/L (1,1 : 722.5 nm)
s::pectrolyserCOD
DW : 3rd RMSE = 54.0 mg/L (P2)
WW : 15th RMSE = 112.2 mg/L (P1)
AW : 2nd RMSE = 57.9 mg/L (P1)
TEH 4-20 mA output
DW : 12th RMSE = 77.2 mg/L (P3)
WW : 12th RMSE = 68.7 mg/L (P3)
AW : 10th RMSE = 101.9 mg/L (P3)
TEH TURBIDITY
DW : 15th RMSE = 111.9 mg/L (P2)
WW : 13th RMSE = 70.7 mg/L (P2)
AW : 15th RMSE = 169.6 mg/L (P1)
TEH-Cond4-20 mA outputs
DW : 13th RMSE = 79.9 mg/L (T2)
WW : 8th RMSE = 41.1 mg/L (T2)
AW : 7th RMSE = 81.8 mg/L (T2)
TEH-CondTURBIDITY-CONDUCTIVITY
DW : 14th RMSE = 90.1 mg/L (T2)
WW : 5th RMSE = 36.7 mg/L (T2)
AW : 11th RMSE = 108.8 mg/L (T2)
TK 4-20 mA output
DW : 6th RMSE = 60.5 mg/L (P2)
WW : 10th RMSE = 50.4 mg/L (P3)
AW : 8th RMSE = 94.0 mg/L (P1)
TK TURBIDITY
DW : 5th RMSE = 56.9 mg/L (P2)
WW : 11th RMSE = 51.8 mg/L (P2)
AW : 12th RMSE = 110.6 mg/L (P2)
TK-Cond4-20 mA outputs
DW : 4th RMSE = 55.3 mg/L (T2)
WW : 2nd RMSE = 28.3 mg/L (T2)
AW : 4th RMSE = 59.1 mg/L (T2)
TK-CondTURBIDITY-CONDUCTIVITY
DW : 2nd RMSE = 53.5 mg/L (T2)
WW : 3rd RMSE = 31.0 mg/L (T2)
AW : 5th RMSE = 72.7 mg/L (T2)
TK-TEH 4-20 mA outputs
DW : 10th RMSE = 74.8 mg/L (T2)
WW : 9th RMSE =41.1 mg/L (T2)
AW : 9th RMSE = 98.7 mg/L (T2)
TK-TEH TURBIDITIES
DW : 11th RMSE = 76.9 mg/L (T2)
WW : 7th RMSE = 38.5 mg/L (T2)
AW : 13th RMSE = 144.5 mg/L (T2)
TK-TEH-Cond4-20 mA outputs
DW : 8th RMSE = 68.7 mg/L (T4)
WW : 4th RMSE = 31.3 mg/L (T3)
AW : 1st RMSE = 51.9 mg/L (T4)
TK-TEH-CondTURBIDITIES-CONDUCTIVITY
DW : 9th RMSE = 72.0 mg/L (T4)
WW : 1st RMSE = 27.6 mg/L (T4)
AW : 6th RMSE = 76.8 mg/L (T4)

Results



100 mg/L
Dry Weather
Wet Weather
All weather
T_K-T_{EH}-$Cond_{TURBIDITIES-CONDUCTIVITY}$
DW : 15th RMSE = 95.3 mg/L (T4)
WW : 10th RMSE = 19.2 mg/L (T3)
AW : 16th RMSE = 94.8 mg/L (T3)
$EFS_{4-20\ mA\ output(s)}$
DW : 2nd RMSE : 33.7 mg/L (P3 - 254 nm)
WW : Not tested
AW : Not tested
$Cond$-$pH_{4-20\ mA\ outputs}$
DW : 12th RMSE = 63.9 mg/L (T2)
WW : 7th RMSE = 13.5 mg/L (T2)
AW : 8th RMSE = 50.4 mg/L (T2)
$Cond$-$pH_{CONDUCTIVITY-pH}$
DW : 13th RMSE = 71.0 mg/L (T2)
WW : 8th RMSE = 15.6 mg/L (T2)
AW : 12th RMSE = 63.6 mg/L (T2)
Kajaani $TS_{4-20\ mA\ output}$
DW : Not tested
WW : Not tested
AW : Not tested
$s::pectrolyser_{ABSORBANCE(S)}$
DW : 1st RMSE = 24.9 mg/L (8,8 : 200, 202.5, 225, 222.5, 227.5, 200, 205 & 230 nm)
WW : 1st RMSE = 6.9 mg/L (2,2 : 200 & 202.5 nm)
AW : 1st RMSE = 21.9 mg/L (2,2 : 200 & 202.5 nm)
$s::pectrolyser_{CODd}$
DW : 9th RMSE = 51.0 mg/L (P2)
WW : 16th RMSE = 115.6 mg/L (P1)
AW : 6th RMSE = 49.5 mg/L (P1)
T_K-T_{EH}-$Cond_{4-20\ mA\ outputs}$
DW : 14th RMSE = 92.4 mg/L (T4)
WW : 5th RMSE = 12.7 mg/L (T4)
AW : 2nd RMSE = 41.8 mg/L (T4)
T_K-$T_{EH\ TURBIDITIES}$
DW : 17th RMSE = 176.8 mg/L (T1)
WW : 15th RMSE = 29.4 mg/L (T1)
AW : 10th RMSE = 52.6 mg/L (T2)
T_K-$T_{EH\ 4-20\ mA\ outputs}$
DW : 16th RMSE = 126.3 mg/L (T1)
WW : 9th RMSE = 17.1 mg/L (T2)
AW : 7th RMSE = 50.4 mg/L (T2)
$T_{EH\ 4-20\ mA\ output}$
DW : 4th RMSE = 45.2 mg/L (P3)
WW : 12th RMSE = 24.3 mg/L (P3)
AW : 11th RMSE = 55.6 mg/L (P3)
T_K-$Cond_{TURBIDITY-CONDUCTIVITY}$
DW : 10th RMSE = 55.0 mg/L (T2)
WW : 2nd RMSE = 10.2 mg/L (T2)
AW : 5th RMSE = 47.4 mg/L (T2)
$T_{EH\ TURBIDITY}$
DW : 5th RMSE = 47.6 mg/L (P3)
WW : 14th RMSE = 26.4 mg/L (P3)
AW : 14th RMSE = 68.5 mg/L (P2)
T_K-$Cond_{4-20\ mA\ outputs}$
DW : 11th RMSE = 55.8 mg/L (T2)
WW : 3rd RMSE = 10.9 mg/L (T2)
AW : 4th RMSE = 42.9 mg/L (T2)
T_{EH}-$Cond_{4-20\ mA\ outputs}$
DW : 6th RMSE = 49.2 mg/L (T2)
WW : 6th RMSE = 13.3 mg/L (T2)
AW : 3rd RMSE = 42.2 mg/L (T2)
$T_{K\ TURBIDITY}$
DW : 3rd RMSE = 39.1 mg/L (P3)
WW : 11th RMSE = 24.1 mg/L (P1)
AW : 15th RMSE = 77.3 mg/L (P1)
$T_{K\ 4-20\ mA\ output}$
DW : 8th RMSE = 50.8 mg/L (P2)
WW : 13th RMSE = 24.5 mg/L (P1)
AW : 13th RMSE = 67.4 mg/L (P2)
T_{EH}-$Cond_{TURBIDITY-CONDUCTIVITY}$
DW : 7th RMSE = 49.9 mg/L (T2)
WW : 4th RMSE = 11.1 mg/L (T2)
AW : 9th RMSE = 52.6 mg/ (T2)