

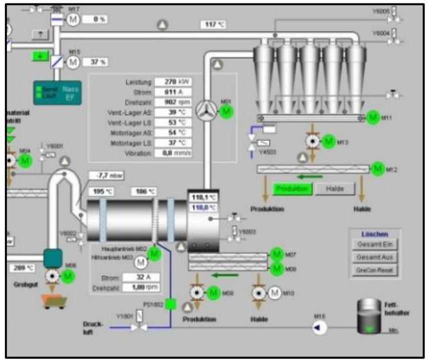


PhD defense – *September 17, 2021*

# Near infrared spectroscopy applied to solid organic waste: how to avoid water effects?

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*Co-supervised by Eric LATRILLE, Ryad BENDOULA and Cyrille CHARNIER*

0.1

# Agenda

Summary of contents

# 1. Introduction, context, scientific objectives

# 1.1 Introduction, context, scientific objectives

## The anaerobic co-digestion process

**Inputs** → **Anaerobic Digestion** → **Outputs**

Biowaste

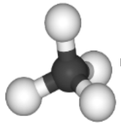
Sludge from sewage treatment

Crop residues

Urban and industrial effluents

Animal manure

New biomass



Biogas ($CH_4$)

- Combined Heat Power (CHP)
- Gas grid injection
- Vehicle fuel

Digestate

Fertilizer

- **Highly diverse biochemical and physical properties**
- **Daily fluctuations of quality/quantity**

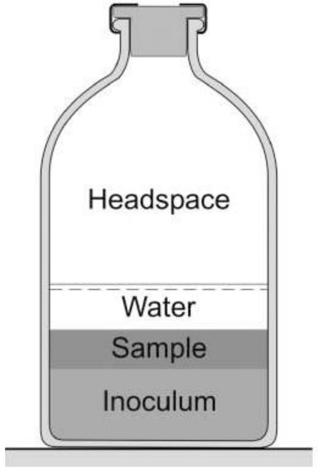
- **How to optimize the feeding recipe?**

- **Requires fast and reliable substrate characterization tools**

# 1.1 Introduction, context, scientific objectives

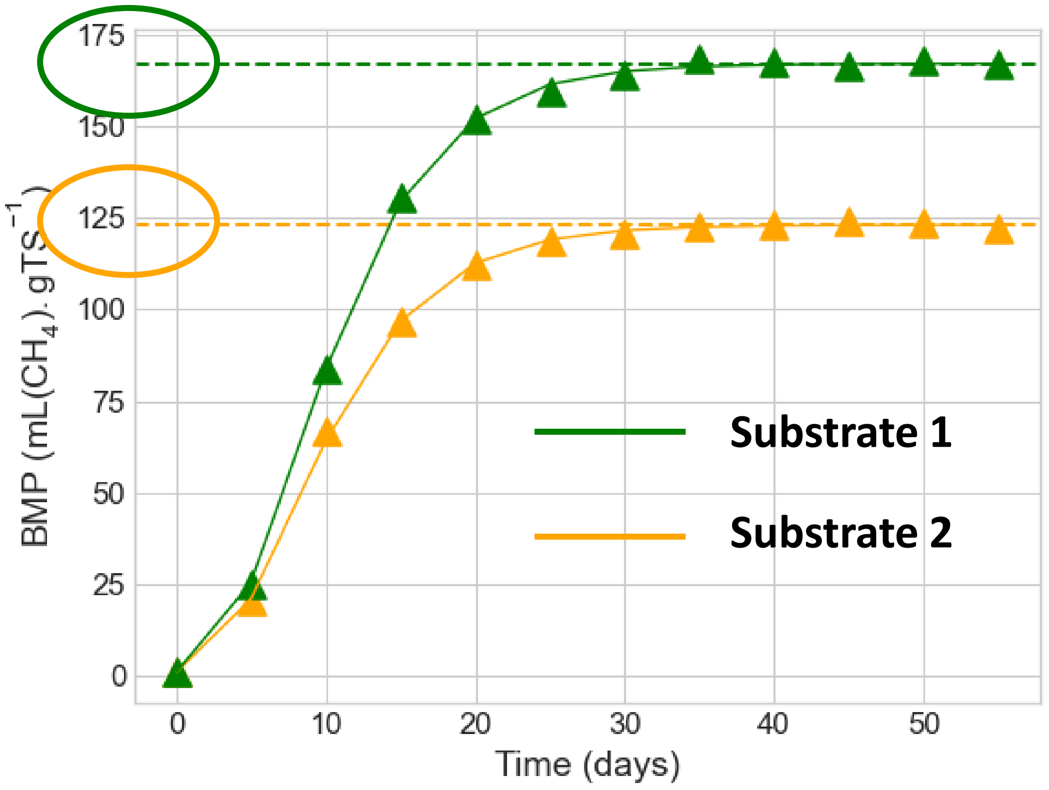
## Substrate characterization: the biochemical methane potential (BMP)[1]

**Organic waste**




**Anaerobic digestion**
**30-60 days**

**Monitoring of gas production**



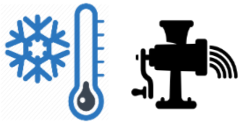

Angelidaki et al., *Water Science Technology*, 2009.

# 1.1 Introduction, context, scientific objectives

## Operational context: a NIRS-based characterization tool (IRSCAN)

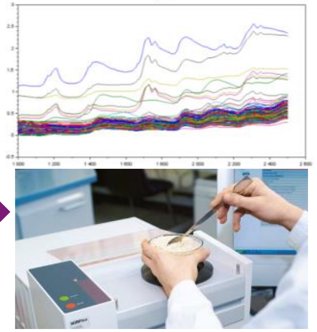
Substrates (organic waste)

Freeze-drying and grinding



0 → 4 days

NIR scan
(reflectance mode & 1000-2500 nm)



Chemometrics

- **Methane potential (BMP)**[1]
- Proteins[2]
- Lipids[2]
- Carbohydrates[2]
- Chemical Oxygen Demand (COD)[2]
- $CH_4$ kinetics[2]

[1] Lesteur et al., *Bioresource Technology*, 2011.
[2] Charnier et al., *Waste Management*, 2016.

### Advantages

- **Fast measurement** (4 days vs. 1-2 months)
- Applicable **on high diversity of waste**
- Accuracy and **reproducibility**
- Possible to optimize feeding strategy

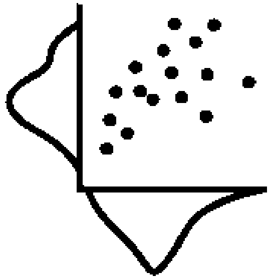
### Hurdles

- **Sample preparation is required** to reduce effects of water and particle size :
  - **Time-consuming step** + additional costs
  - **Loss of volatile fraction** during drying
  - **Limits online applications**

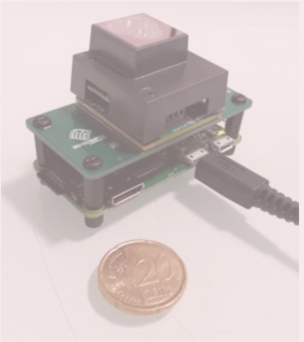
# 1.1 Introduction, context, scientific objectives

## Operational context: online and on-site analysis of substrates

➢ Can we **avoid freeze-drying steps**, and **analyze fresh matter** by NIRS directly?



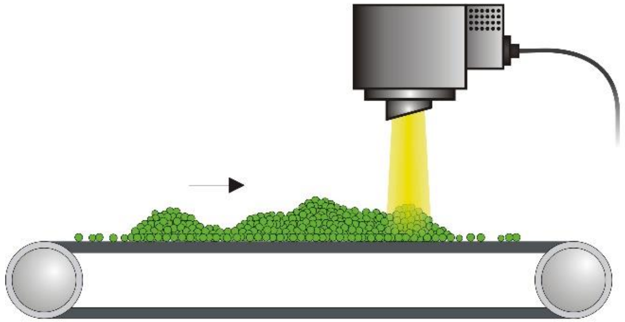
1) Can **modeling strategies be found to account for water effects?**



2) Are **handheld spectrometers suitable** for characterizing diverse organic waste?

➢ **Potential applications:**

➢ **Online** analysis



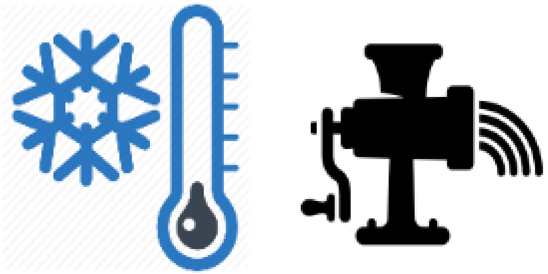
➢ **On-site** analysis

# 1.2 Introduction, context, scientific objectives

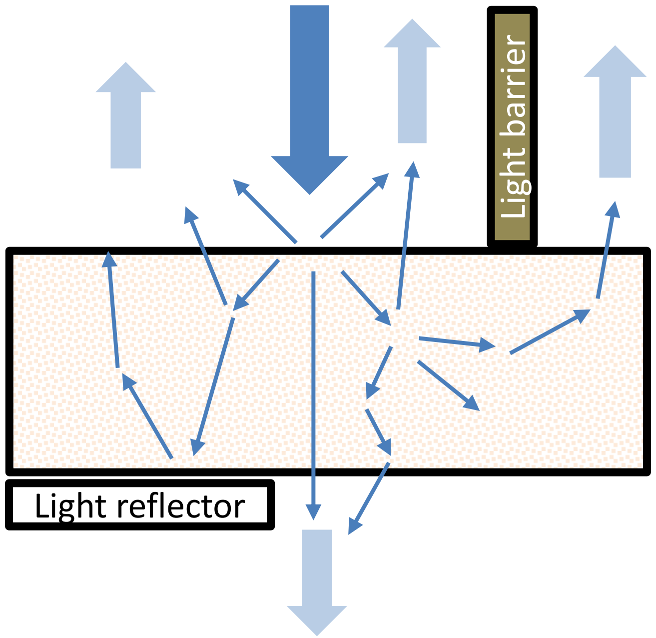
## How to build robust models against water effects?

| Can the influencing factor be controlled? | Can the measurement method be less influenced by the factor? | Can the model pipeline be less influenced by the factor? |
| --- | --- | --- |

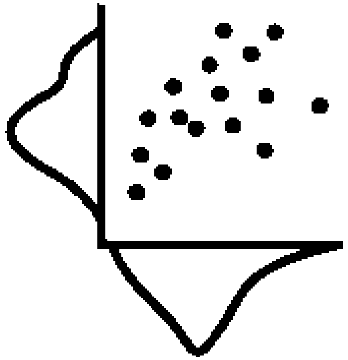
**Sample preparation**
(grinding, drying, dilution, filtering)



**Measurement mode**
(reflectance/transmittance/interactance, distance/contact, polarization)

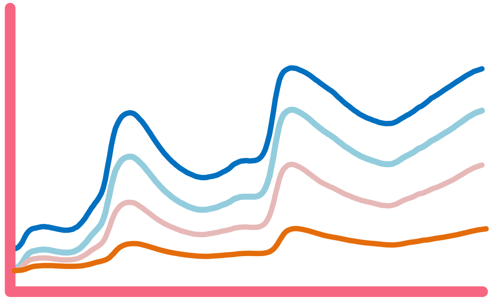
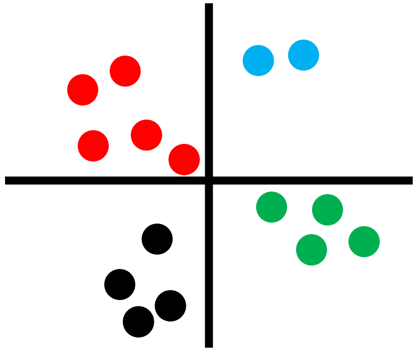



**Pre-processing, modeling**

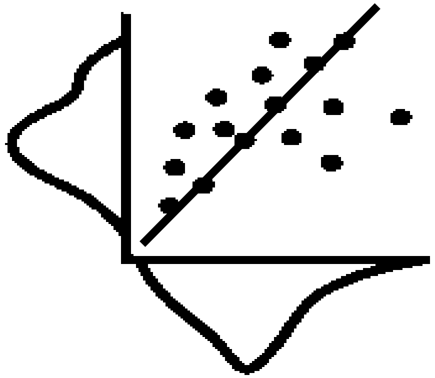


## Scientific objectives

- 1) To develop a <u>better understanding of the moisture content effects</u> on NIRS applied to a wide range of organic materials

- 2) To find <u>new ways of building models that are robust</u> to moisture content effects

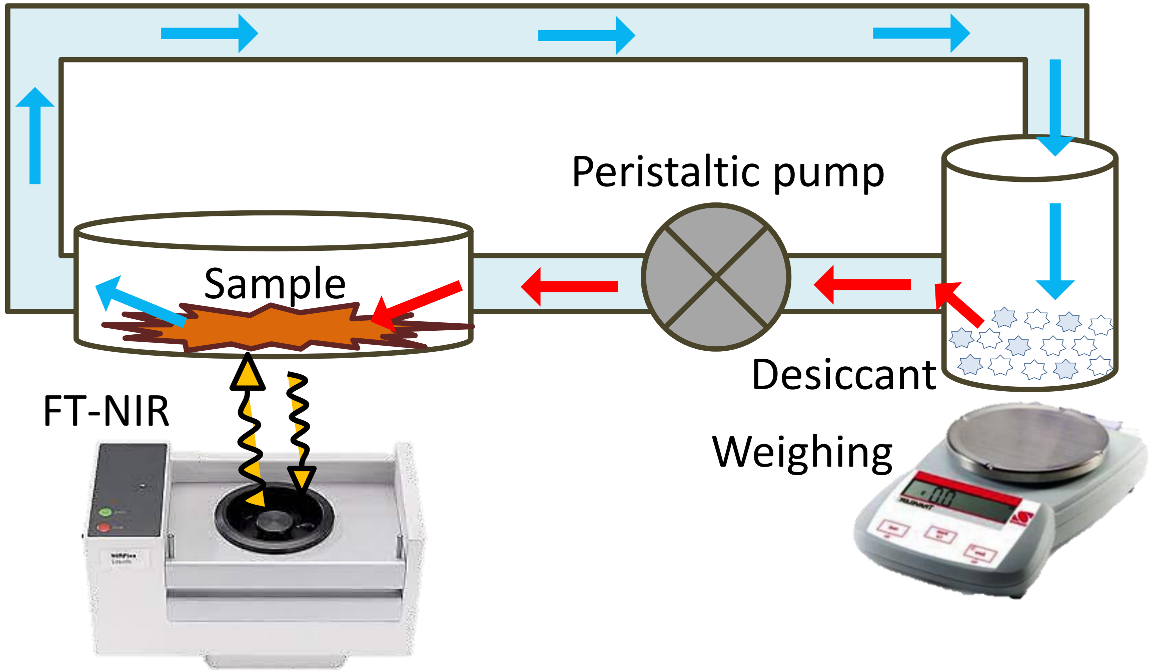


# 2. Materials & Methods

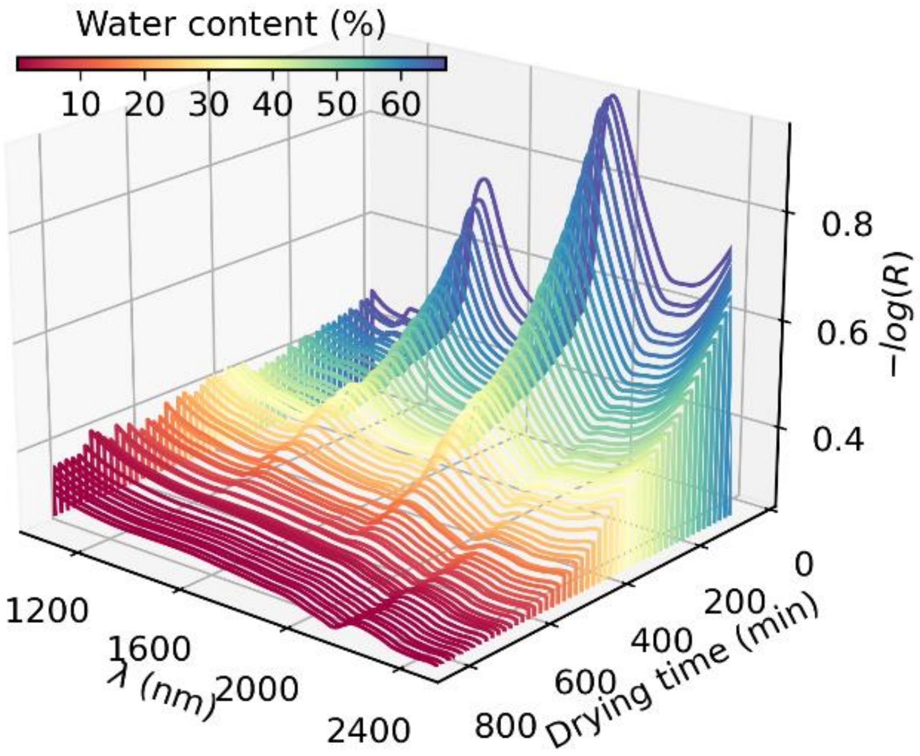
# 2.1 Materials & Methods

## An innovative system to collect spectral variations related to water variations

- **Closed circuit air-drying system with NIRS and water content monitoring**




- **Evolution of NIR spectra with water content %**

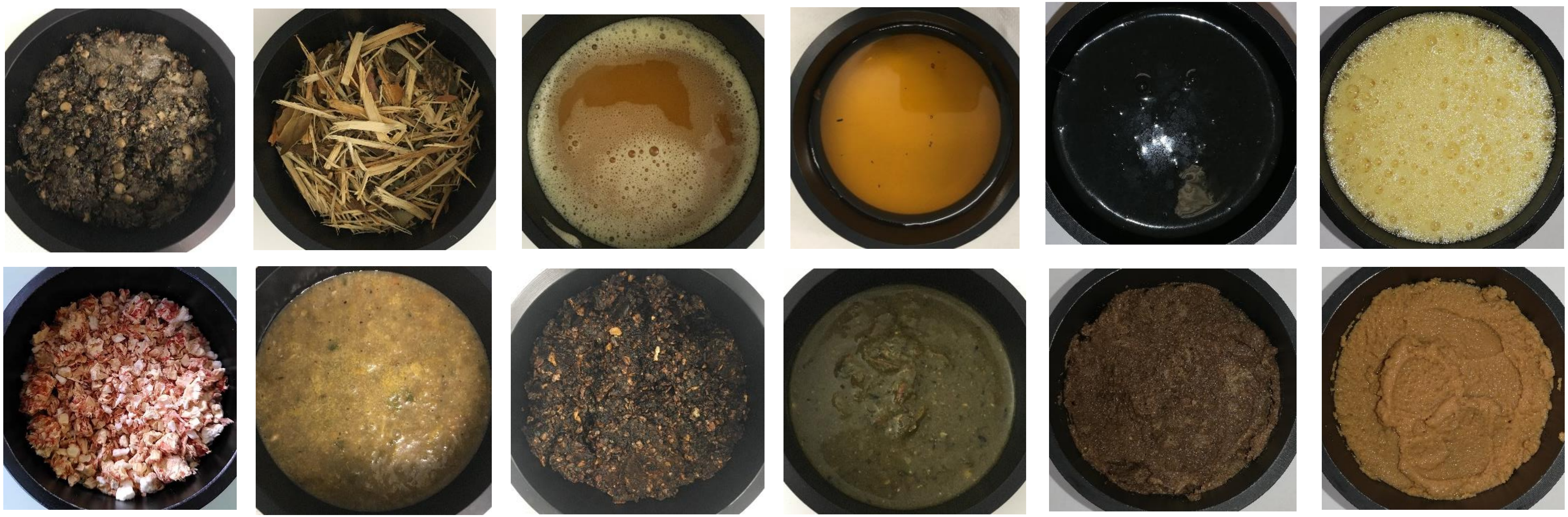



- **89 substrates, 120 000 spectra, DM% = 1-99%**
- Analysis of each substrate with IR-SCAN (**freeze-dried/ground spectra + characterization in lipids/proteins/carbohydrates/COD**)

# 2.2 Materials & Methods

## Analyzed substrates

➢ A **wide range of physical properties and biochemical composition**



[6] d

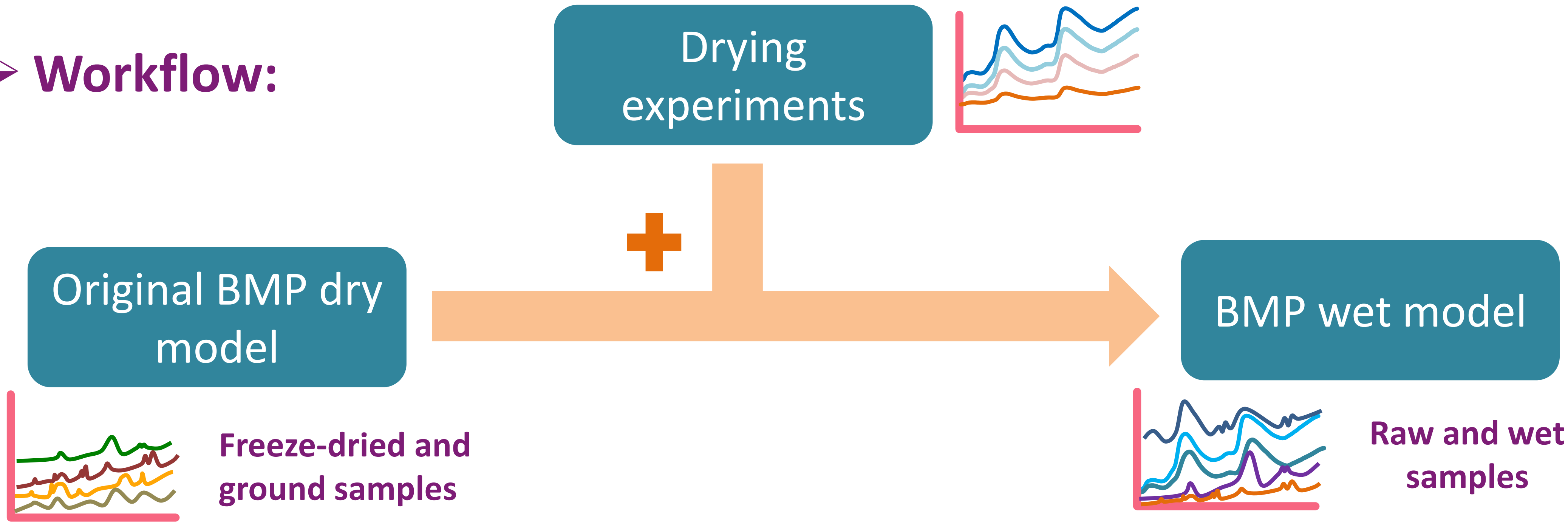
# 3.1 Results – Global correction of models

# 3.1 Global correction of models

## Objective, Materials & Methods

- **Objective:**
  - **Evaluate <u>global correction methods to account for moisture content</u> variations** in a calibration model (*i.e.*, a **« one global model for all »**)
  - **BMP prediction**

- **Workflow:**



# 3.1 Global correction of models

## Objective, Materials & Methods

## ➢ Methods evaluated:

**Feature selection** *(cut water bands)*
Wu et al., Soil Science, 2009.

**Scaling, skewing** (GLSW)
Bro et al., Journal of Chemometrics, 2003.
Martens et al., Journal of Chemometrics, 2003.

**Orthogonal projections** *(EPO, OSC-EPO)*
Roger et al., Chem. Intel. Lab. Systems, 2003.
Preys et al., Chem. Intel. Lab. Systems, 2008.

**Transfer** (*PDS*)
Wang et al., Analytical Chemistry, 1991.
Ji et al., Eur. Jour. of Soil Science, 2015.

**Model update**
Andries et al., Journal of Chemometrics, 2019.

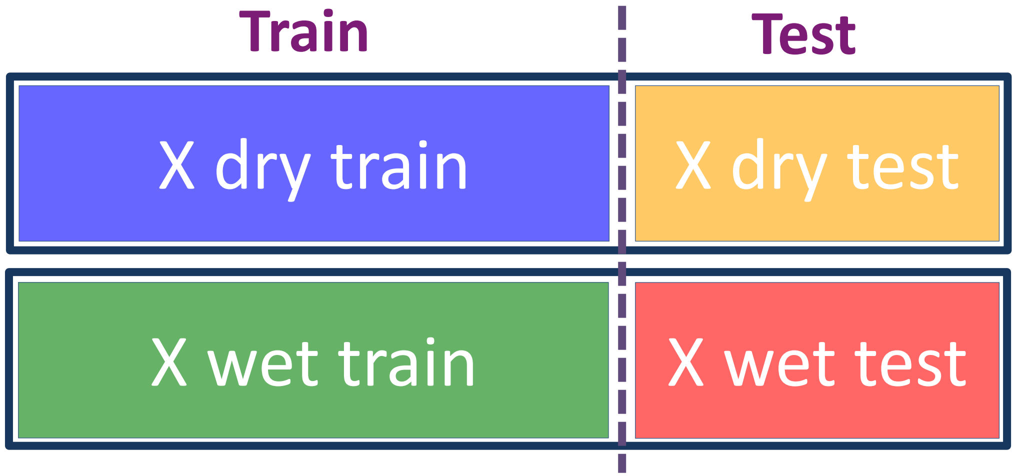
**Repeatability file**
Tillman et al., Jour. of Near Infrared Spectroscopy, 1998.

**Stacking**

## ➢ Datasets:

**Freeze-dried and ground** samples = **X dry**

**Raw** samples analyzed during drying = **X wet**

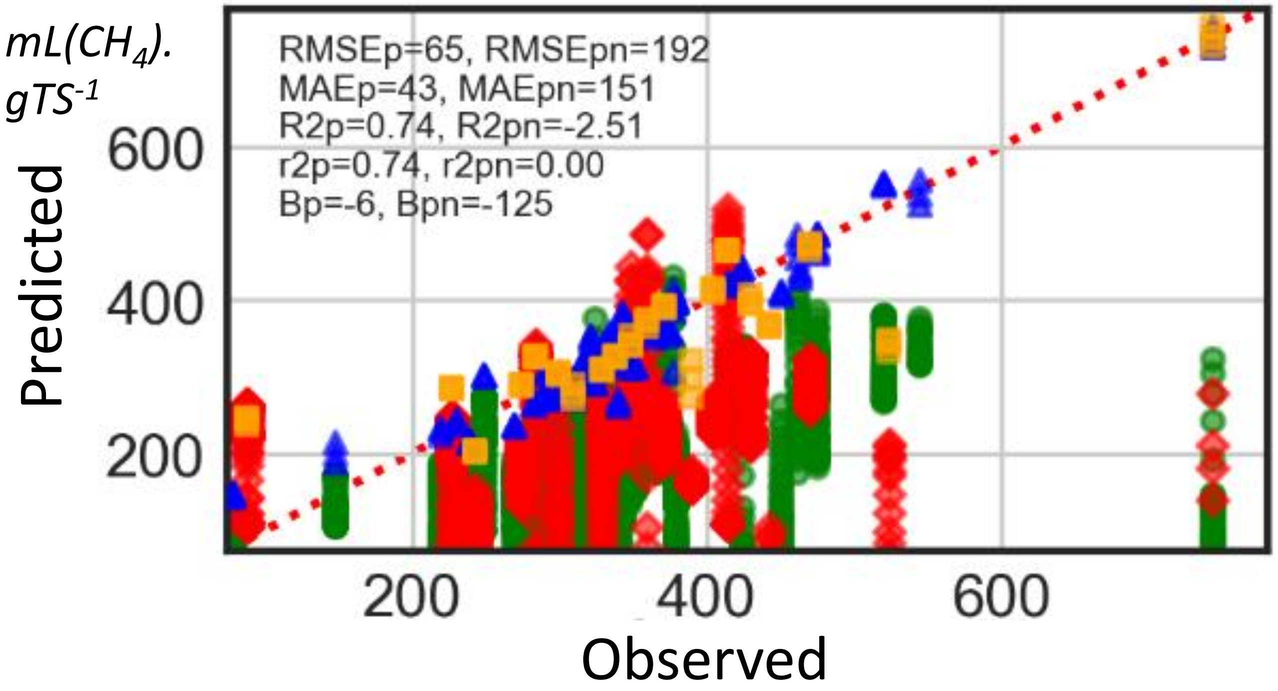


# 3.1 Global correction of models

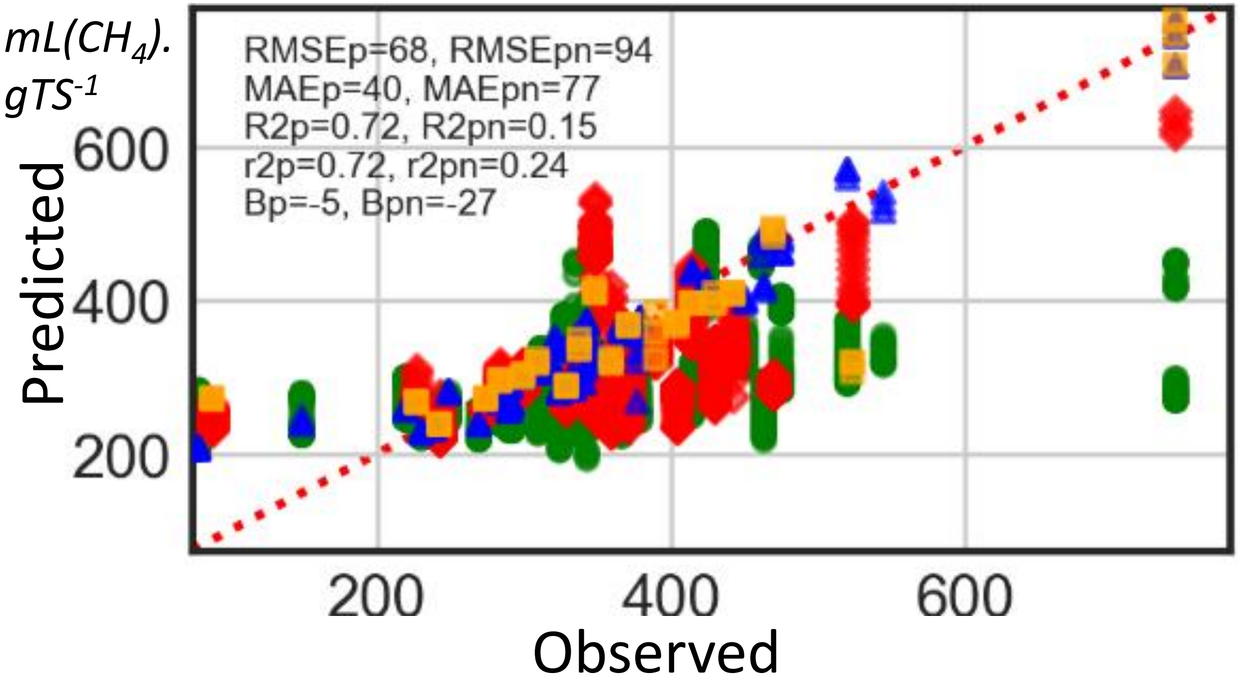
## Results – model performances

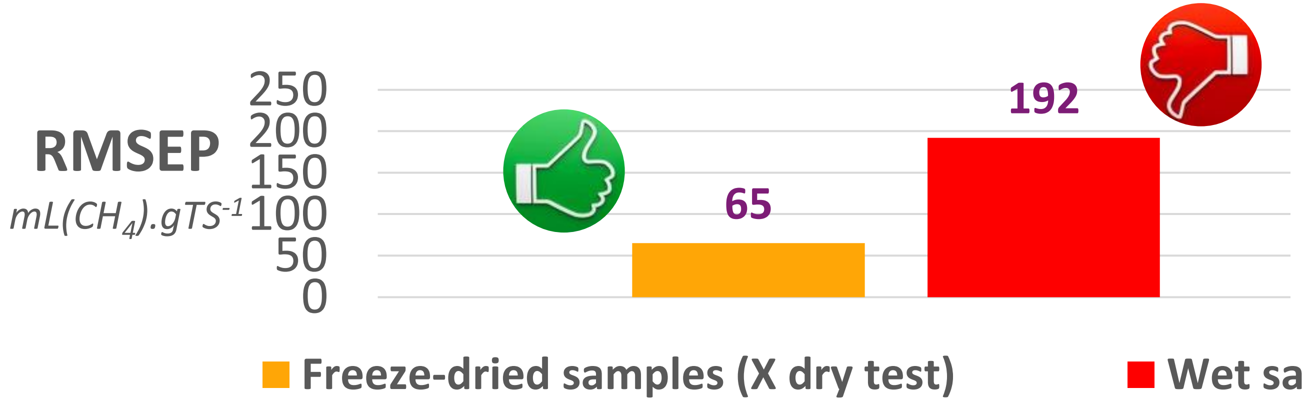
Identity line | X dry train | X dry test | X wet train | X wet test

### Original model (no correction)




### With correction (Repeatability File)



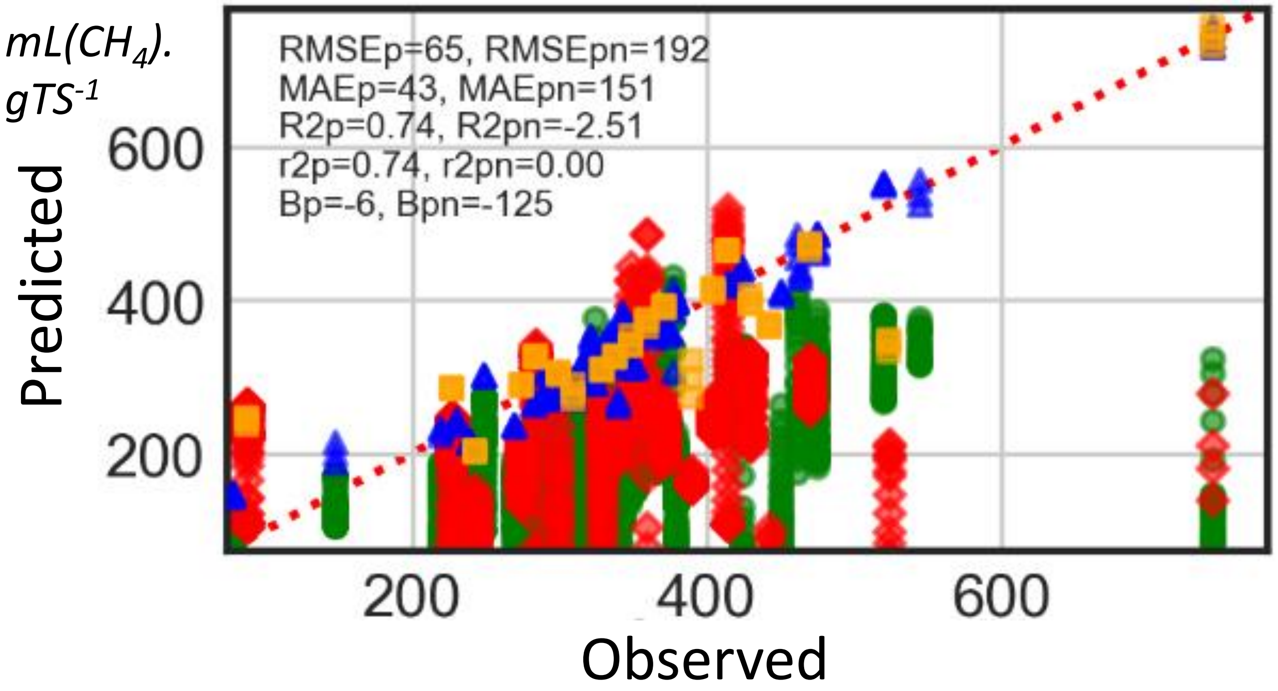



# 3.1 Global correction of models

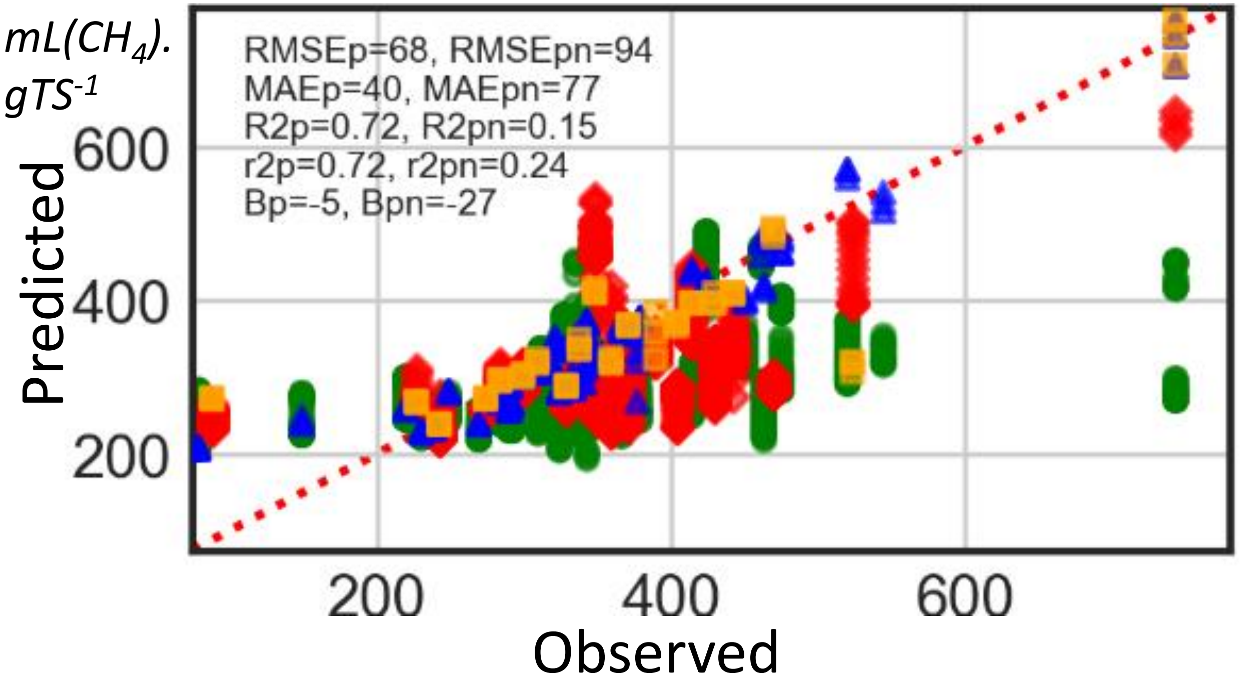
## Results – model performances

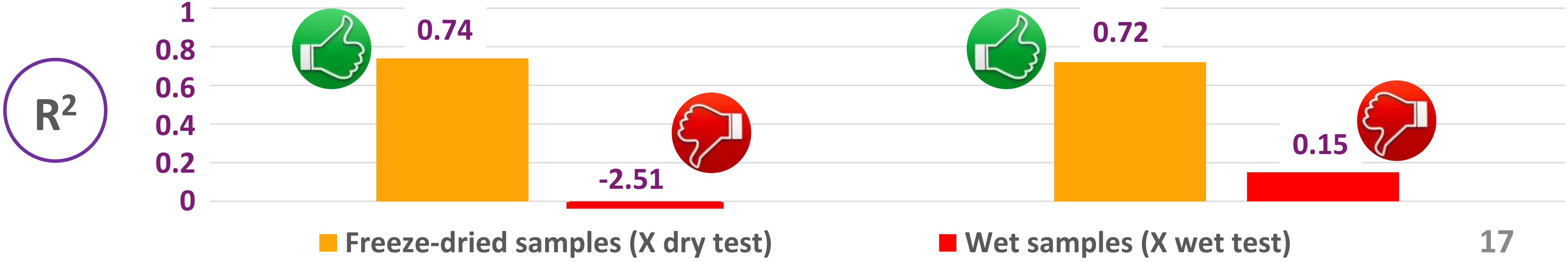
Identity line · X dry train · X dry test · X wet train · X wet test

### Original model (no correction)



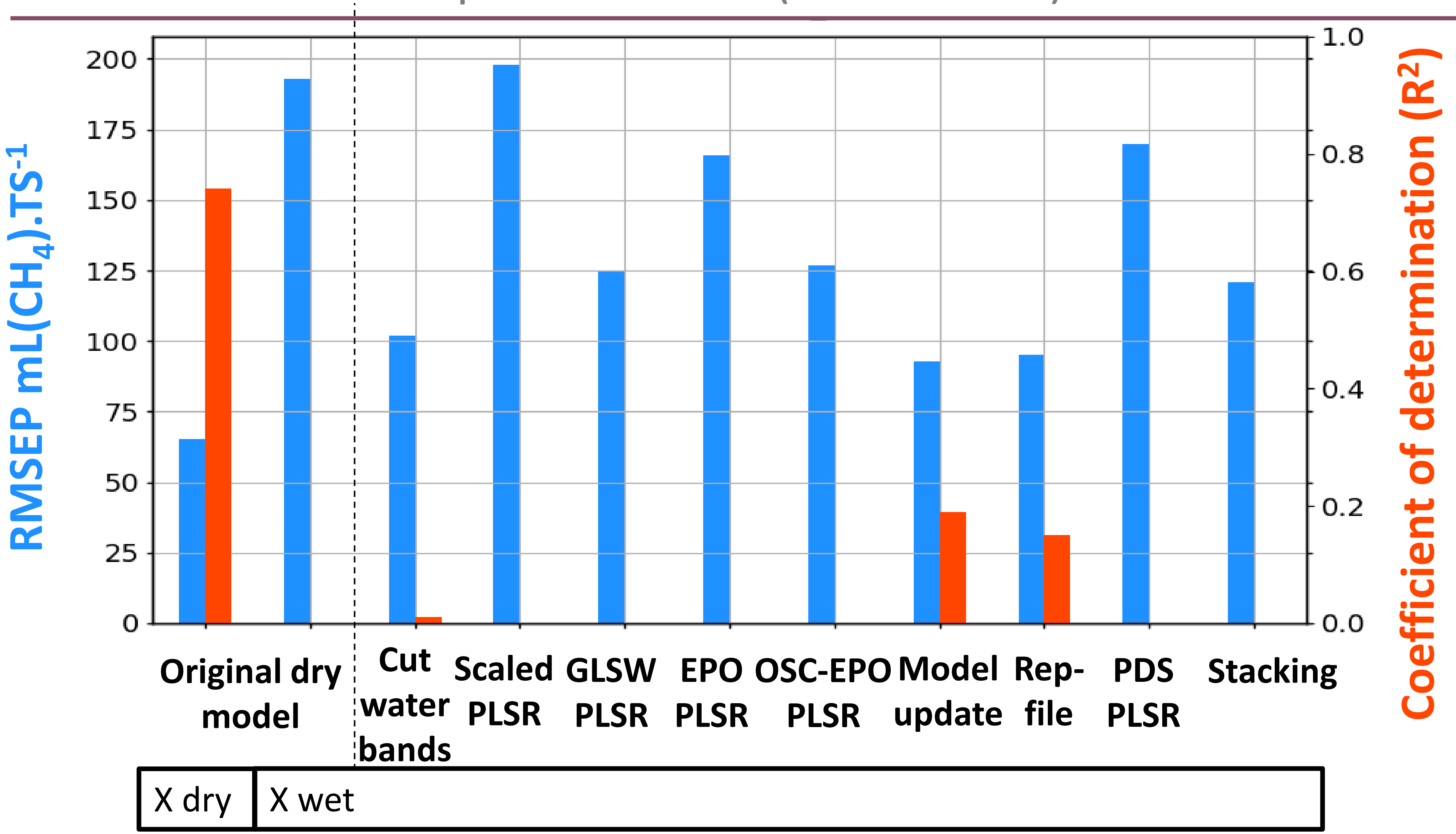

### With correction (Repeatability File)



# 3.1 Global correction of models

## Results – model performances (all methods)



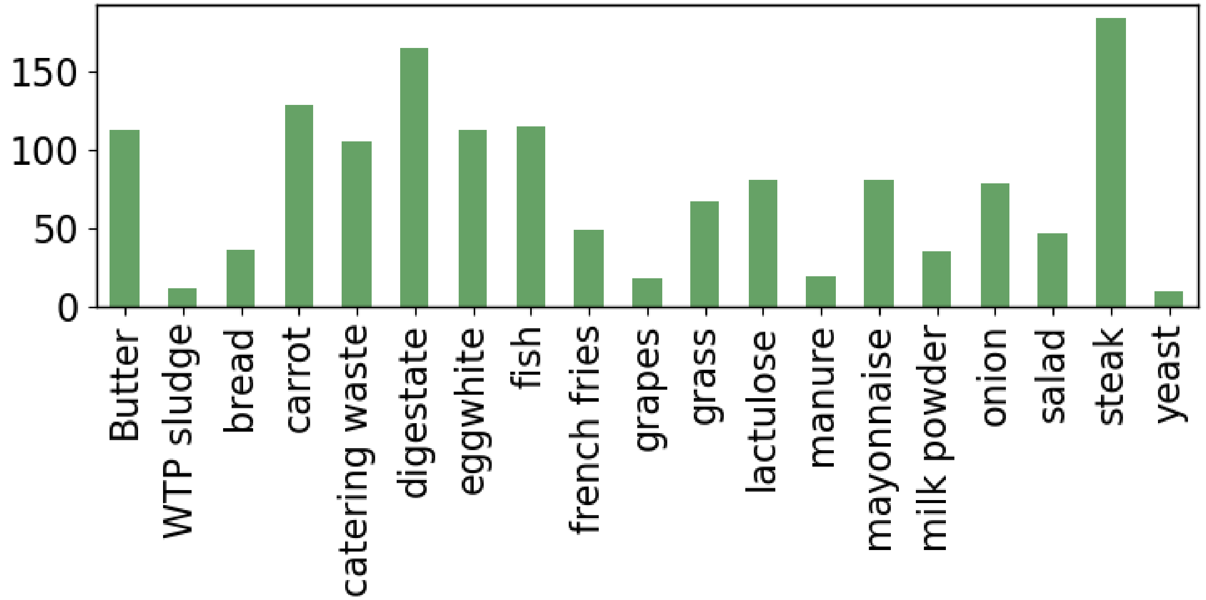

➢ None of the global correction methods allowed significant improvements

# 3.1 Global correction of models

## Results – prediction quality differs according to substrates

- **Prediction error depends on substrate:**

**RMSEP** per substrate




- **Implies:**
  i. **Different sensitivities** to moisture content effects
  ii. **Different types** of moisture content effects

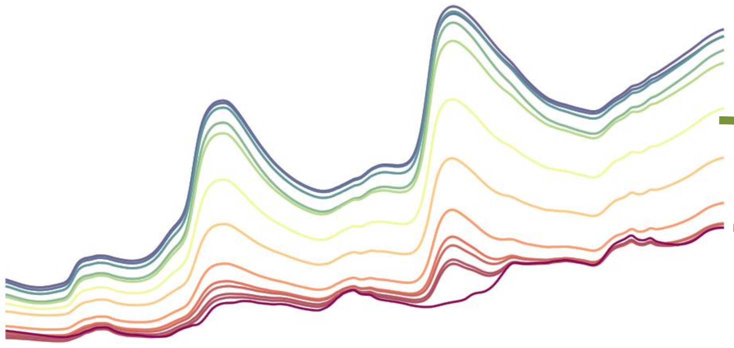
- Conclusion:
  - **A need to better assess moisture content effects according to substrate types**

# 3.2 Results – non-linearity of water effects

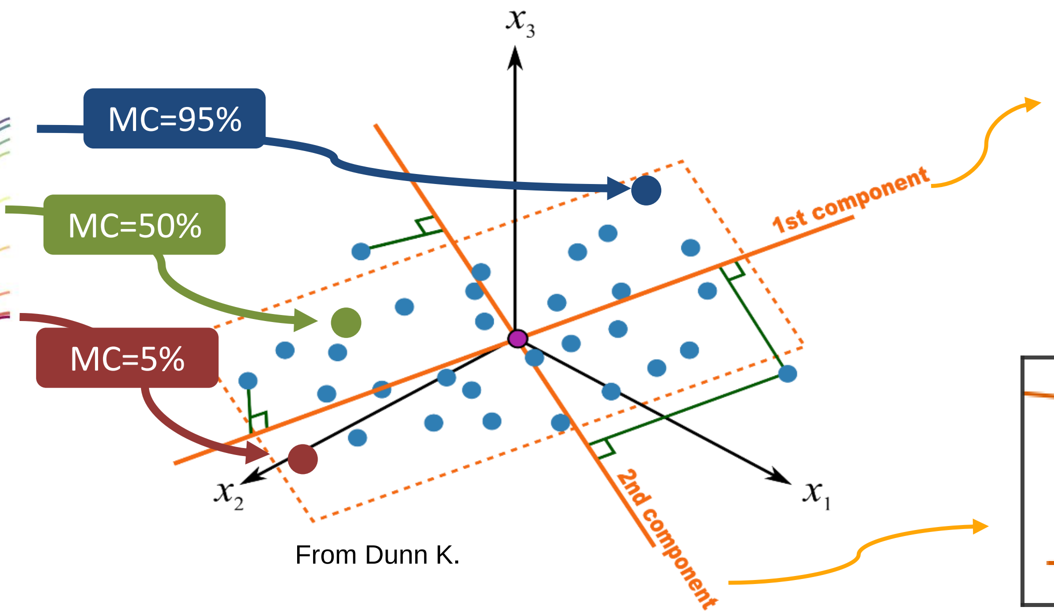
# 3.2 Non-linearity of water effects

## Objective, Materials & Methods

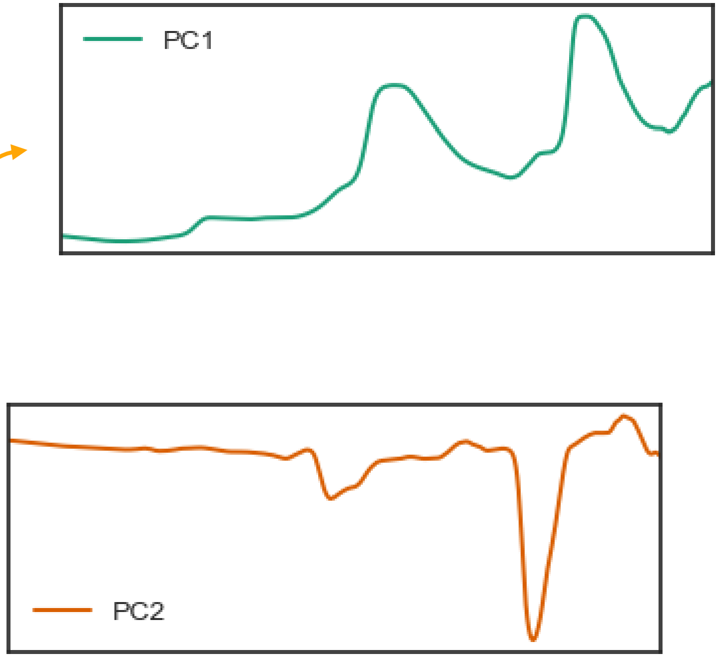
- **Objective:**
  - **Analyze moisture content effects according to 1) substrate type and 2) moisture content level**
- **Using principal components analysis (PCA):**



Spectra during drying



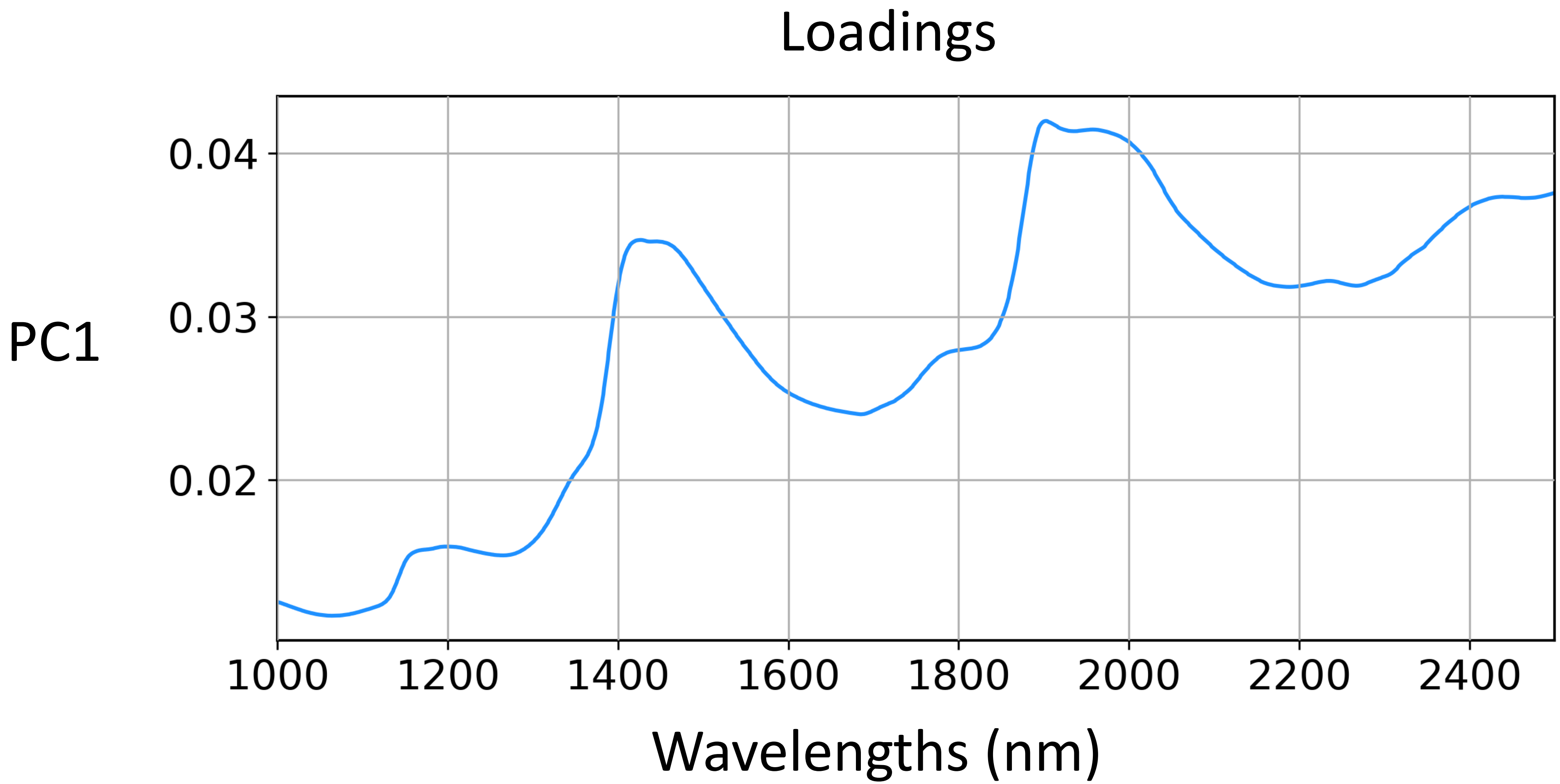

Scores




Loadings

# 3.2 Non-linearity of water effects

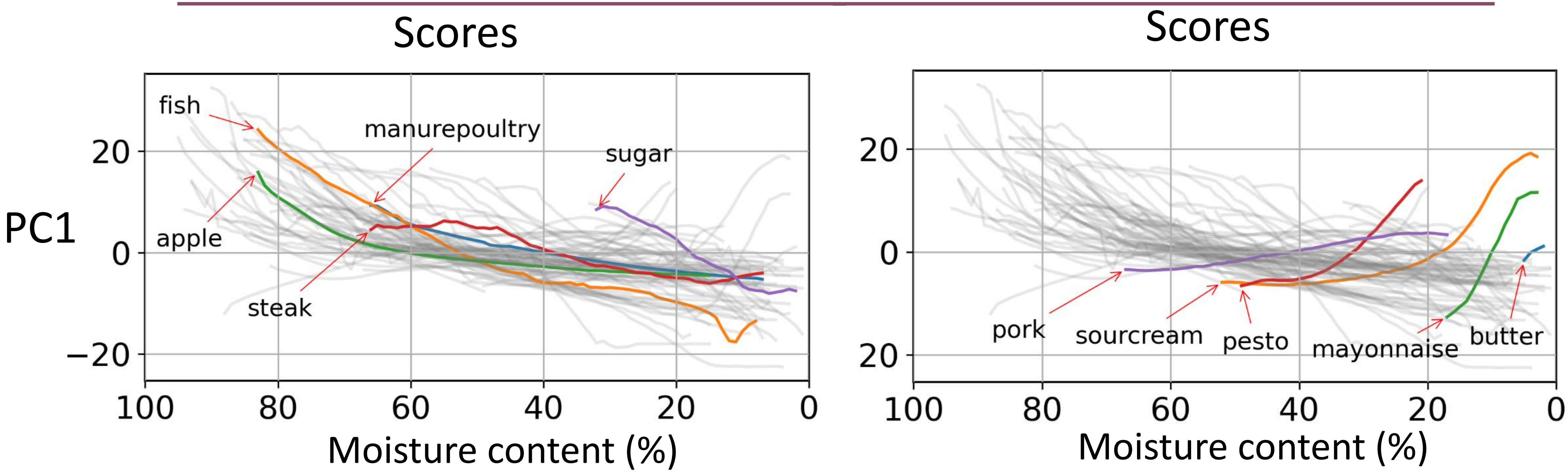
## Water affects physical properties (*ie.*, scattering)




- **Explained variance (91.6%)**

# 3.2 Non-linearity of water effects

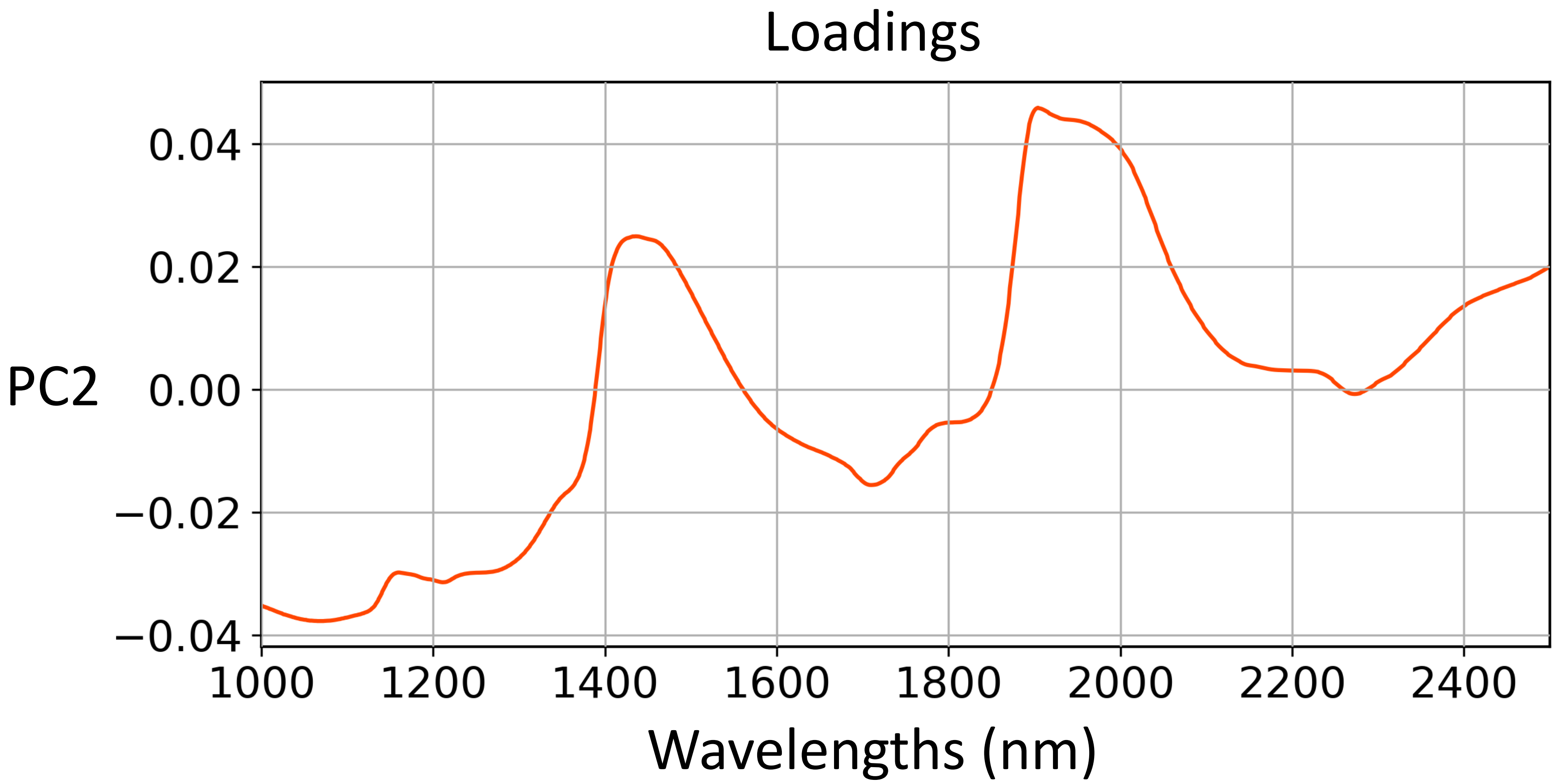
## Water affects physical properties (*ie.*, scattering)




- **Level of scattering evolves non-linearly with moisture content**
- **Dependence on biochemical composition: most substrates show decrease along drying, but high fat content samples show an increase**

# Non-linearity of water effects

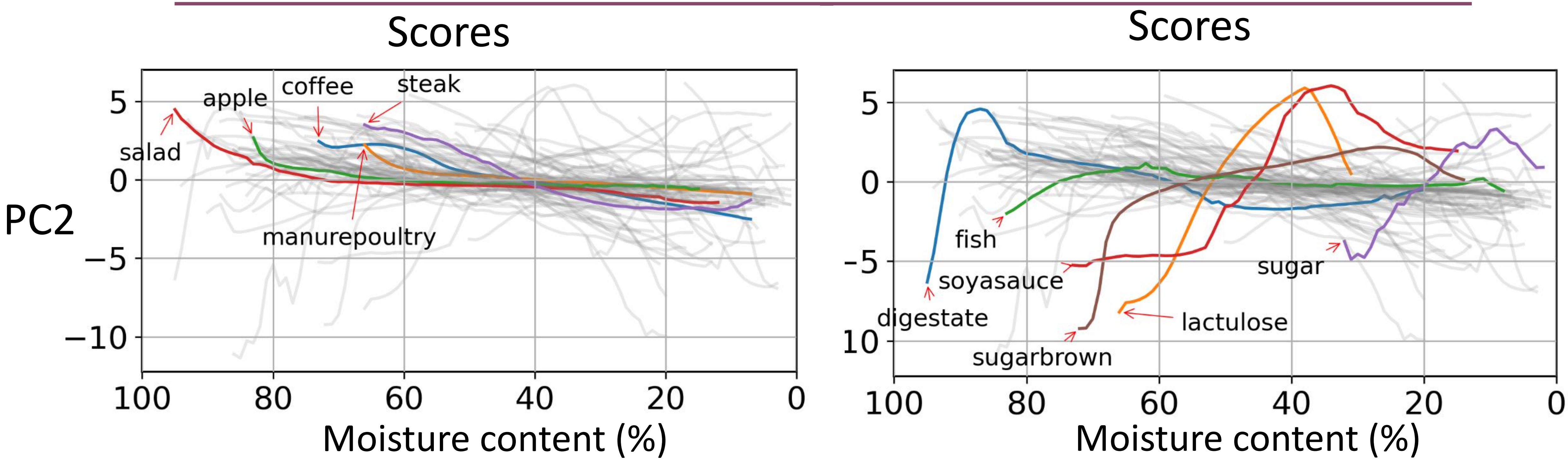
Water affects chemical composition (*ie.*, absorption)




- **Explained variance (6.5%)**

# 3.2 Non-linearity of water effects

## Water affects chemical composition (*ie.*, absorption)




- **OH absorption decrease along drying**
- **Saturation of water OH bands at high water content levels: forward scattering too high**

# 3.2 Non-linearity of water effects

## Conclusion

- **Water effects are complex:**
  - **Chemical** effects (absorption)
  - **Physical** effects (scattering)

- **Water effects depend on**
  - the **substrate type** (biochemical and physical properties)
  - the **moisture content level**

- **Physical effects account for the most variance: a need to better understand these effects**

# 3.3 Results - Water effects on light scattering

# 3.3 Water effects on light scattering

## Objective, Materials & Methods

- **Objective:**
  - **How does water modify light scattering?**
  - **Study physical effects independently from chemical effects**

- **Proposed approach:**

**Criteria:**

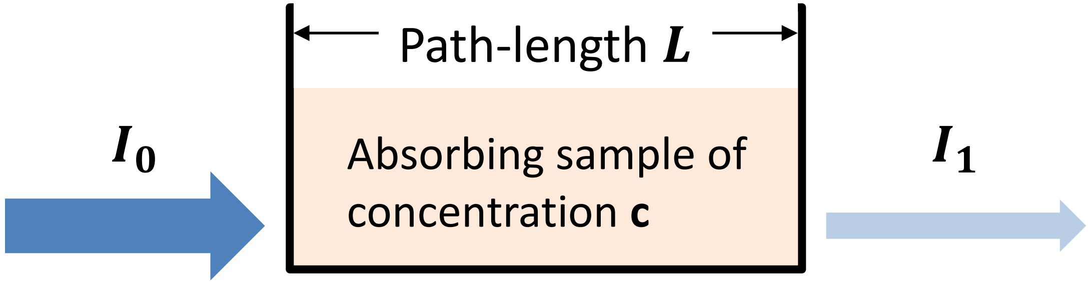
- Scattering media (particulate)
- Limited chemical interactions (no solubilization)
- No absorption (dry mass)

**Aluminum paper pellets mixed with water**

# Water effects on light scattering

## The Bouguer-Beer-Lambert (BBL) law framework

### ➢ Transmission measurements:




$$A = -log(T) = -log\left(\frac{I_1}{I_0}\right) = \varepsilon_\lambda . L . c$$

$A$ the **absorbance**, $T$ the **transmittance**, $\varepsilon_\lambda$ the **extinction coefficient**

### ➢ BBL law holds in very strict conditions[1-2]:

- Homogeneous and fully transmitting medium
- Low concentrations
- Independence of absorbers
- Use of monochromatic light

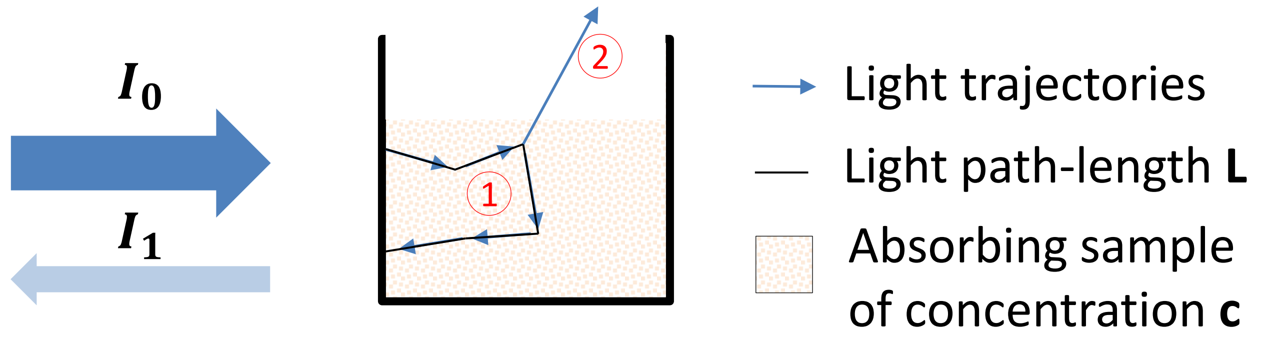
[1] Swinehart et al., Jour. of Chemical Education, 1962.
[2] Mayerhöfer et al., ChemPhysChem, 2020.

# Water effects on light scattering

## What happens with scattering materials?

- **In scattering media (powder, suspension), light scattering** results in **two phenomena**[1]

    1) **Path-length modifications**
    2) **Photons loss**




- One way of modeling[2]:
    1) multiplicative effect ($kL$)
    2) additive effect ($f$) :

$$A = -log(R) = -log\left(\frac{I_1}{I_0}\right) = \varepsilon_\lambda . kL . c + f$$

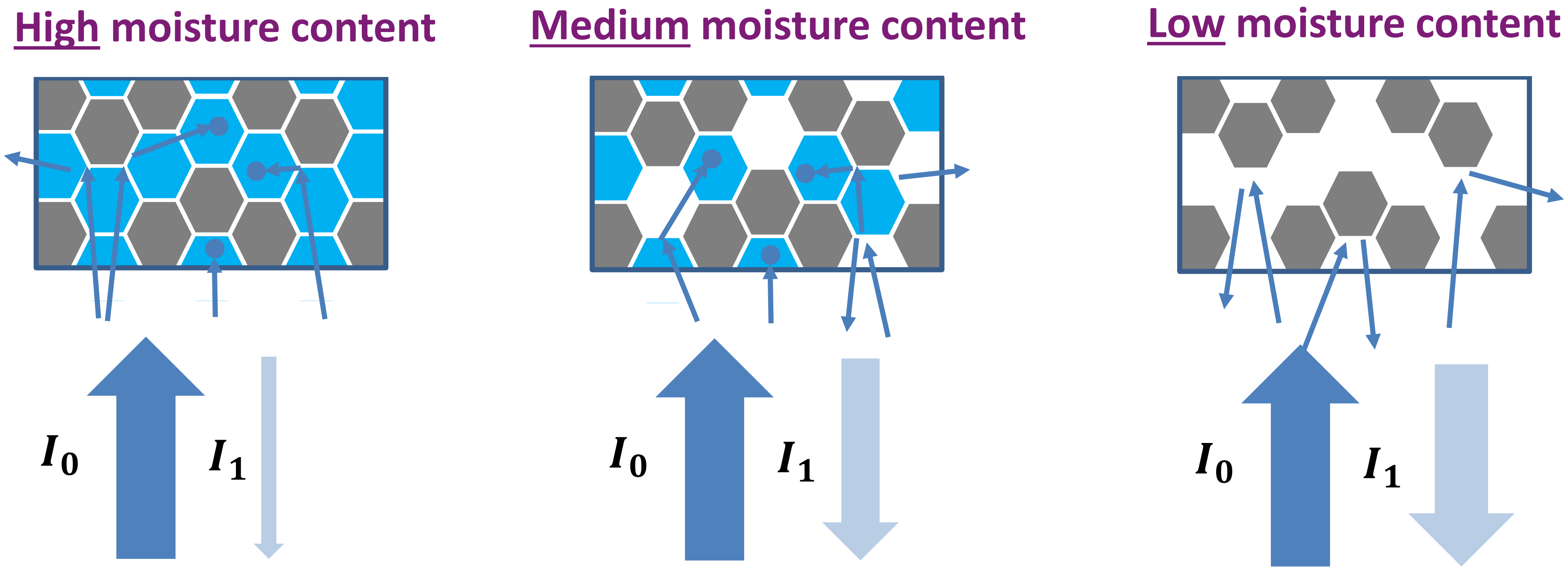
With $k$ and $f$ constants

[1] Gobrecht et al., Advances in Agronomy, 2014.
[2] Martens et al., Analytical Chemistry, 2003.

# 3.3 Water effects on light scattering

## What about when moisture content varies?

- **Forward scattering level is directly related to moisture content**




- **Water acts as a guide for photons**
- **Intuition was that it involved a geometrical relationship**

# Water effects on light scattering

## New modeling of light path-length in the BBL law

Hypothesis: **Light path-length is directly related to water content by a power law**

$$L_{\lambda,c} = L_0 . c^{a_\lambda}$$

With $c$ water content, $L_0$ and $a_\lambda$ constants

$$\Rightarrow A_{\lambda,c} = \varepsilon_\lambda . L_0 . c^{a_\lambda + 1} + f_{\lambda,c}$$

# Water effects on light scattering

## New modeling of light path-length in the BBL

Hypothesis: **Light path-length is directly related to water content by a power law**

$$L_{\lambda,c} = L_0 . c^{a_\lambda}$$

With $c$ water content, $L_0$ and $a_\lambda$ constants

$$\Rightarrow A_{\lambda,c} = \varepsilon_\lambda . L_0 . c^{a_\lambda+1} + f_{\lambda,c}$$

- **To validate this, additive effects $f_{\lambda,c}$ were first removed using extended multiplicative scatter correction (EMSC)[1] to obtain $A_{\lambda,c} - f_{\lambda,c}$**

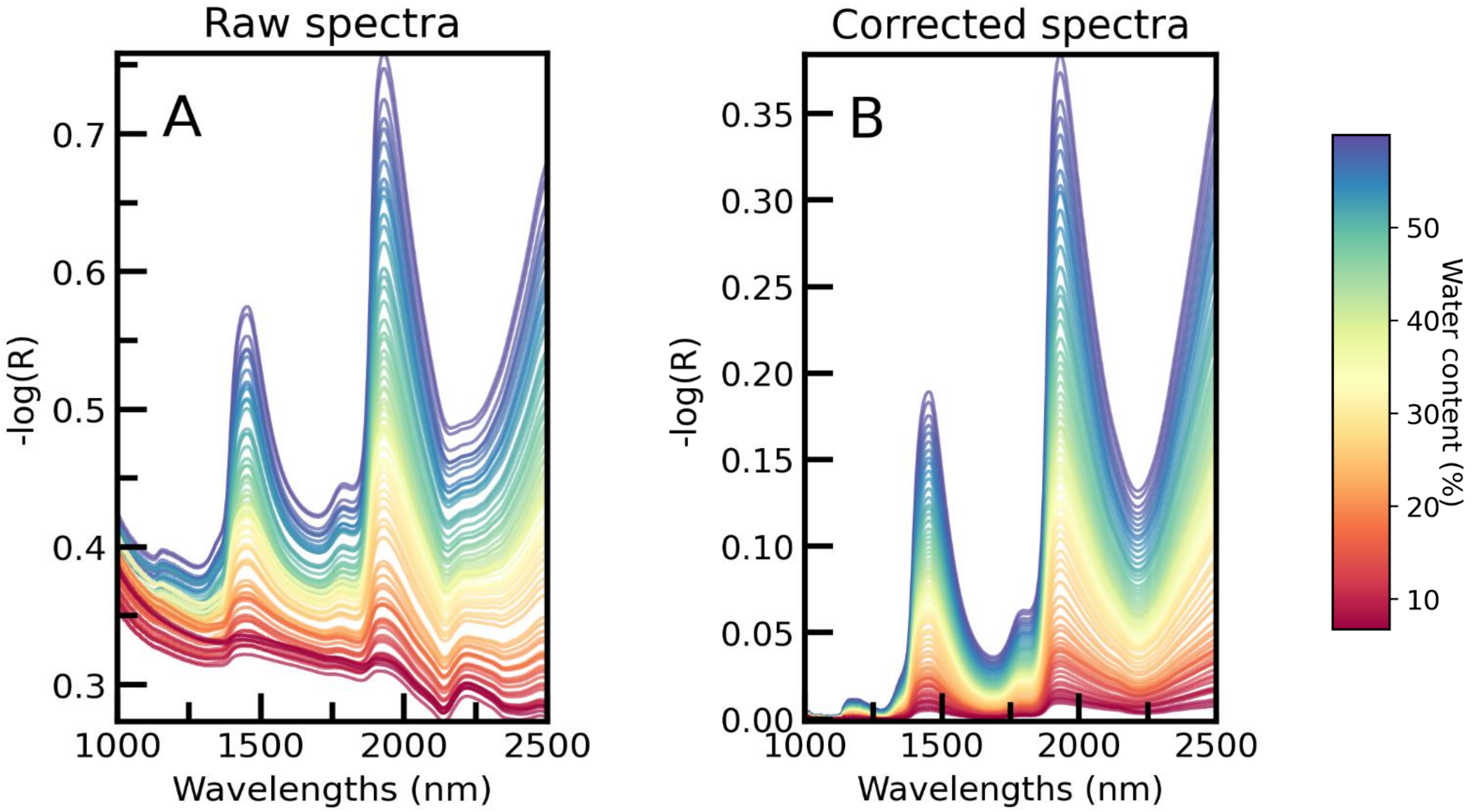
- **Then, a log-log least squares regression was run between $log(A_{\lambda,c} - f_{\lambda,c})$ and $log(c)$:**

$$\boldsymbol{log(A_{\lambda,c} - f_{\lambda,c})} = log(\varepsilon_\lambda . L_0) + (a_\lambda + 1) . \boldsymbol{log(c)}$$

[1] Martens et al., Analytical Chemistry, 2003.

# 3.3 Water effects on light scattering

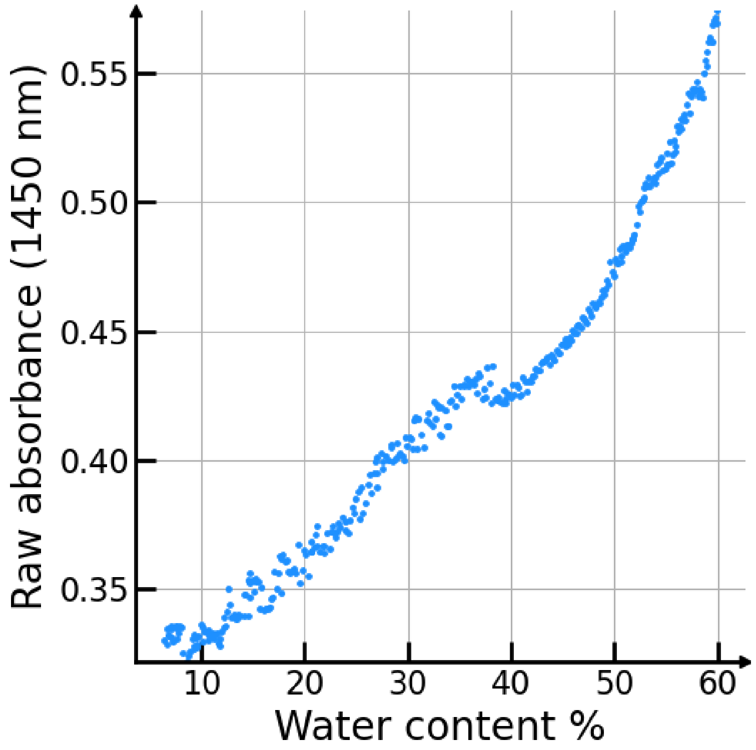
## Correction of additive effects in spectra using EMSC



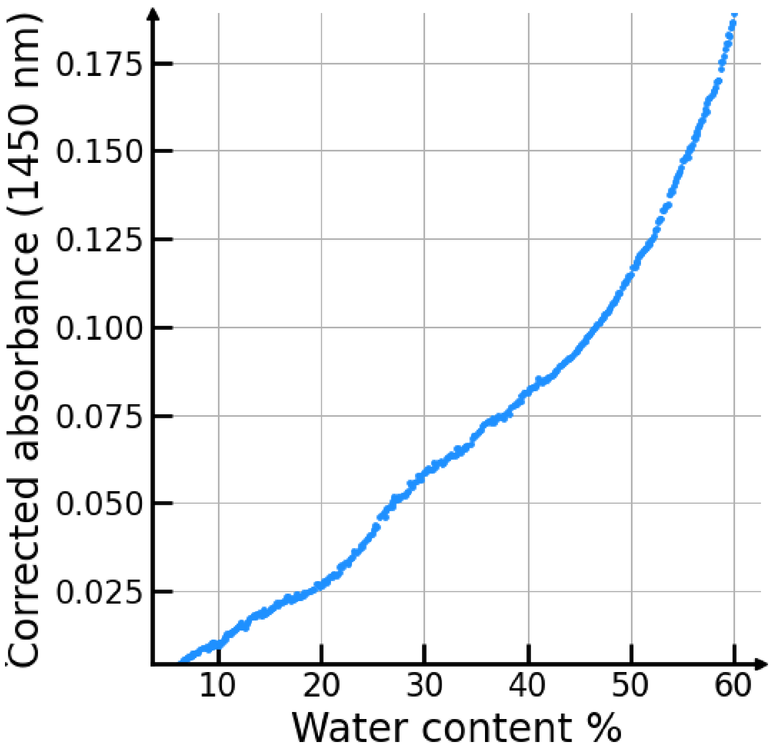
# 3.3 Water effects on light scattering

## Results for one wavelength

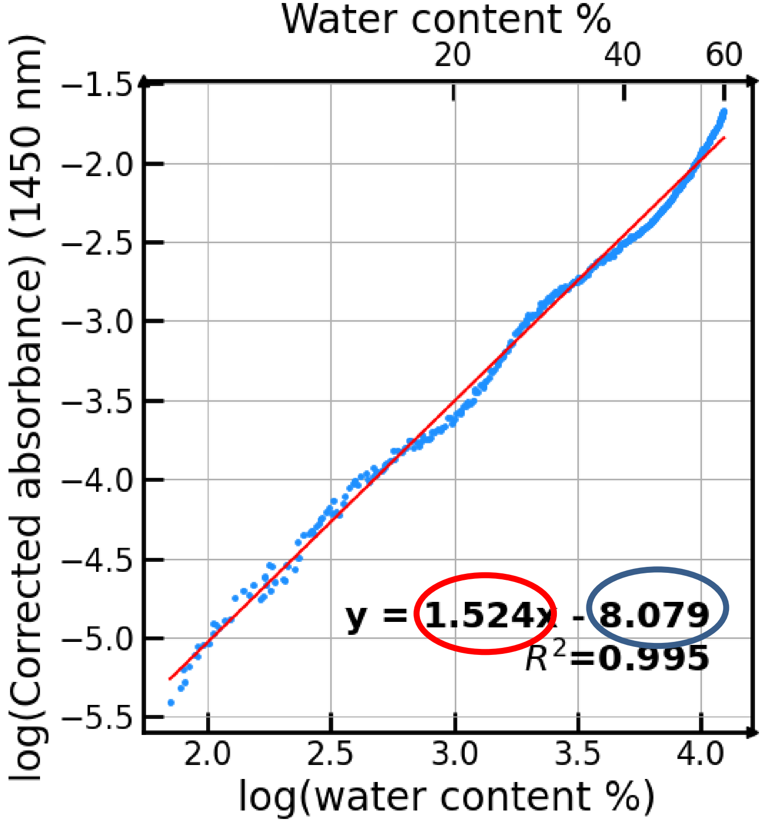
**Raw absorbance**




**Corrected absorbance**




**Log-log plot**

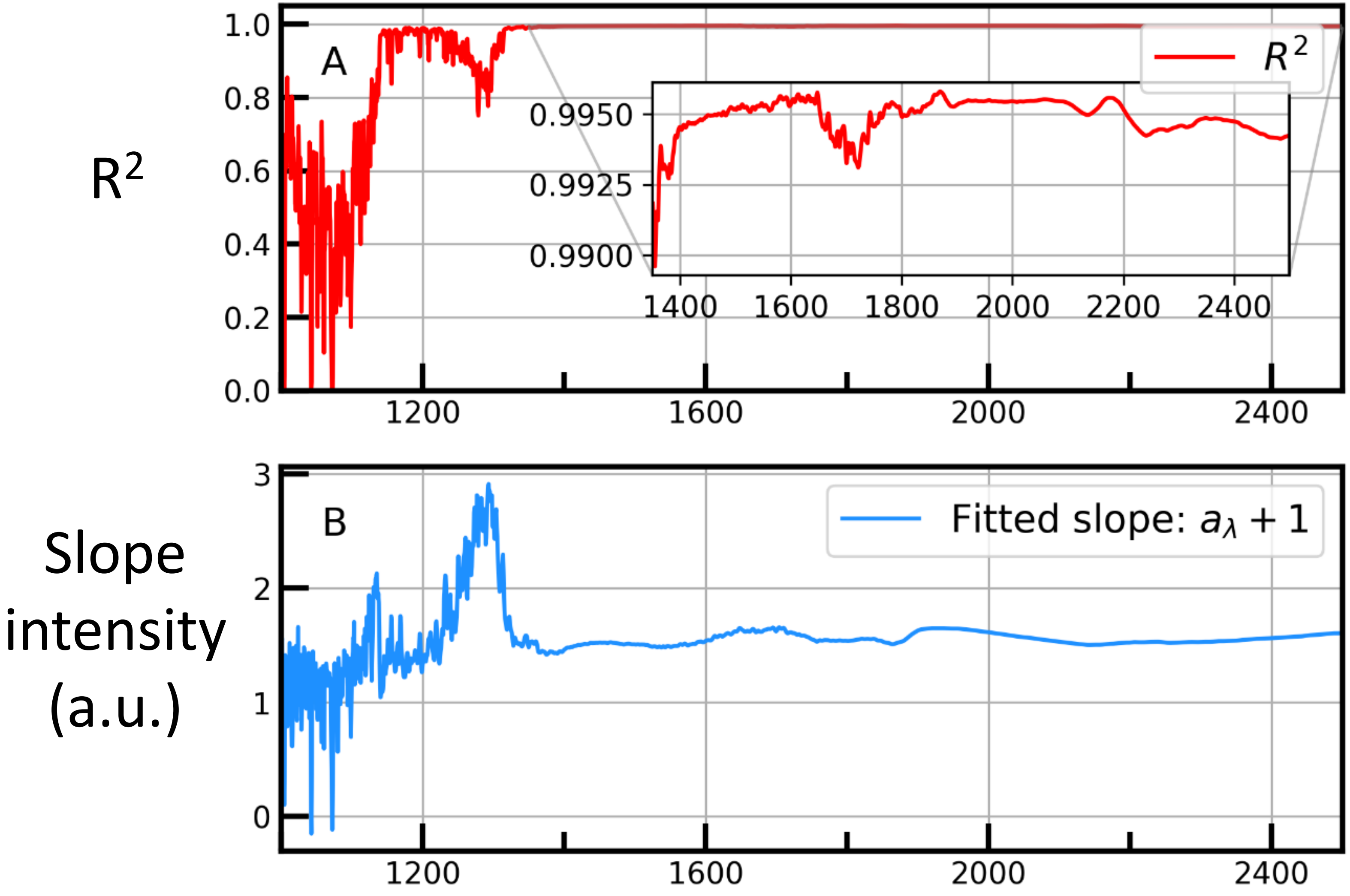



➢ **Analysis at a given wavelength (1450 nm) shows very good fit**

$$\log(A_{\lambda,c} - f_{\lambda,c}) = \log(\varepsilon_{\lambda}.l_0) + (a_{\lambda}+1).\log(c)$$

# 3.3 Water effects on light scattering

## Results for all wavelengths



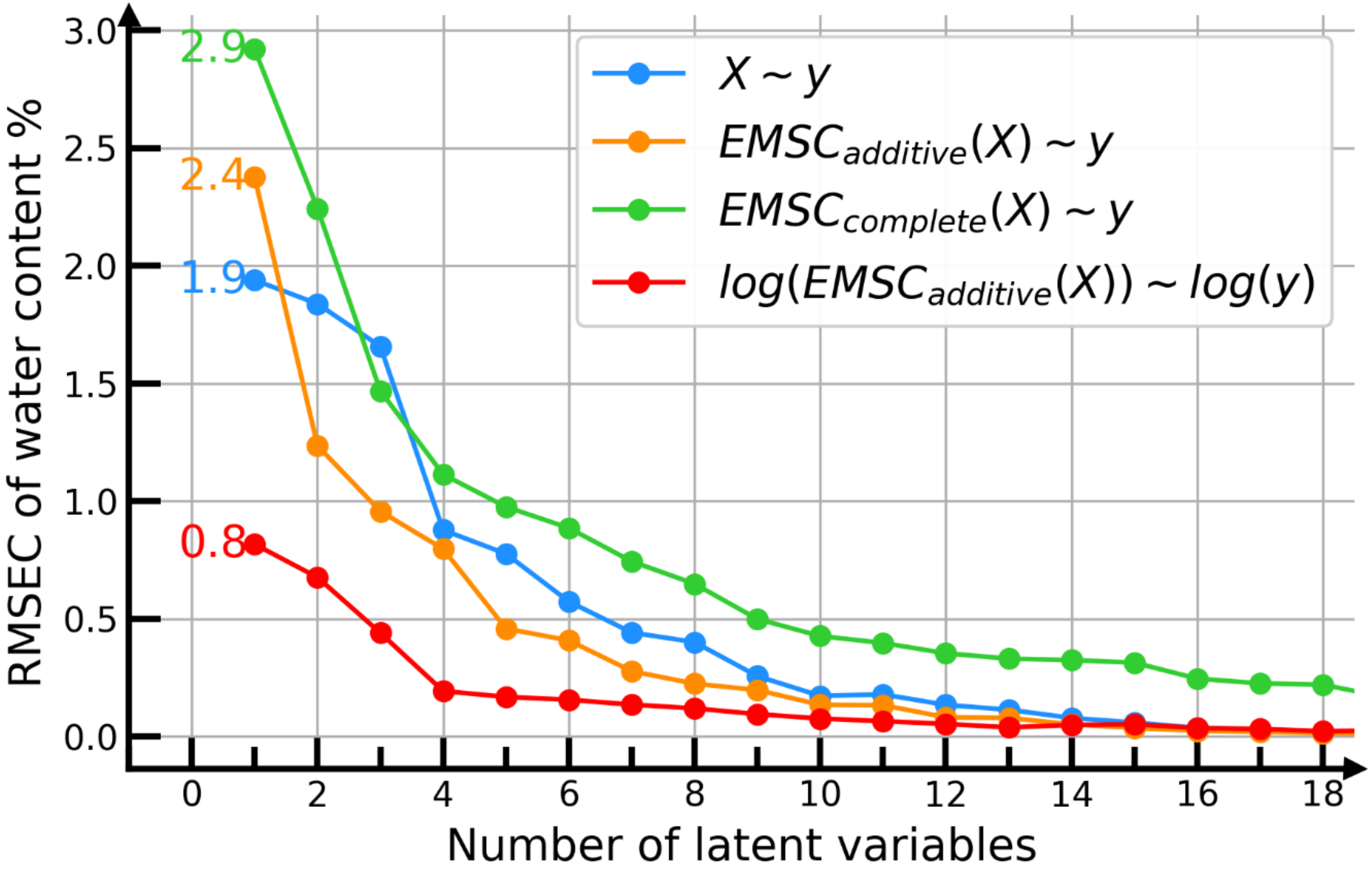

**Good fit for all wavelengths** (>1350nm)

**Stable slope values** (~1.5)

➢ **This further validates the power law**

# Water effects on light scattering

## Implications for quantitative calibrations




- **Inadequacy of linear models**
- **Log transform could provide simpler models**

# 3.3 Main conclusions of former studies

## Conclusions

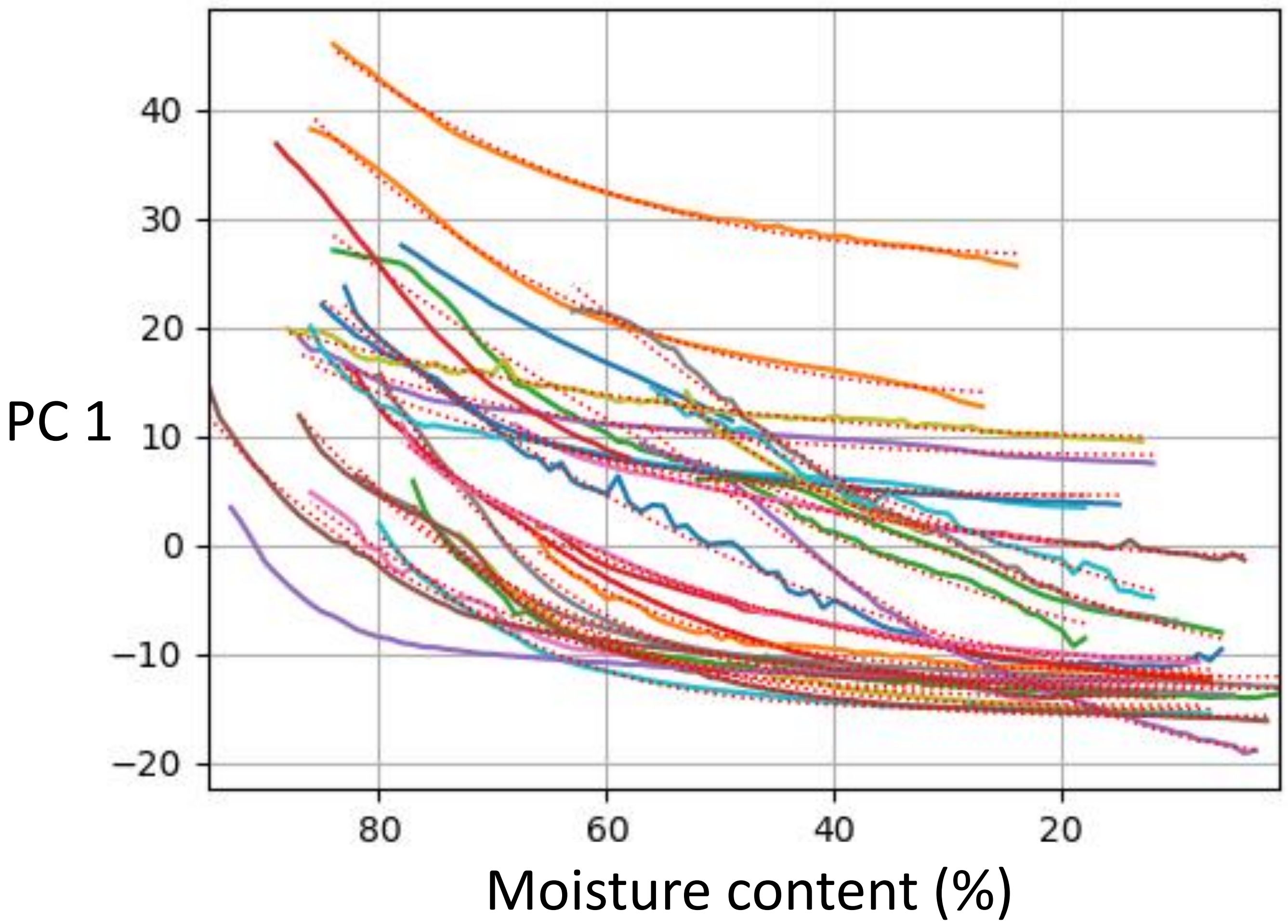
- Global **linear models were not reliable**
- Analysis of water effects
  - A **clear non-linearity** and a **dependence on both moisture content and substrate type**
  - **Scattering modifications can be modeled by a simple power law**

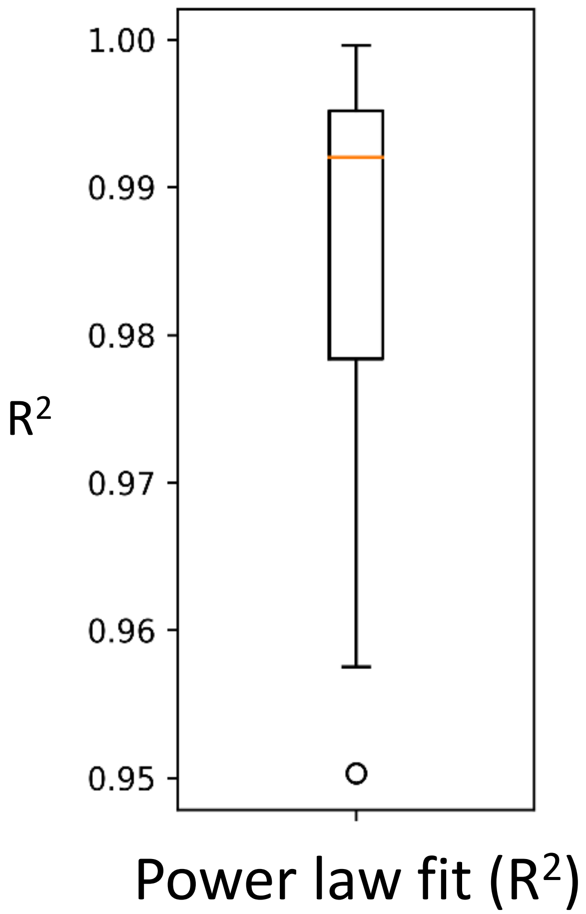
- Investigate the possibility of **building** **<u>local models</u>** (based on both **substrate type** and **moisture content**)

# 3.4 Results – Local modeling

# 3.4 Local modeling

## Local group of homogeneous samples

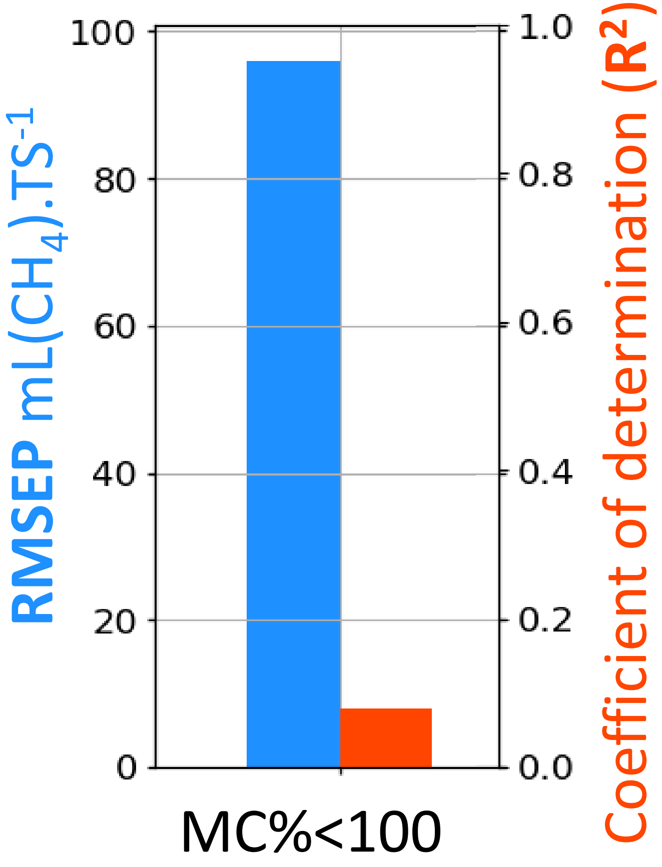



- 37(/89) selected substrates follow a power-law type relationship

# 3.4 Local modeling

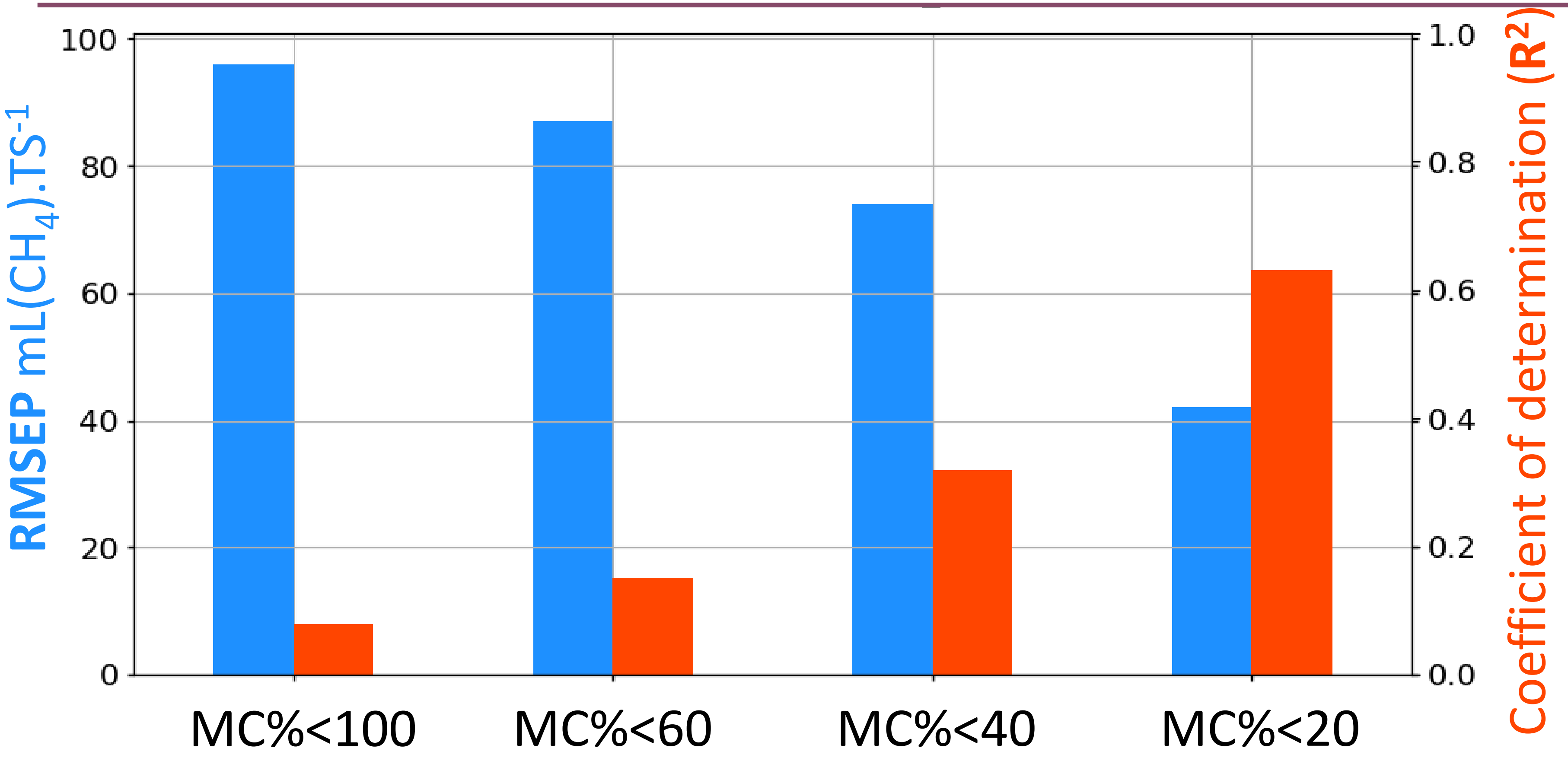
## Models built on this local group




- **Local model still does not provide satisfactory results**
- Power relationship not well modeled by PLS?
  → **non linear methods**
- Biochemical footprint hidden by water?
  → **reduce moisture content range**

# 3.4 Local modeling

## Models built on this local group (reduced moisture content range)

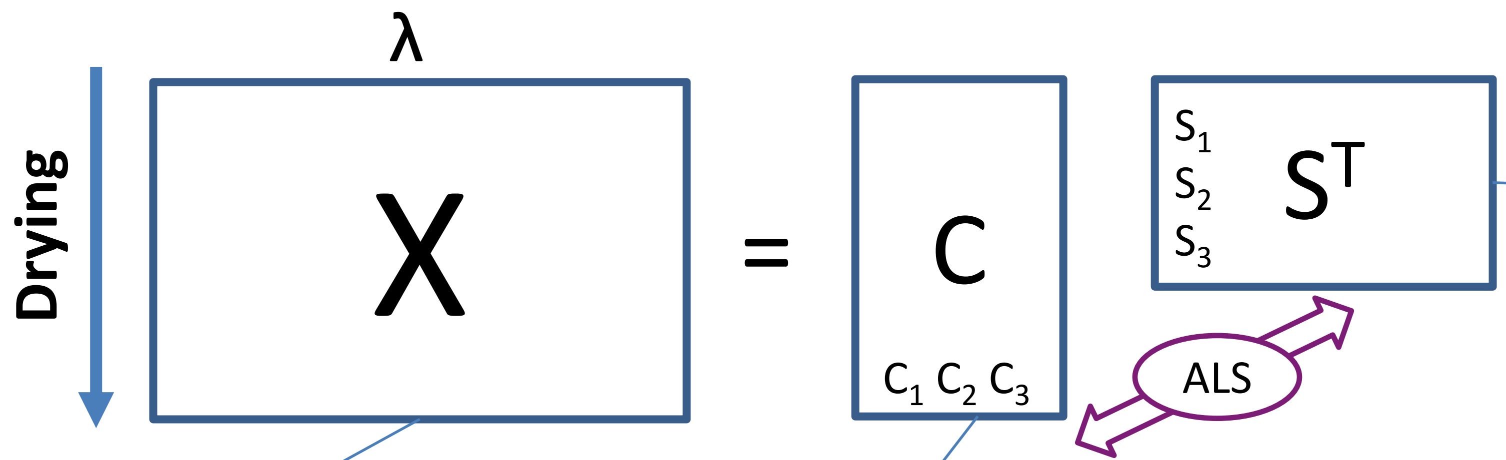


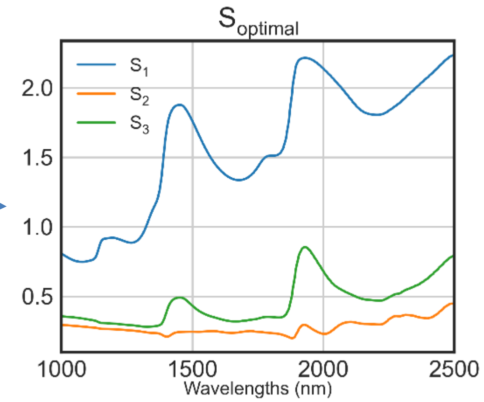

➢ More satisfactory models with reduced moisture content range

# 3.4 Local modeling

## Potential of MCR-ALS to further refine local groups

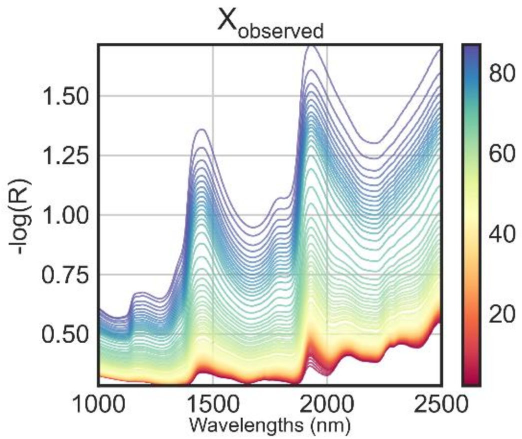
### ➢ Adding the power law constraint to MCR-ALS framework[1]

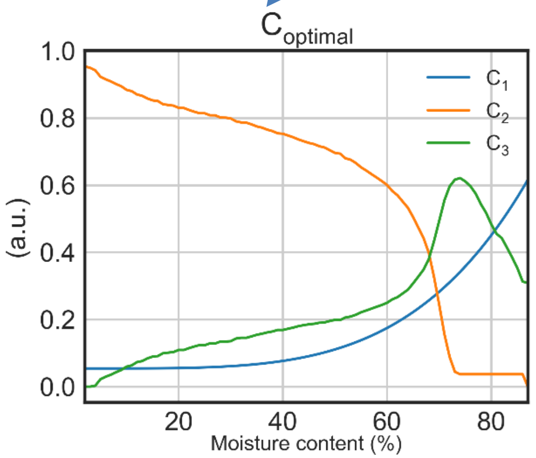



**Spectra constraints:**

- Non-negativity



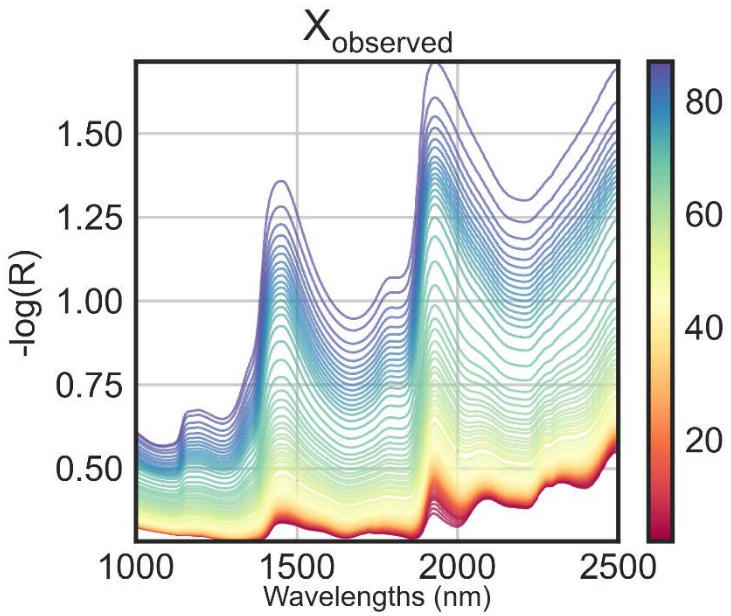

**Concentration constraints:**

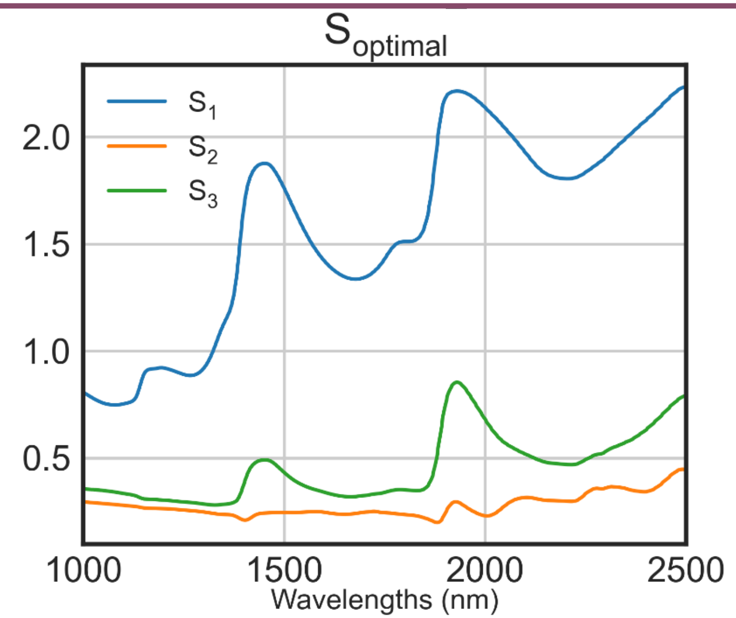
- Non-negativity
- Closure
- Unimodality
- **Hard modeling constraint (power law on $C_1$)**
  - $C_1(MC\,\%) = k_1.(MC\%)^{k_2} + k_3$

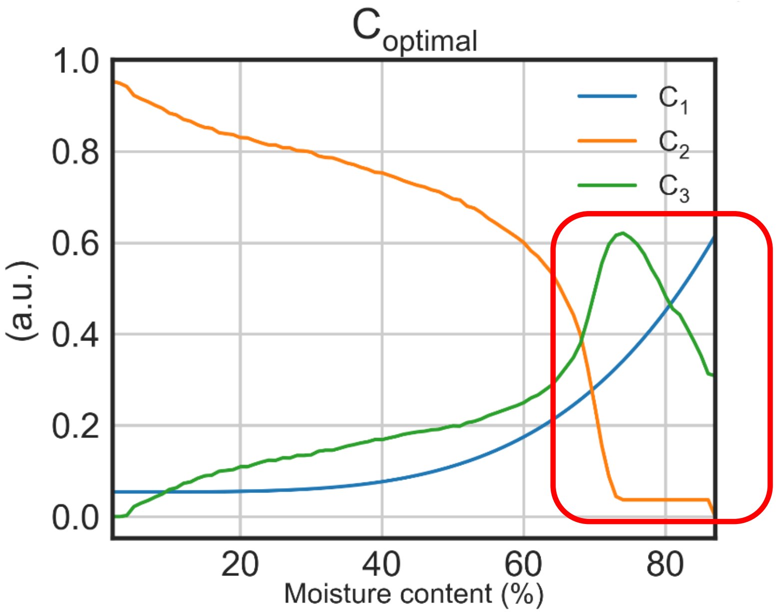
# 3.4 Local modeling

## Potential of MCR-ALS to further refine local groups

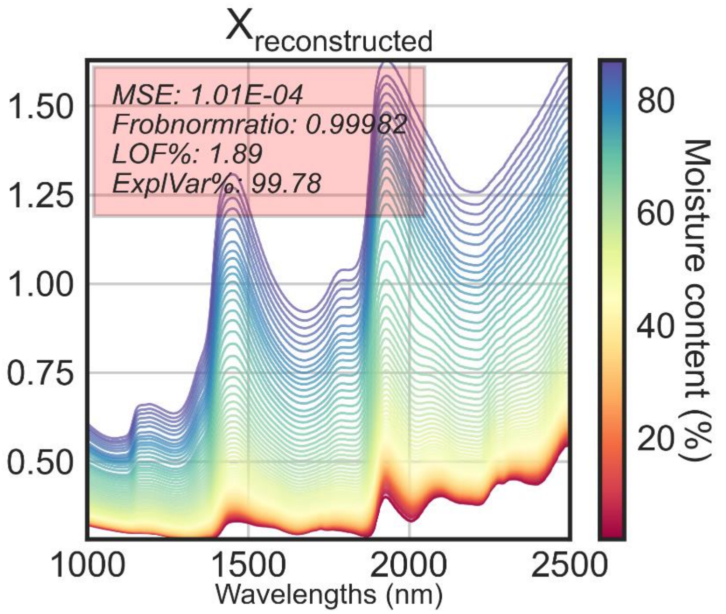
Wheat chaff




**Non-linearity**




[6] d

# 4. Conclusions and perspectives

# 4.1 Conclusions and perspectives

## Conclusions

- **Objective 1) To develop a better understanding of the moisture content effects on NIRS applied to a wide range of organic materials**
  - A new experimental set-up for analyzing water effects
  - Moisture content effects shown to be complex with both physical and chemical effects
  - Relating the path-length (power law) directly to moisture content could allow to better model the scattering modifications induced by water

- **Objective 2) To find new ways of building models that are robust to moisture content effects**
  - Global correction methods are insufficient due to non-linearity of effects
  - Local modeling holds promises

# 4.1 Conclusions and perspectives

## Perspectives

- **Fundamental knowledge on water effects:**
  - Investigate the modified BBL law in more complex systems: how to deal with chemical interaction? How to remove additive effects?
- **Quantitative calibrations on wet samples:**
  - Develop the knowledge-based local approach with the help of MCR-ALS
  - Evaluate the potential of non-linear methods (local PLS, SVM, RT, RF, CNN)
  - Use NIRS measurements during drying as one predictor (N-way methods)
- **On-site and online applications:**
  - Sample preparation and measurements configurations are complementary strategies to reduce water effects
  - Pursue the evaluation of low-cost and handheld spectrometers applied to wet substrates

# Thank you!

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