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Prediction of the BMP of maize silages using NIRS from wet and dried samples

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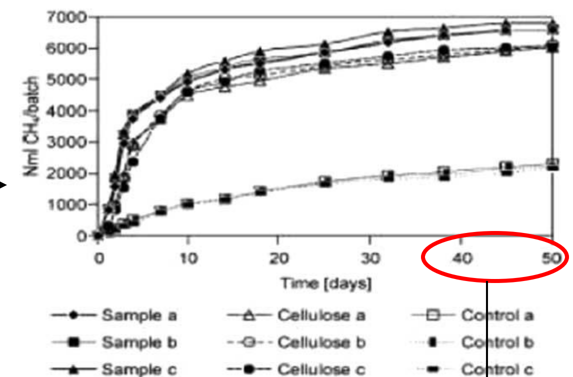
Introduction

Biogas and biomethane measurements (ABP and BMP)



ABP: anaerobic biogasification potential
➔ biogas ($mL_{biogas} \cdot g_{substrate}^{-1}$)

BMP: biochemical methane potential
➔ biomethane ($mL_{CH4} \cdot g_{substrate}^{-1}$)

40-50 days

Introduction

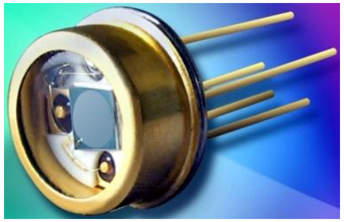
NIRS is successfully used for various applications: nutritional value, quality & authenticity, process controlling & monitoring…

Advantages: **easy**, **fast**, non-destructive analytical technique.

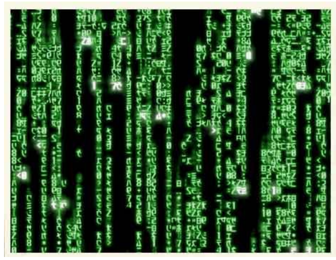
Light Source

Monochromator

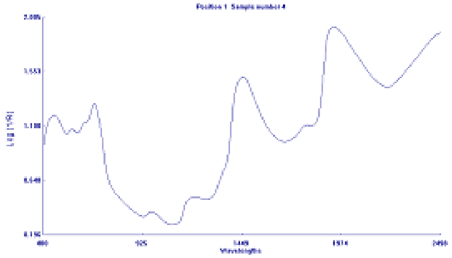
Sample



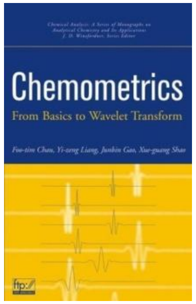
Detector



Processor



Data



Data treatments

Concentration

Adapted from *Handbook of Near-Infrared Analysis, 3rd ed.*

The most used energy crop: maize silages

Water content

Organic content

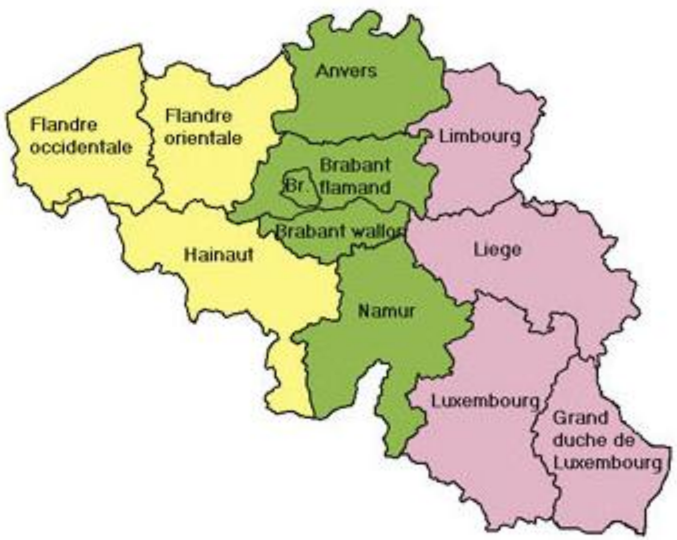
Variety
Cultural practices
Maturity stages

Various ABP and BMP

Material and methods

Biomass production

Maize



3 years

9 fields

25 varieties

3/4 harvesting dates for 4 specific varieties (FAO Index 240-340)

→ Around 400 samples

Sample pretreatments

Harvested maize

↓ Ensiling

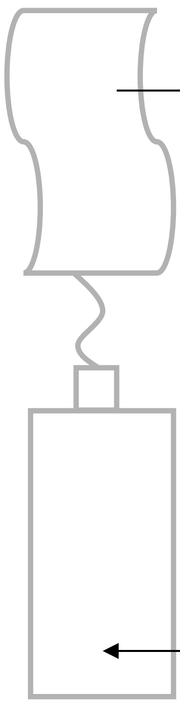
Wet maize silage

↓ Drying (70°C, 48h) / Grinding (Centrifugal mill, 1mm mesh)

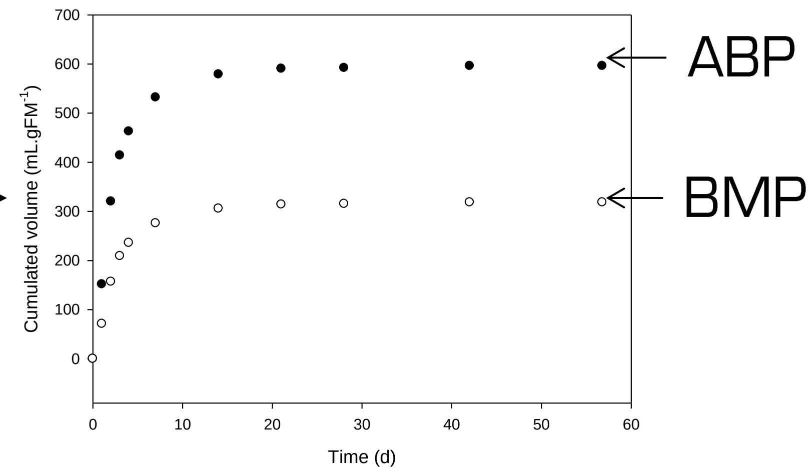
Dry maize powder

Material and methods

Anaerobic digestion (VDI-4630)



Biogas volume
&
Composition (CH_4, CO_2)



Substrate

ABP: anaerobic biogasification potential
→biogas ($mL_{biogas}.g_{substrate}^{-1}$)

BMP: biochemical methane potential
→biomethane ($mL_{CH4}.g_{substrate}^{-1}$)

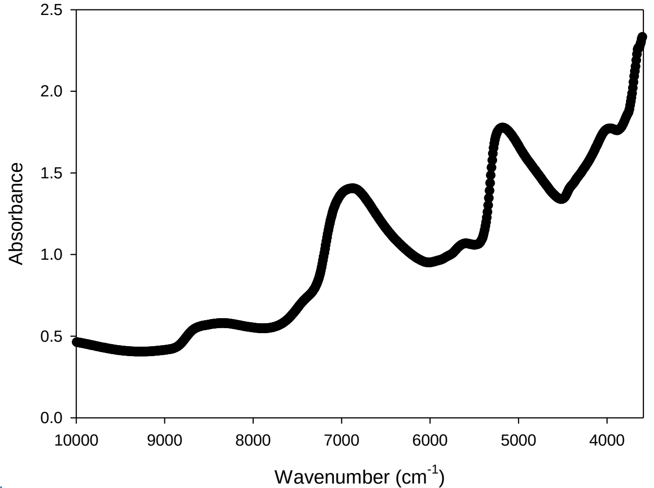
Inoculum: sludge from AD of a sewage treatment plant

NIRS

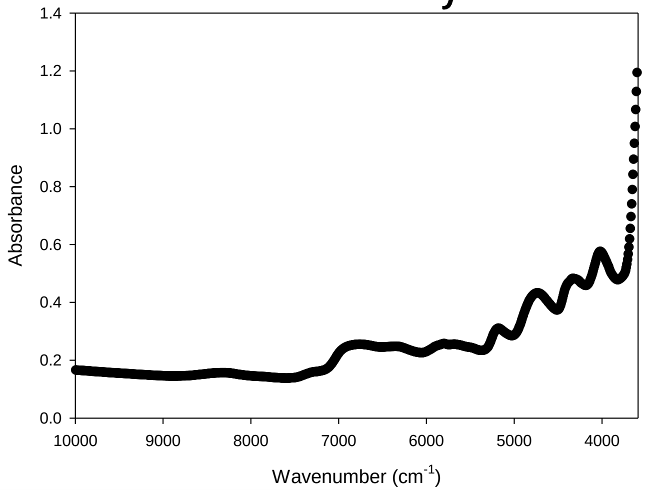
Brüker MPA
- integrating sphere
- sampling cup 97mm
- rotation
- triplicate

Range: 10000-3600 cm^{-1}
Sample scans: 64 scans
Resolution: 16 cm^{-1}

Wet maize silages
➔NIR wet



Dry maize powder
➔NIR dry



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Material and methods

Biochemistry

Analysed on dry maize powder

Fat — Soxhlet extraction with hexane
Gravimetrically measured after evaporation

NDF
ADF
ADL — Van Soest method with an automatic device (Ankom 2000 fiber analyser)

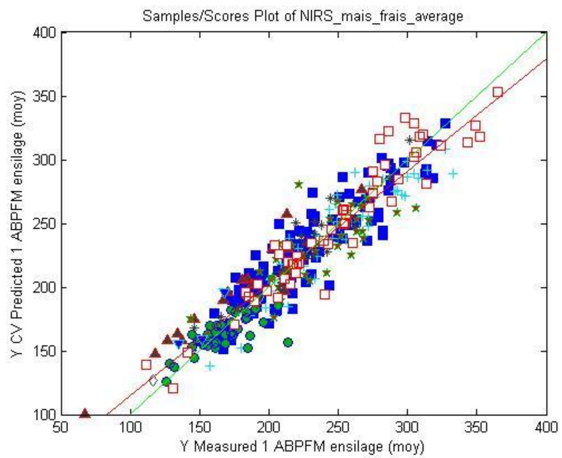
Carbon
Nitrogen
Sulfur — TruSpec Elemental analyser

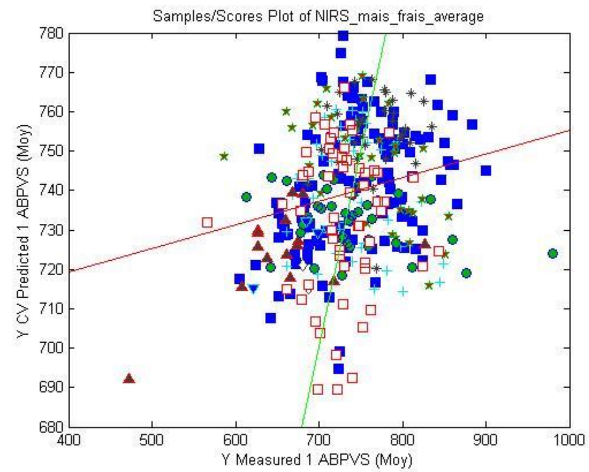
NIR wet→ABP/BMP wet silages:

expressed per unit of

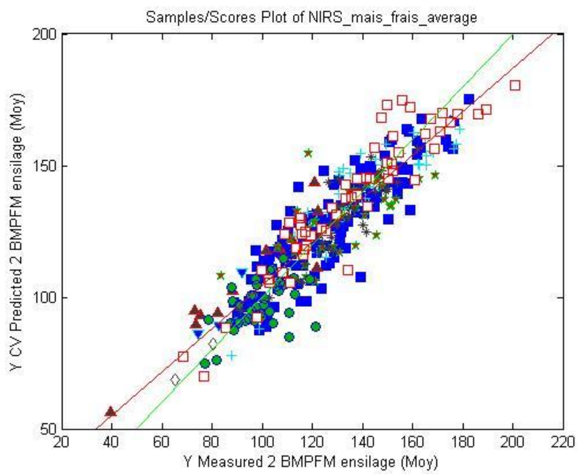
Fresh matter | **Volatile Solids**

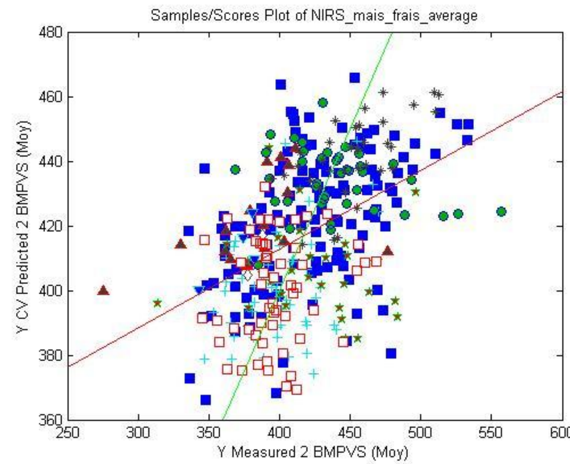
Biogas





Biomethane

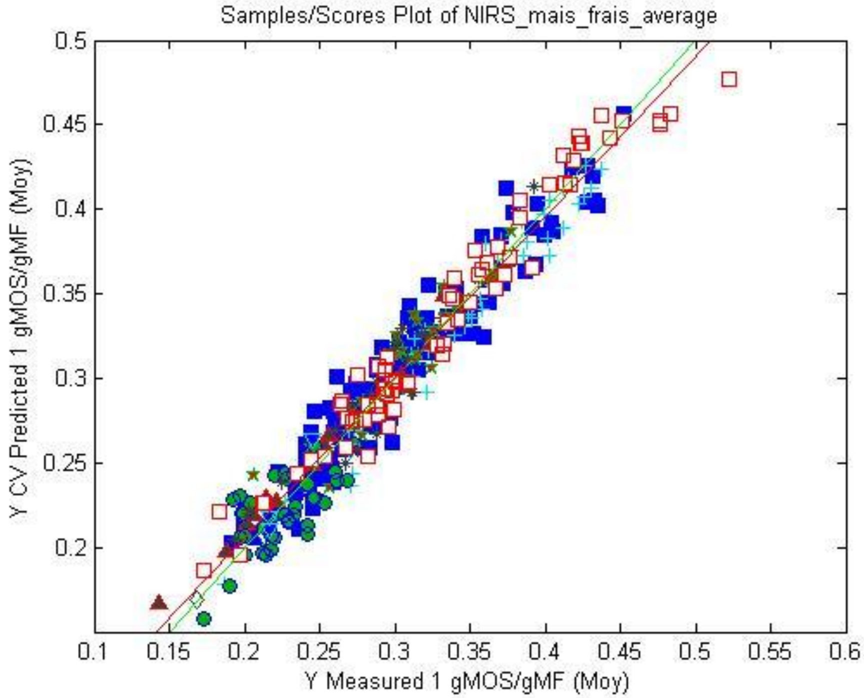




(Mayer, 2012)

NIR wet➔VS wet silages:

VS (gVS.gFM^{-1}) prediction



VS: volatile solids
FM: fresh matter

(Mayer, 2012)

Reason for weak prediction for ABP_{VS} and BMP_{VS}

Statistic	VS	ABP_{FM}	ABP_{VS}	BMP_{FM}	BMP_{VS}
Unit	($gVS.gFM^{-1}$)	($mL.gFM^{-1}$)	($mL.gVS^{-1}$)	($mL.gFM^{-1}$)	($mL.gVS^{-1}$)
N	375	364	363	364	363
Minimum	0.1312	68	515	39	300
Maximum	0.5060	365	900	201	534
Range	0.3748	297	386	161	233
Mean	0.3037	225	741	126	417
Median	0.2982	222	740	125	413
SD	0.0641	48	55	25	40
RSD	21.11	21.33	7.42	19.84	9.59
Kurtosis	-0.22	-0.16	0.84	-0.05	-0.06
Skewness	0.30	-0.13	-0.20	0.10	0.32
SEL	0.0092	10	32.73	5	18
RSEL	3.03	4.44	4.42	3.97	4.32
SEL/SD	14	21	60	20	45
R^2max	97.95	95.93	65.13	95.49	79.93

$$R^2_{Max} = \frac{SD^2 - SEL^2}{SD^2}$$

(Dardenne, 2010)

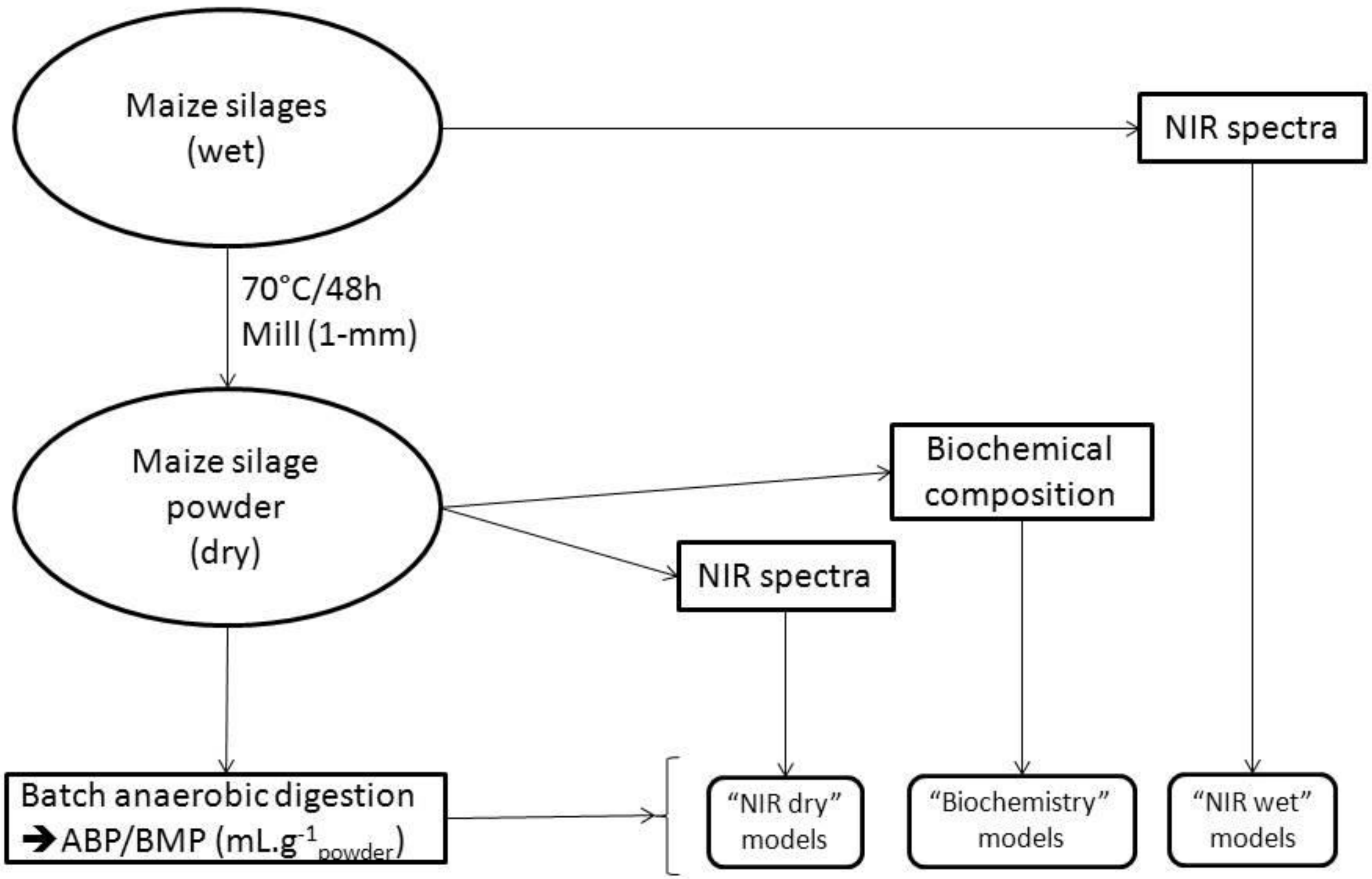
Problem: for ABP_{VS} and BMP_{VS}: SEL is too high compared to SD

➔ decrease SEL value for ABP_{VS} and BMP_{VS}

Proposed solution : analysing dry matter solely

➔sample drying and grinding

Results & Discussion



ABP/BMP of **dry powder**

Regression method	PLS		PLS		PLS	
X Block	NIR dry		NIR wet		Biochemistry	
Y	ABP	BMP	ABP	BMP	ABP	BMP
Y unit	($mL_{Biogas}.g^{-1}_{powder}$)	($mL_{CH4}.g^{-1}_{powder}$)	($mL_{Biogas}.g^{-1}_{powder}$)	($mL_{CH4}.g^{-1}_{powder}$)	($mL_{Biogas}.g^{-1}_{powder}$)	($mL_{CH4}.g^{-1}_{powder}$)
N	50	50	50	50	39	39
Min	488	283	488	283	488	283
Mean	550	307	550	307	544	304
Max	595	323	595	323	590	320
SD	29.2	11.6	29.2	11.6	27.4	10.4
RSD (%)	5.3	3.8	5.3	3.8	5.0	3.4
SEL	7.5	3.8	7.5	3.8	6.1	3.5
RSEL (%)	1.4	1.2	1.4	1.2	1.1	1.2
RSEL/RSD (%)	26	33	26	33	22	34
R2max	93.4	89.5	93.4	89.5	95.0	88.6
Wavenumber range	9303-3826cm^{-1}	9303-3826cm^{-1}	9303-3749cm^{-1}	9303-3749cm^{-1}	-	-
Pretreatment X	SNV-Det-1D-MC	SNV-Det-1D-MC	1D-MC	1D-MC	Autoscale	Autoscale
Pretreatment Y	MC	MC	MC	MC	MC	MC
Cross-validation	Random subsets	Random subsets	Random subsets	Random subsets	Random subsets	Random subsets
LVs	4	4	4	4	3	3
RMSEC	9.6	4.8	17.2	7.4	11.2	4.6
R^2C	87.7	80.9	60.5	54.3	82.8	80.1
RPDC	2.9	2.3	1.6	1.5	2.4	2.2
RMSECV	11.9	5.7	21.5	9.1	14.3	5.7
R^2CV	81.8	73.2	41.6	34.3	73.7	70.2
RPDCV	2.3	1.9	1.3	1.2	1.9	1.8
BiasCV	-0.11	-0.01	0.73	0.27	1.14	0.33

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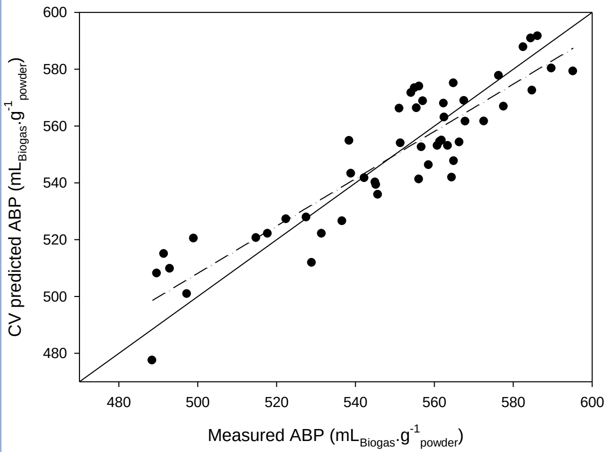
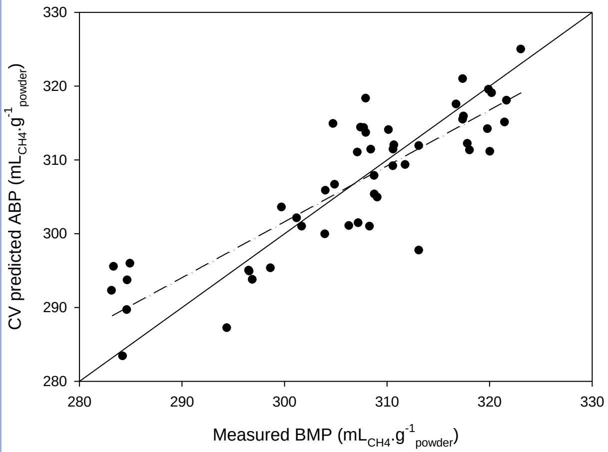
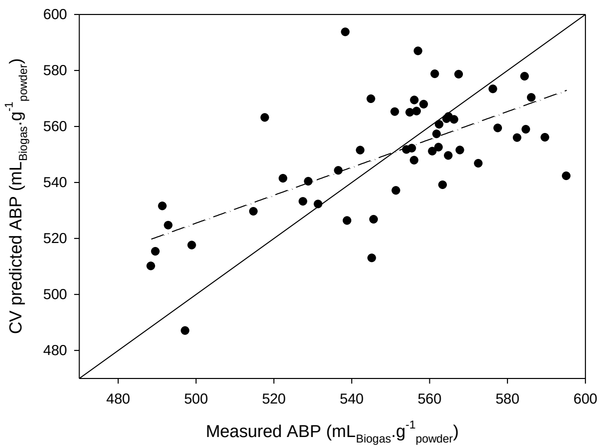
Results & Discussion

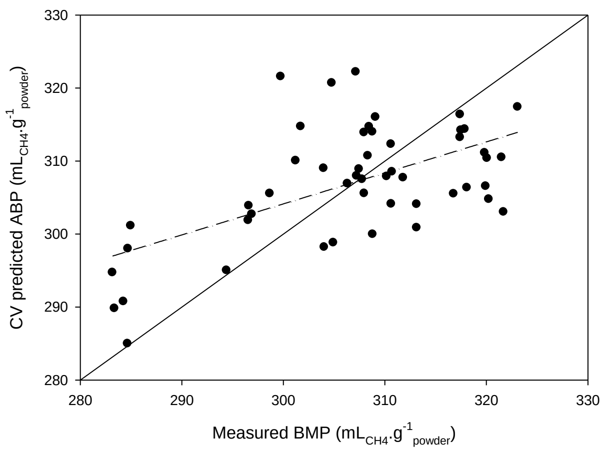
"NIR dry"



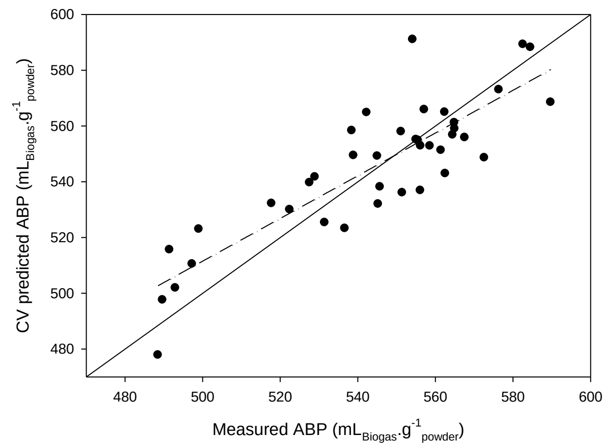


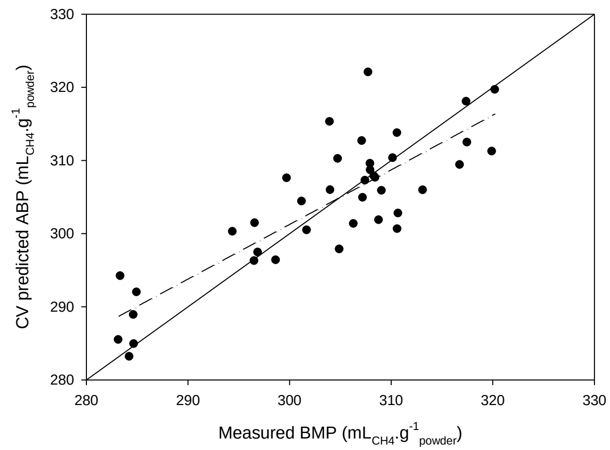
"NIR wet"





"Biochemistry"





Results & Discussion

Dataset

Better SEL ➔ better R^2_{max} ➔ better prediction performance *a priori*

Modelling

Performance: "NIR dry">"Biochemistry">"NIR wet"

For "NIR wet": more spectrum replicates and more acquisition time should be required

Low number (3-4) of Latent Variables for all models

Low number of samples (N=50): currently improved

Biogas (ABP) prediction better than biomethane (BMP) prediction

Method

Loss of volatile compounds (EtOH, Volatile Fatty Acids…)

Results & Discussion

		Wet	Dry
Maize silage	Pros	• Raw matter used in biomethanation ➢ Include all biochemical fractions ➢ Particule size considered	• Easy to analyse with biochemical methods • Homogeneous
	Cons	• Not stable over time: loss of water, volatile compounds • Difficult to analyse with conventional biochemical methods • Heterogeneous, subsampling variability	• Pretreatment of the raw matter (drying and grinding) ➢ Loss of volatile compounds • Time-consuming (48h)
NIRS	Pros	• Immediately analysable • Sensitive to water	• Sensitive to the absorbance of the dry organic fractions
	Cons	• Information can be diluted by water absorption ➢ cautious setup of the acquisition method	• Information loss for water and volatile compounds
ABP/BMP	Pros	• Bioexploitation of all compounds ➢ practical interest	• Sensitive to the dry organic fraction ➢ scientific interest
	Cons	• Dilution by water of the biochemical composition ➢ not feasable for accurate measure of ABPVS and BMPVS	• Lost organic compounds not analysed • Bioconversion kinetics affected

Conclusion

Prediction of biogas and biomethane potential (ABP and BMP) of maize silages with Near Infrared Spectroscopy (NIRS) is achievable

➔ Improvement by using better NIR spectra of wet biomass

➔ Same approach for other energy crops possible

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UCL Université catholique de Louvain

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