It is possible to asses the degradation stage of bio-based materials with an "objective" approach?

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outline

- degradation
- state-of-the-art assesment of degradation degreee
- alternatives
- case studies:
    - paper
    - weathered wood surface
    - waterlogged wood
- conclusion

goals

- to apply more objective approaches (such as NIR spectroscopy) for the evaluation of degradation degree of bio-based materials
- to present some "success stories" of such methodologies:
    - paper degradation by fungi
    - weathering wood surface
    - waterlogged wood

To "ignite*" discussion on the methodolog(ies) for the <u>objective</u> determination of the degradation degree

***in collaboration with COST FP1404**

degradation

Bio-based materials undergo **modification during their service** life caused by mechanical, environmental or biological agents.

In a consequence significant changes within physical, mechanical and chemical properties are occurring and **drop of material performance** is expected.

*On the other hand biodegradability is becoming a **desirable feature** for several everyday products, such as packaging or wastes.*

STATE-OF-THE-ART

The commonly used method(s) for assessment of the degradation stage

- visual assessment according to standards (ex. prEN 252, CEN/TS 12037)
- visual assessment according to “custom” rules
- mould/fungus index
- measurement of mass loss
- measurement of breaking length
- measurement of other properties (strength, water uptake, colour, shape…)
- …

Rating scale according to prEN 252 (2012)

(*and according to COST Action FP1303 TS Hannover, Germany*)

Rating	Description	Definition
0	Sound	No change perceptible by the means at the disposal of the inspector in the field. If only a change of color is observed, It shall be rated 0.
1	Slight attack	Perceptible changes, but very limited in their intensity and their position or distribution: changes which only reveal them-selves externally by superficial degradation, softening of the wood being the most common symptom.
2	Moderate attack	Clear changes: softening of the wood to a depth of at least 2 mm over a wide surface (covering at least 10 square centime-ters) or by softening to a depth of at least 5 mm over a limited surface area (covering less than 1 square centimeter).
3	Severe attack	Severe changes: marked decay in the wood to a depth of at least 3 mm over a wider surface (covering at least 25 square centimeters) or by softening to a depth of at least 10 mm over a more limited surface area.
4	Failure	Impact failure of the stake in the field.

problems of “subjectivity”

The result of assessment (may?) depend on:

- **the person**
- training & personal experiences
- mood
- tiredness/fatique
- the time of measurement
- ???

The degradation is not always visible without aid (such as microscope)!!!

repeatability and reproducibility test

Repeatability: the variation in measurements taken by a single person or instrument on the same or replicate item and under the same conditions

Reproducibility: the variation induced when different operators, instruments, or laboratories measure the same or replicate specimen

For example:

- *10 samples*
- *each measured 2 times*
- *by 2 different operators*

\+ *ANOVA*

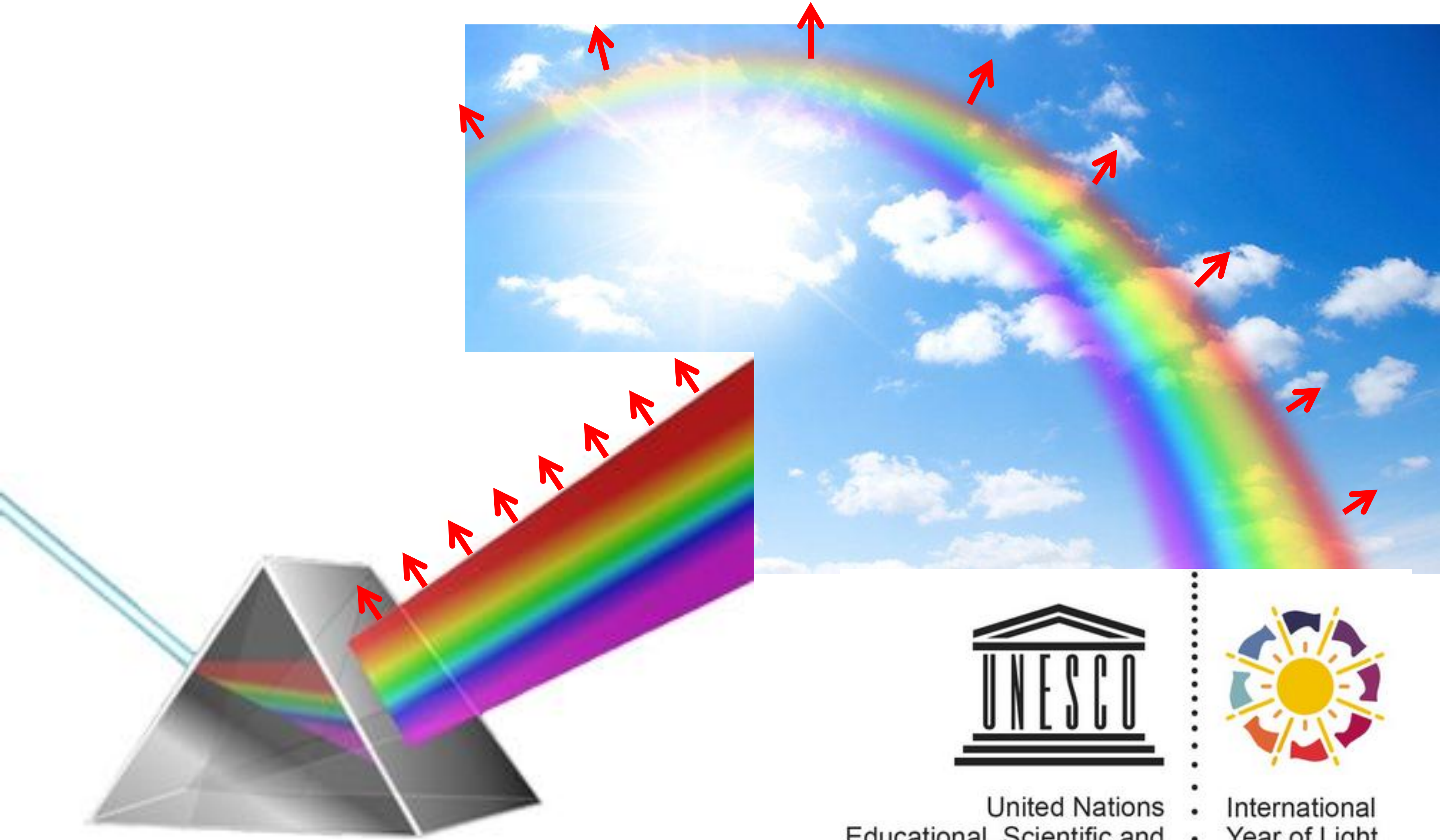
$$SS_{Tot} = \sum \left(x_{ijk} - \bar{x}\right)^2$$

$$SS_{Part} = n_{Op} \cdot n_{Rep} \sum \left(\bar{x}_{i..} - \bar{x}\right)^2$$

$$SS_{Op} = n_{Part} \cdot n_{Rep} \sum \left(\bar{x}_{.j.} - \bar{x}\right)^2$$

$$SS_{Rep} = \sum \sum \sum \left(x_{ijk} - \bar{x}_{ij}\right)^2$$

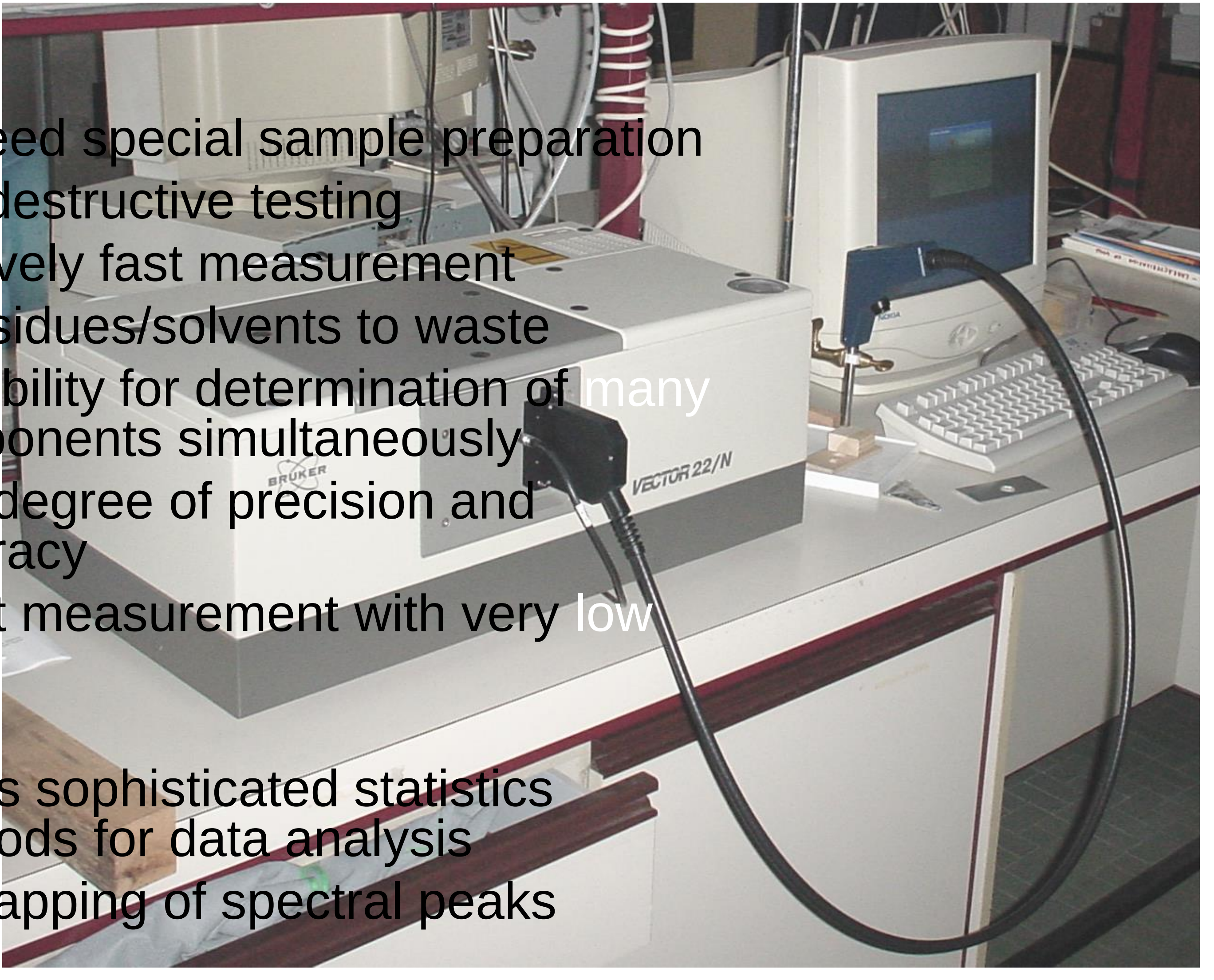
our alternative (one of…)



United Nations
Educational, Scientific and
Cultural Organization

International
Year of Light
2015

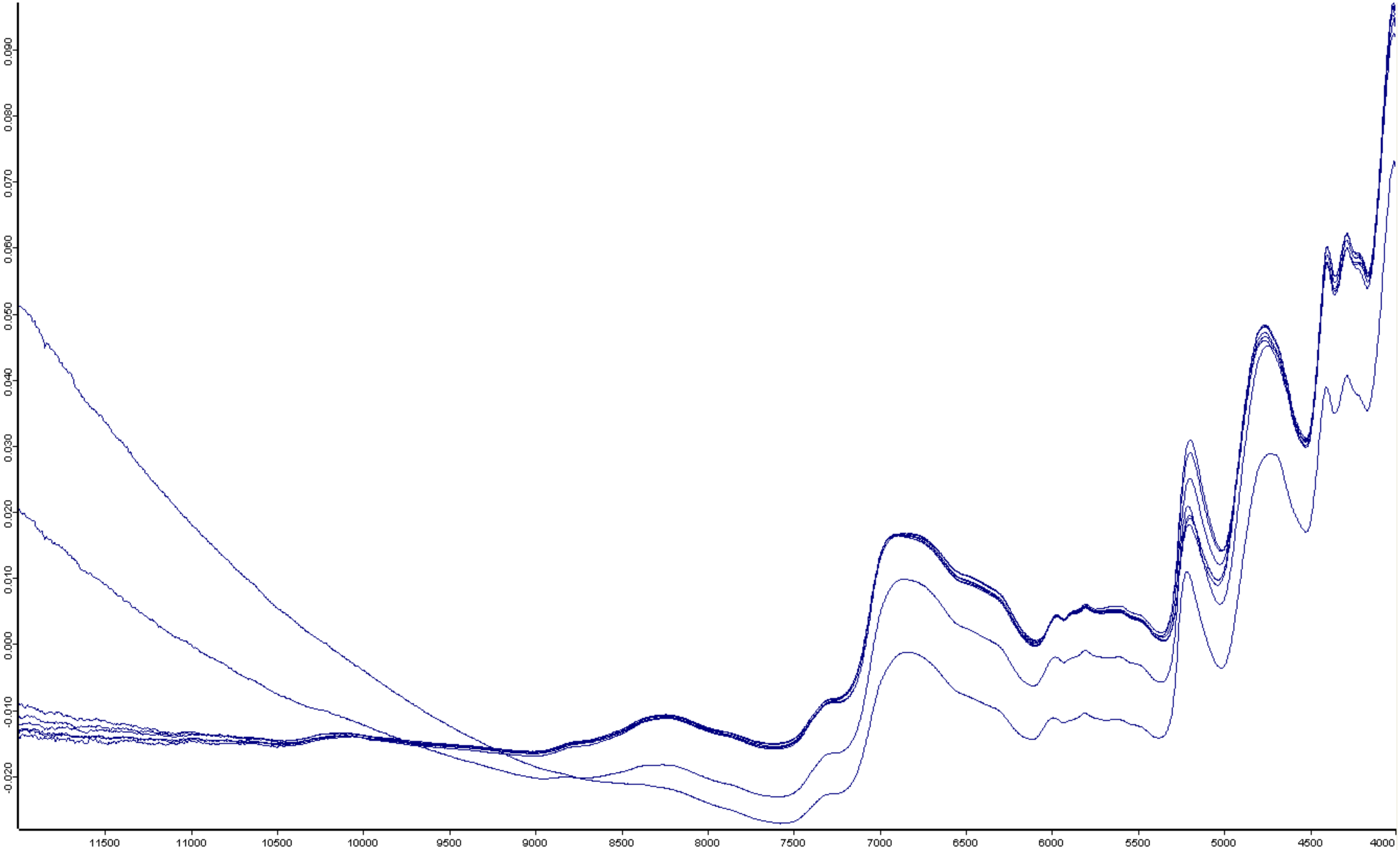
NIR technique



- no need special sample preparation
- non-destructive testing
- relatively fast measurement
- ro residues/solvents to waste
- possibility for determination of many components simultaneously
- high degree of precision and accuracy
- direct measurement with very low cost

- needs sophisticated statistics methods for data analysis
- overlapping of spectral peaks

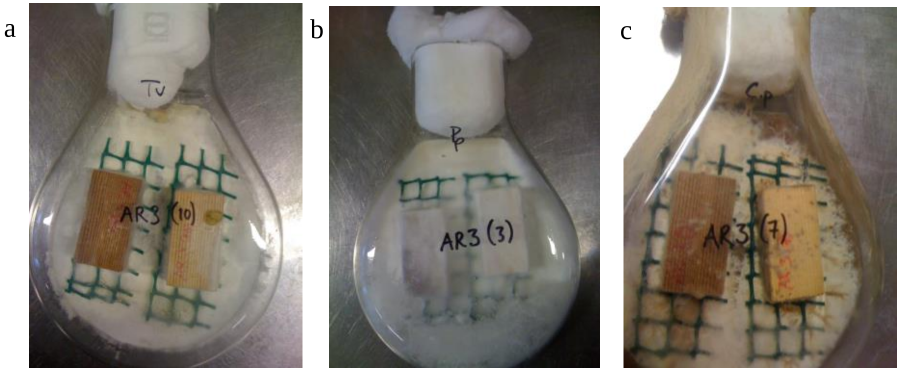
Raw spectra


0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
-0.010
-0.020
11500
11000
10500
10000
9500
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000

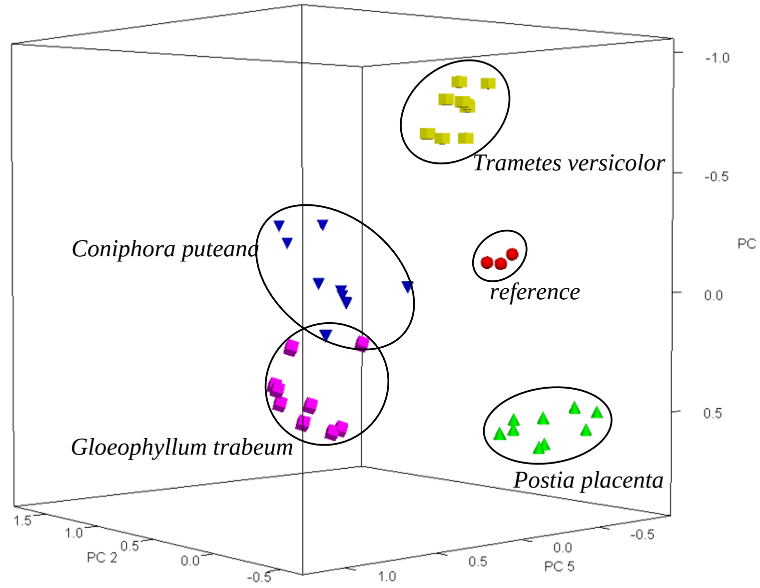
NIR band assignment (wood)

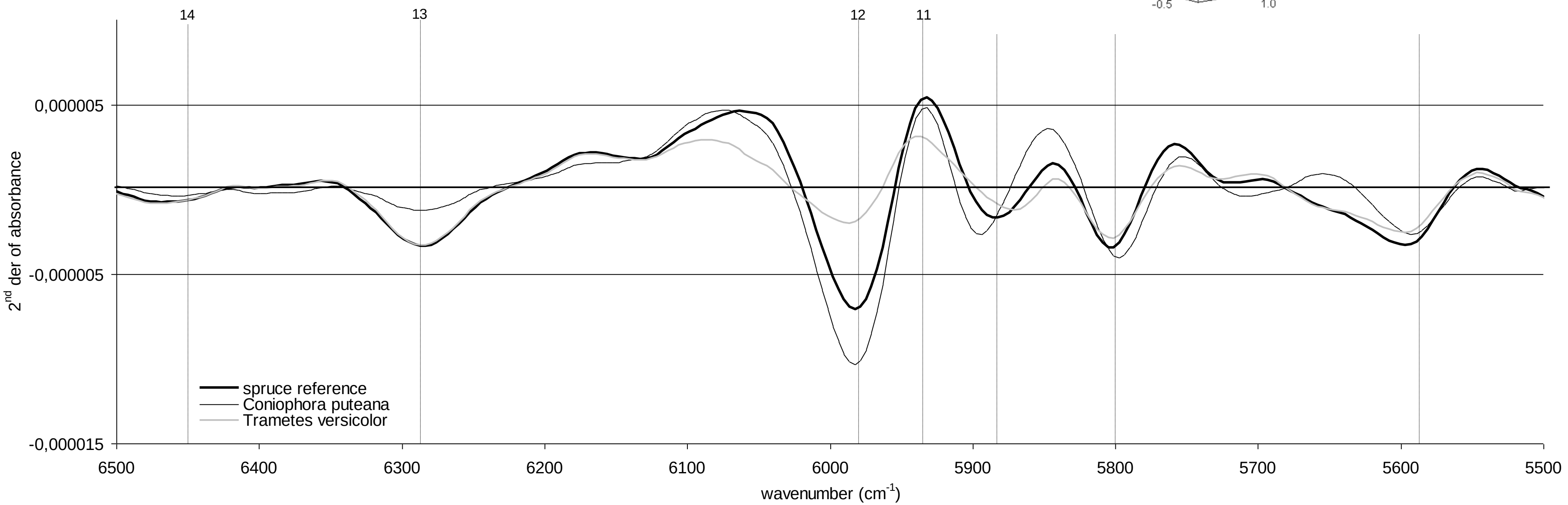
code	wavenumber (cm^{-1})	band assignment
1	4198	CH deformation in holocellulose
2	4280	CH stretching + CH deformation in semi- and crystalline region in cellulose
3	4404	CH_2 stretching + CH_2 deformation of cellulose
4	4620	OH stretching + CH deformation of cellulose
5	4890	OH stretching + CH deformation of cellulose
6	5219	OH stretching + OH deformation of water
7	5464	OH stretching + CH stretching semi- or crystalline regions of cellulose
8	5587	CH stretching semi- or crystalline regions of cellulose
9	5800	CH stretching in furanose/pyranose due to hemicelluloses
10	5883	CH stretching in aliphatic chains
11	5935	CH stretching of aromatic skeletal in lignin
12	5980	CH stretching of aromatic skeletal in lignin
13	6287	OH stretching in crystalline region in cellulose
14	6450	OH stretching in crystalline region in cellulose
15	6722	OH stretching in semi-crystalline region in cellulose
16	6785	OH stretching in semi-crystalline region of cellulose
17	7008	OH stretching in amorphous region in cellulose
18	7309	CH stretching in aliphatic chains
19	7418	CH stretching in aliphatic chains

Proof of idea study: vacuum TM wood decay



a) *Trametes versicolor*, b) *Postia placenta* and c) *Coniophora puteana*





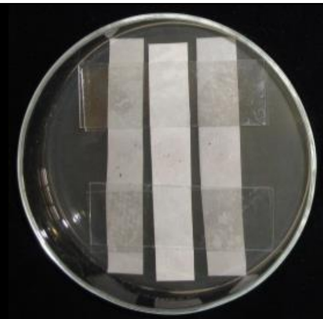
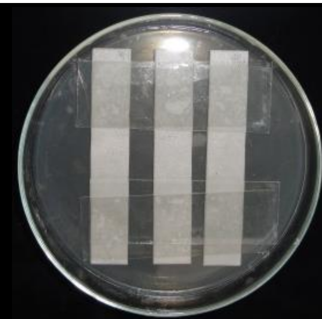
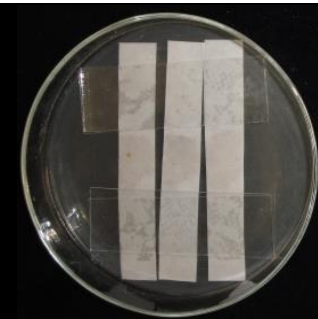
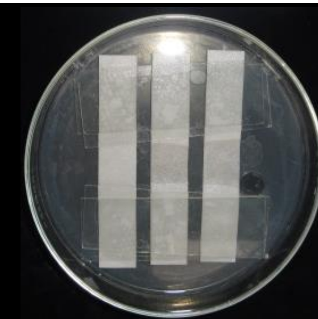
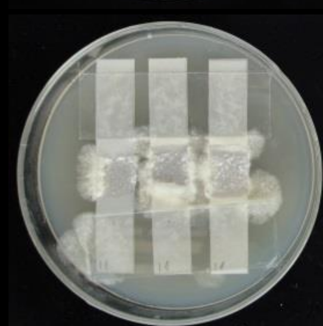
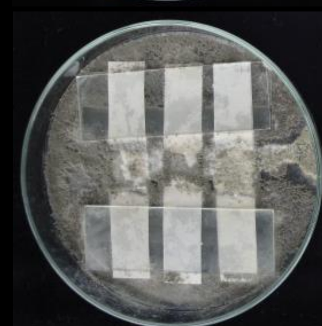
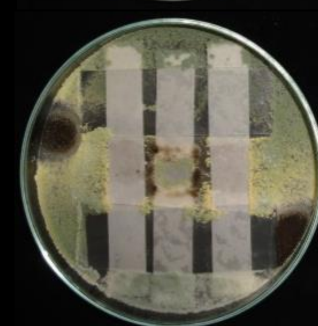
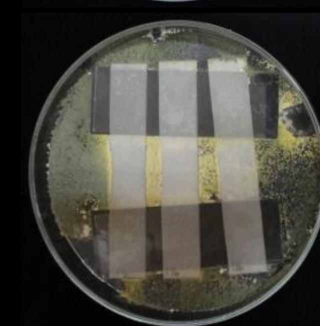
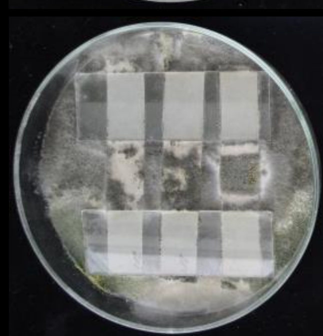
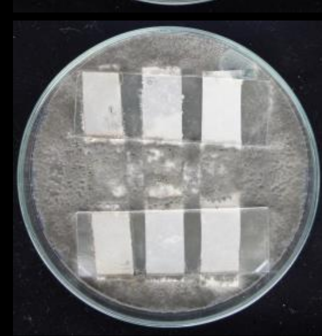
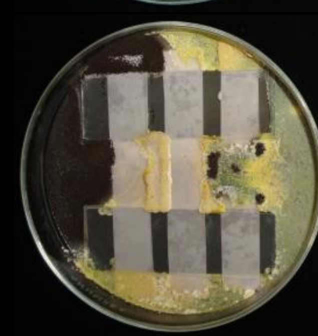
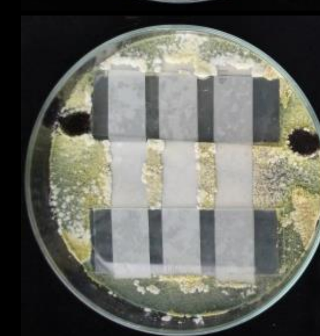
PLS for mass loss; r^2 = 94.43 RMSECV = 3.48 RPD = 4.24

CASE STUDY #1: PAPER WITH ADDITIVES DEGRADED BY FUNGI

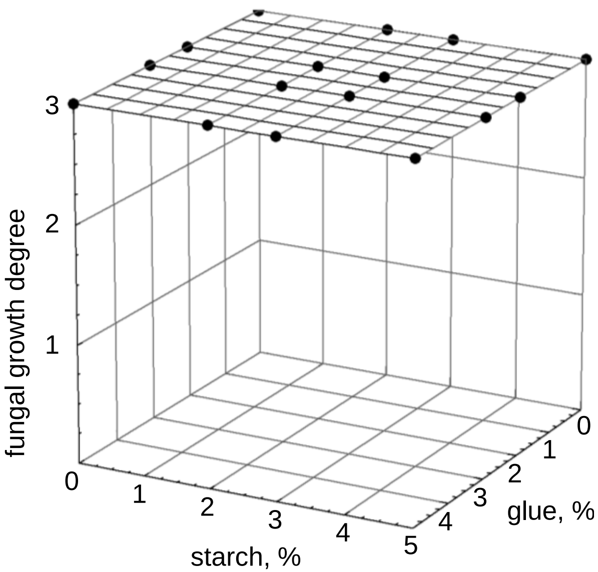
materials & methods

- 16 paper types of coniferous sulphate bleached pulp with varying content of additives (0, 2, 3, and 5% addition of cationic starch and resin adhesive).
- *Chaetomium globosum* and a mixture (1:1:1) of *Aspergillus niger, Penicillium funiculosum, Trichoderma viride* as degrading fungi
- visual evaluation of the fungal growth according to the four point scale:
  - grade “3” no presence of fungi
  - grade “0” very abundant growth with surface entirely colonized by fungus mycelium
- samples measured in ten independent repetition series on the 2^{nd}, 4^{th}, 7^{th}, 10^{th} and 14^{th} day after infestation
- breaking length of paper was measured according to ISO 1924-1 standard, simultaneously to the mycological tests

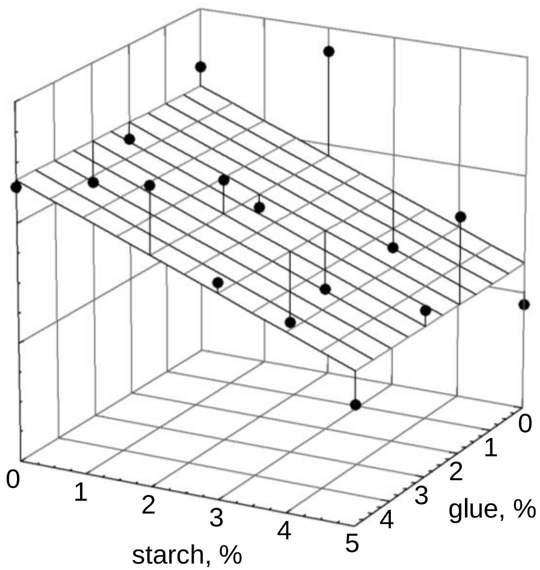
paper samples along the test

additives	*Ch. globosum*		mixture of *A. niger, T. viride, P. funiculosum*	
	without	cationic starch 5% + resin adhesive 5%	without	cationic starch 5% + resin adhesive 5%
2nd day				
7th day				
14th day				

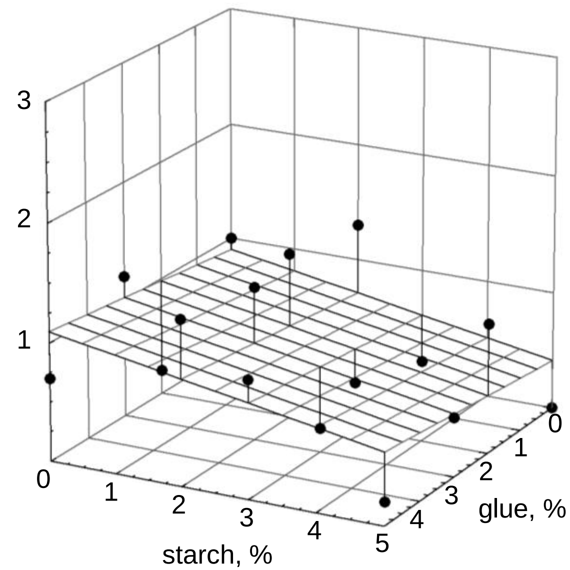
fungi growth degree/index



0 days

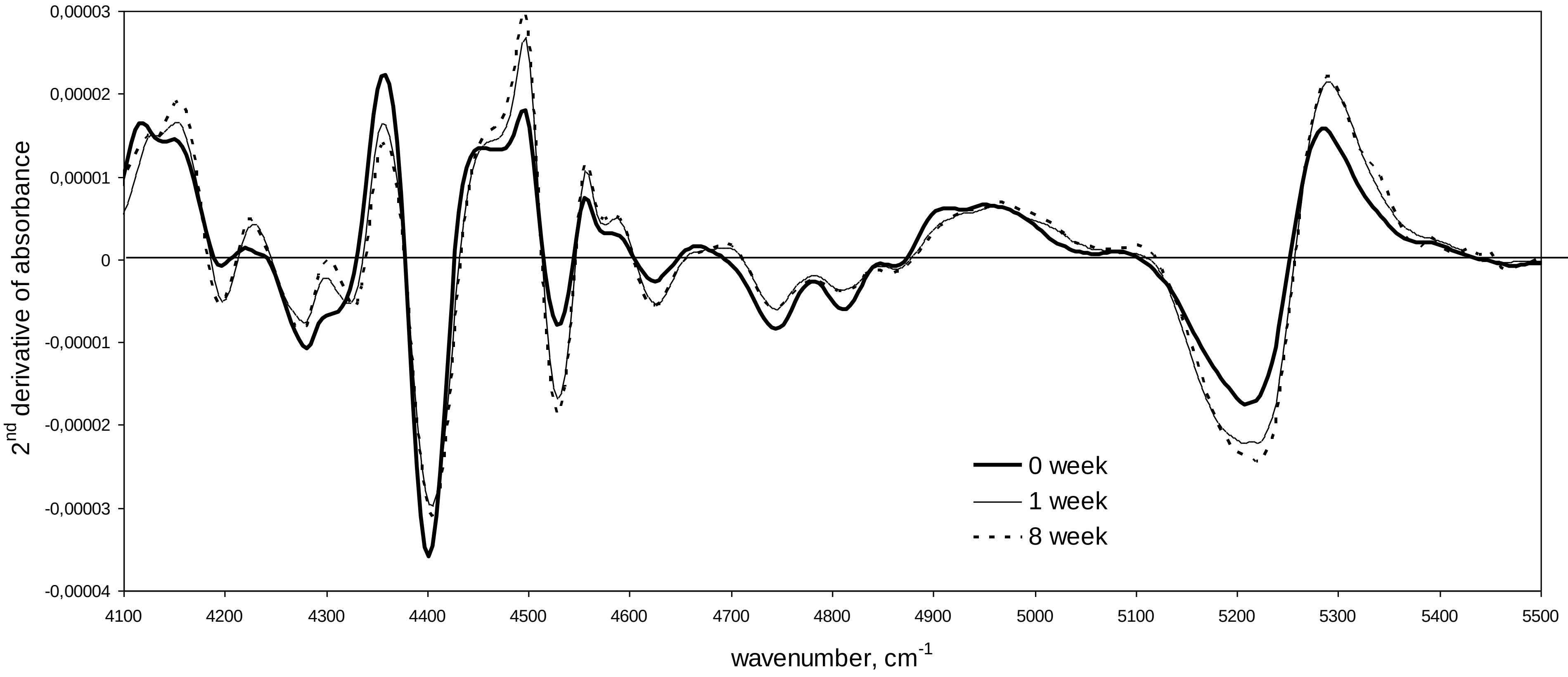


7 days

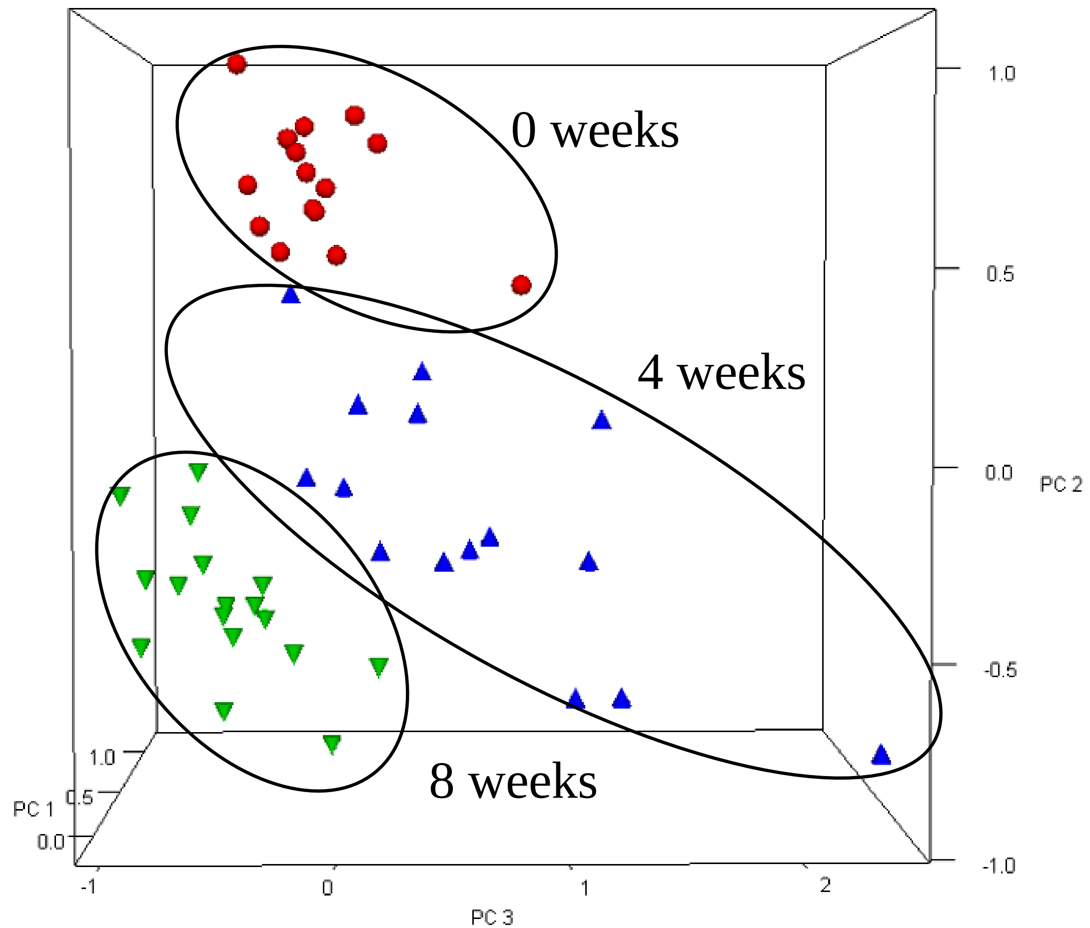


14 days

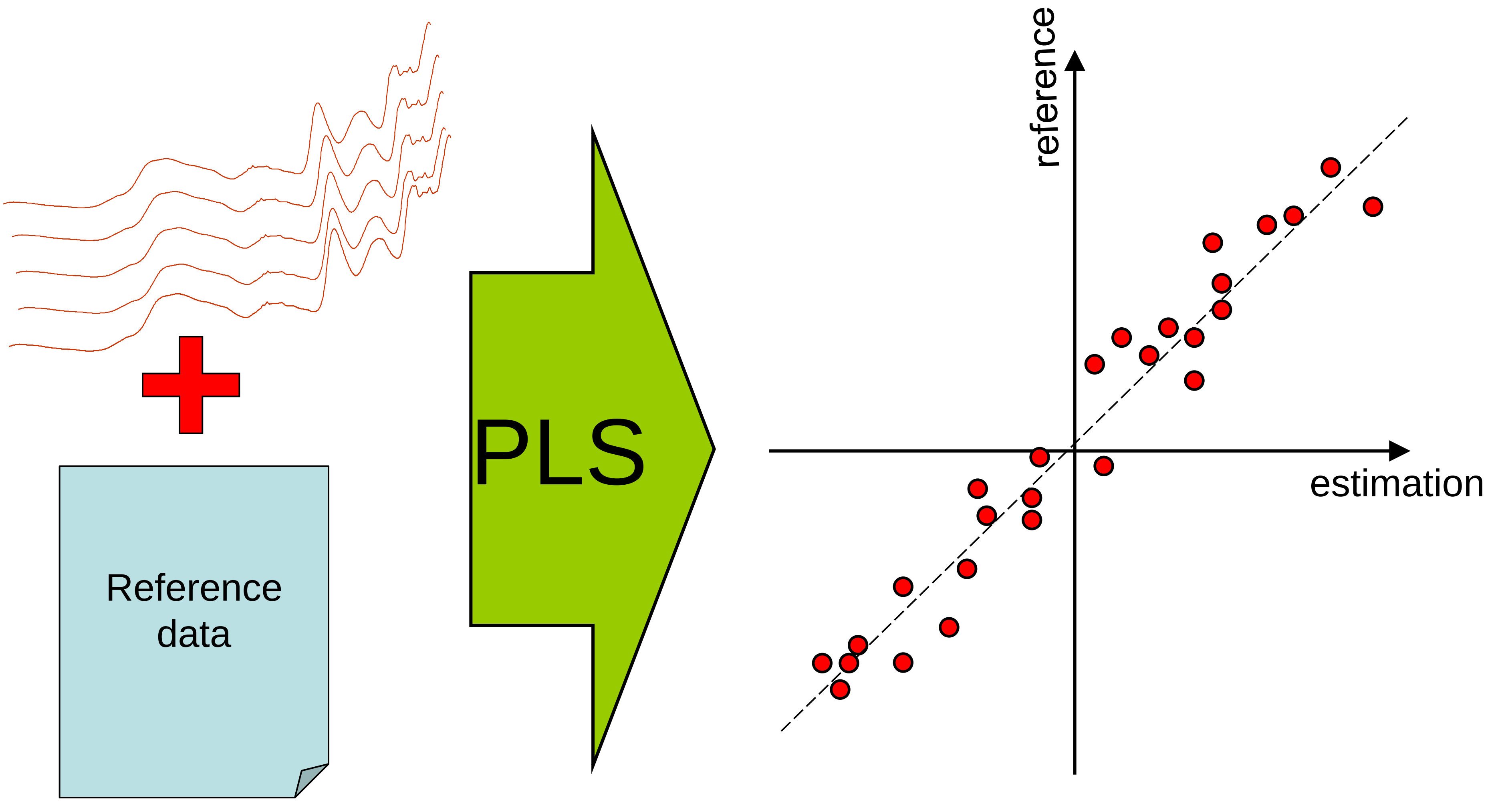
Effect of time: NIR spectra



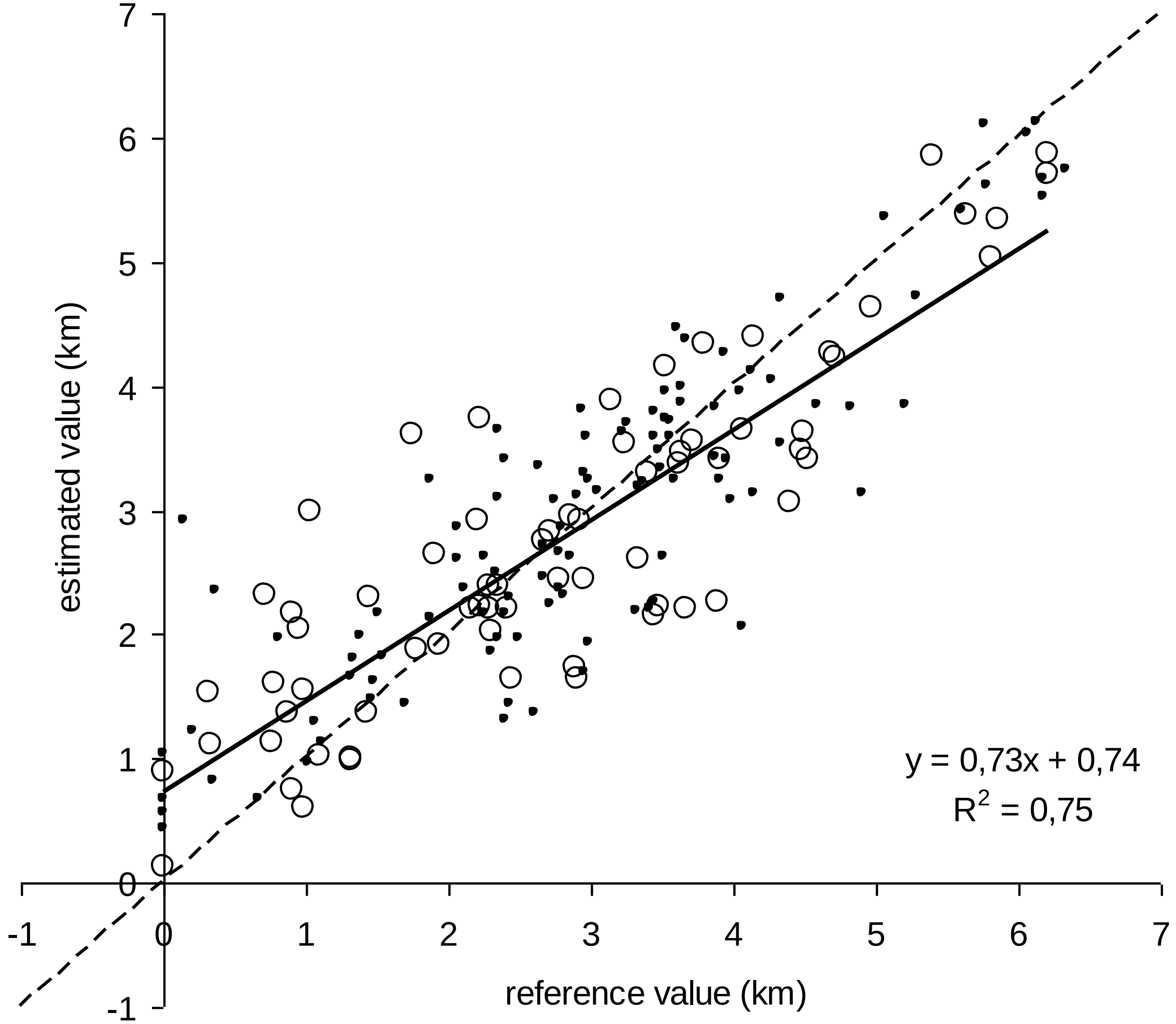
Effect of time: PCA discrimination



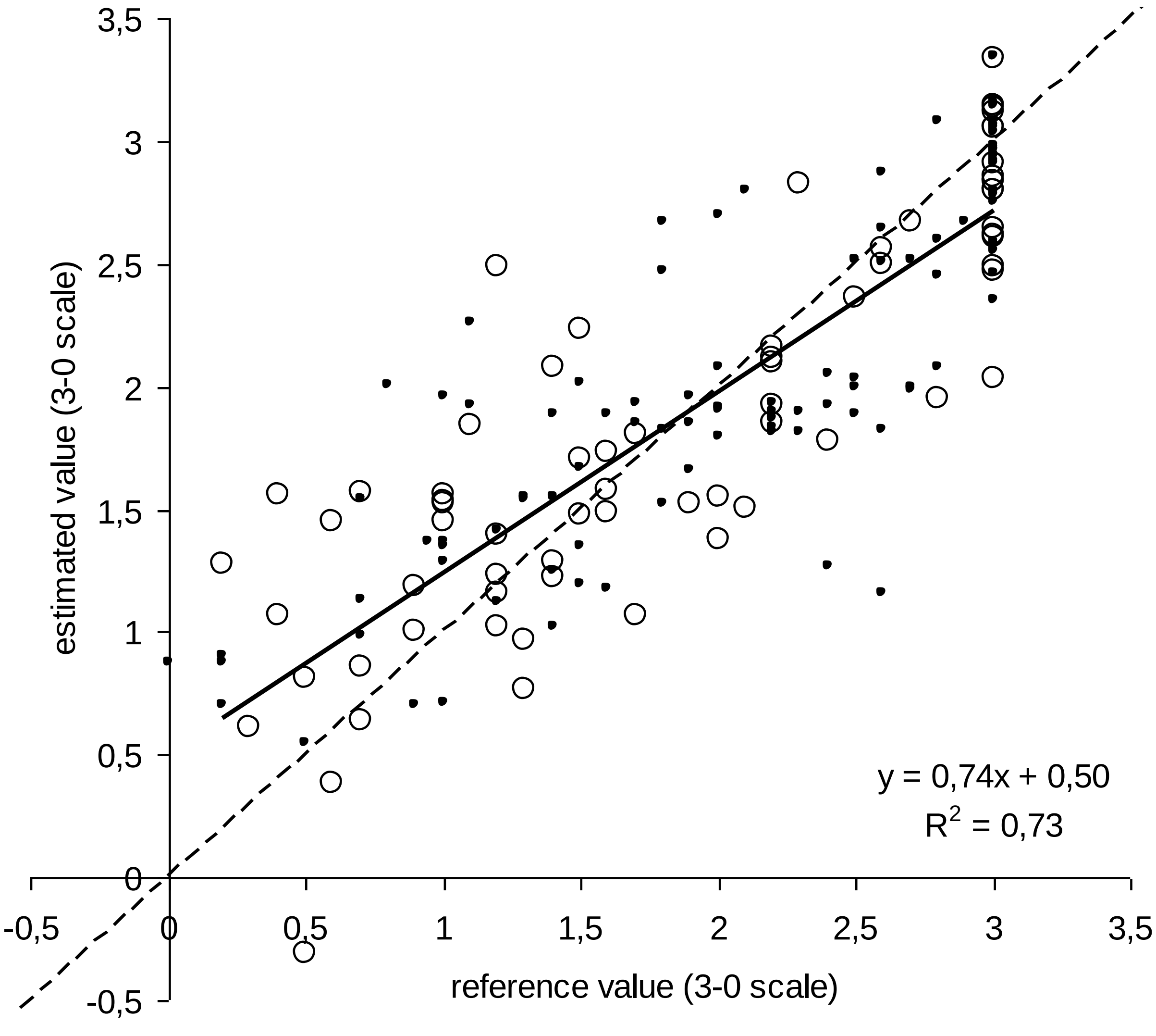
Partial Last Squares



NIR prediction of breaking length



NIR prediction of fungi growth degree

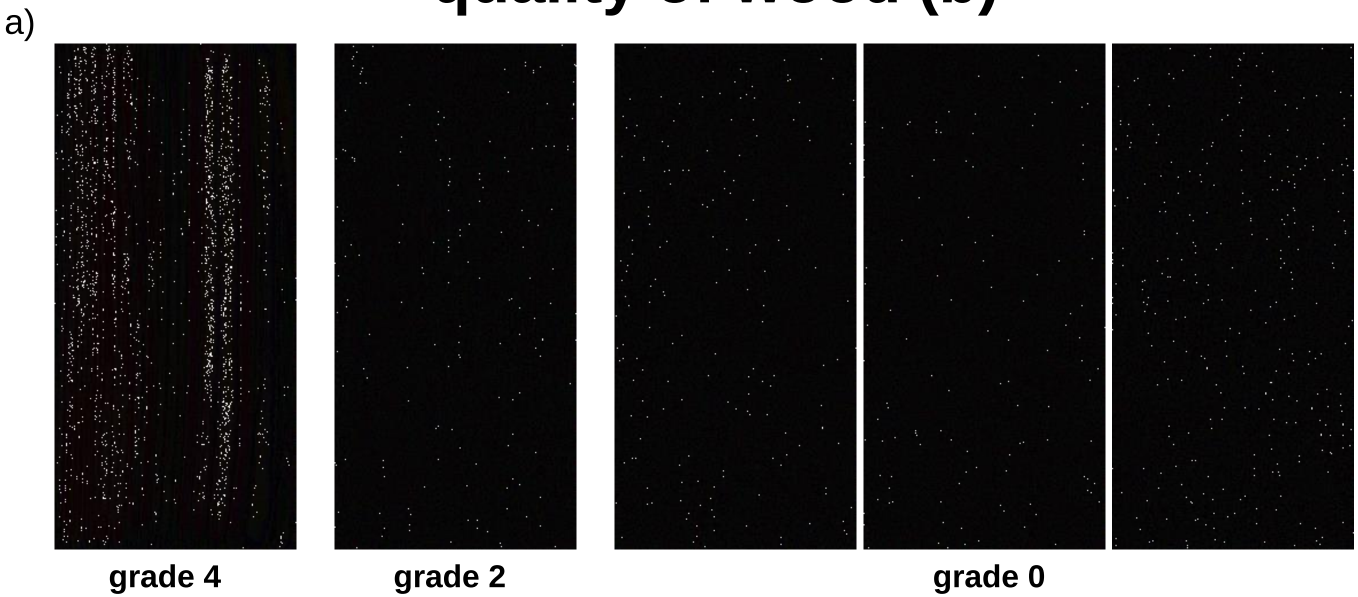


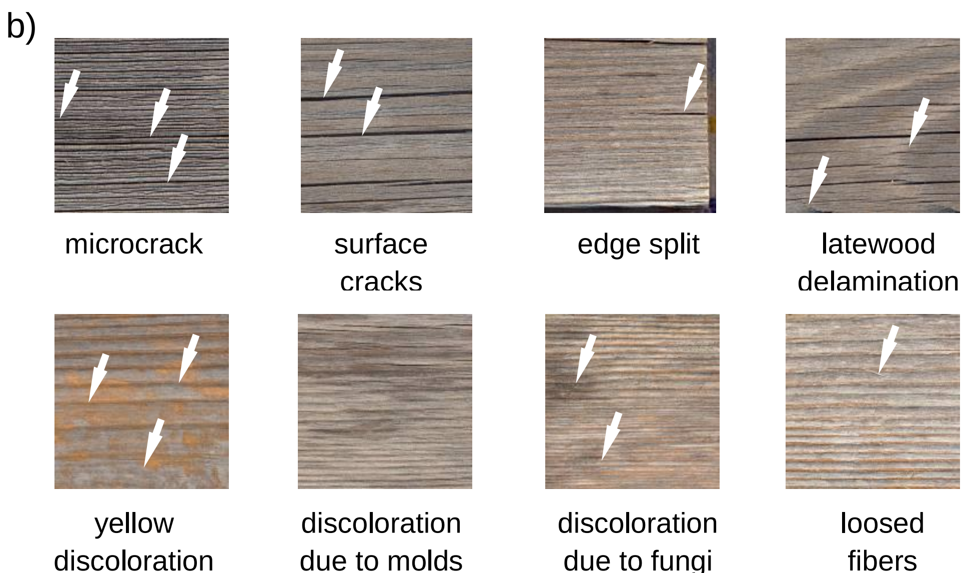
CASE STUDY #2: LONG-TERM SURFACE WEATHERING

wood samples exposed to natural weathering to the south direction in Reggio Emilia

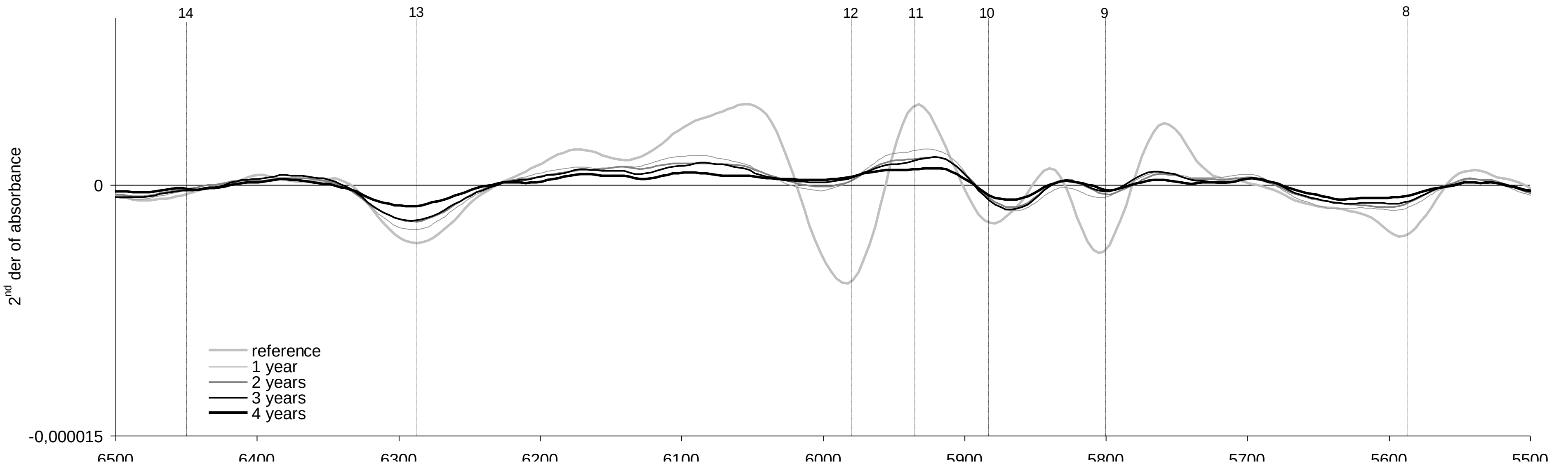
0 years | 1 year | 2 years | 3 years | 4 years

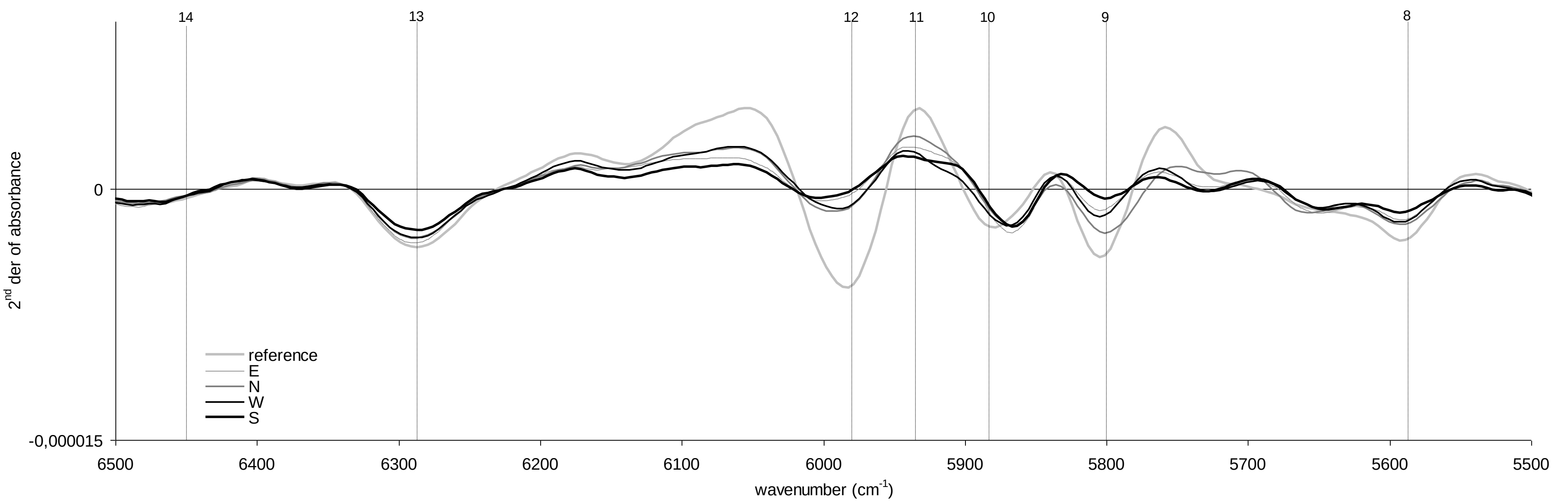
quality grades as provided by experts panel during visual assessment (a), surface defects degrading the aesthetical quality of wood (b)



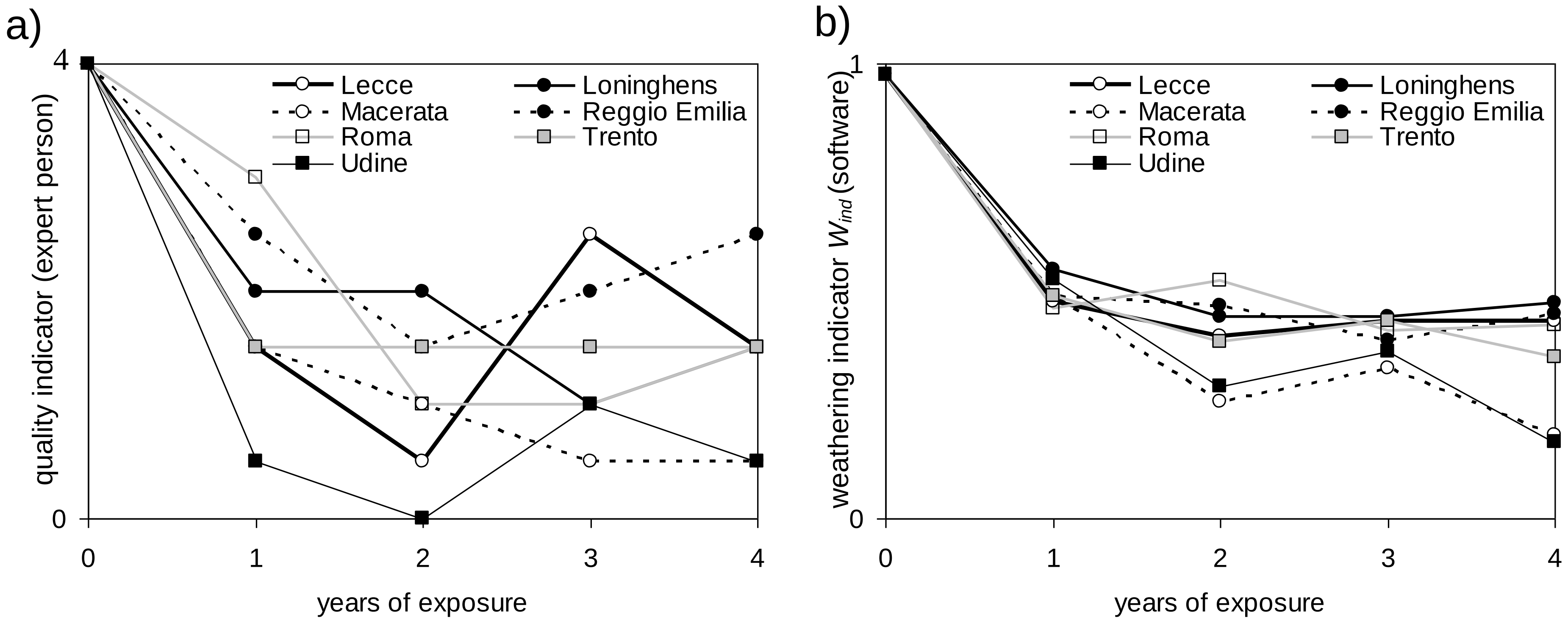


NIR monitoring of wood weathering





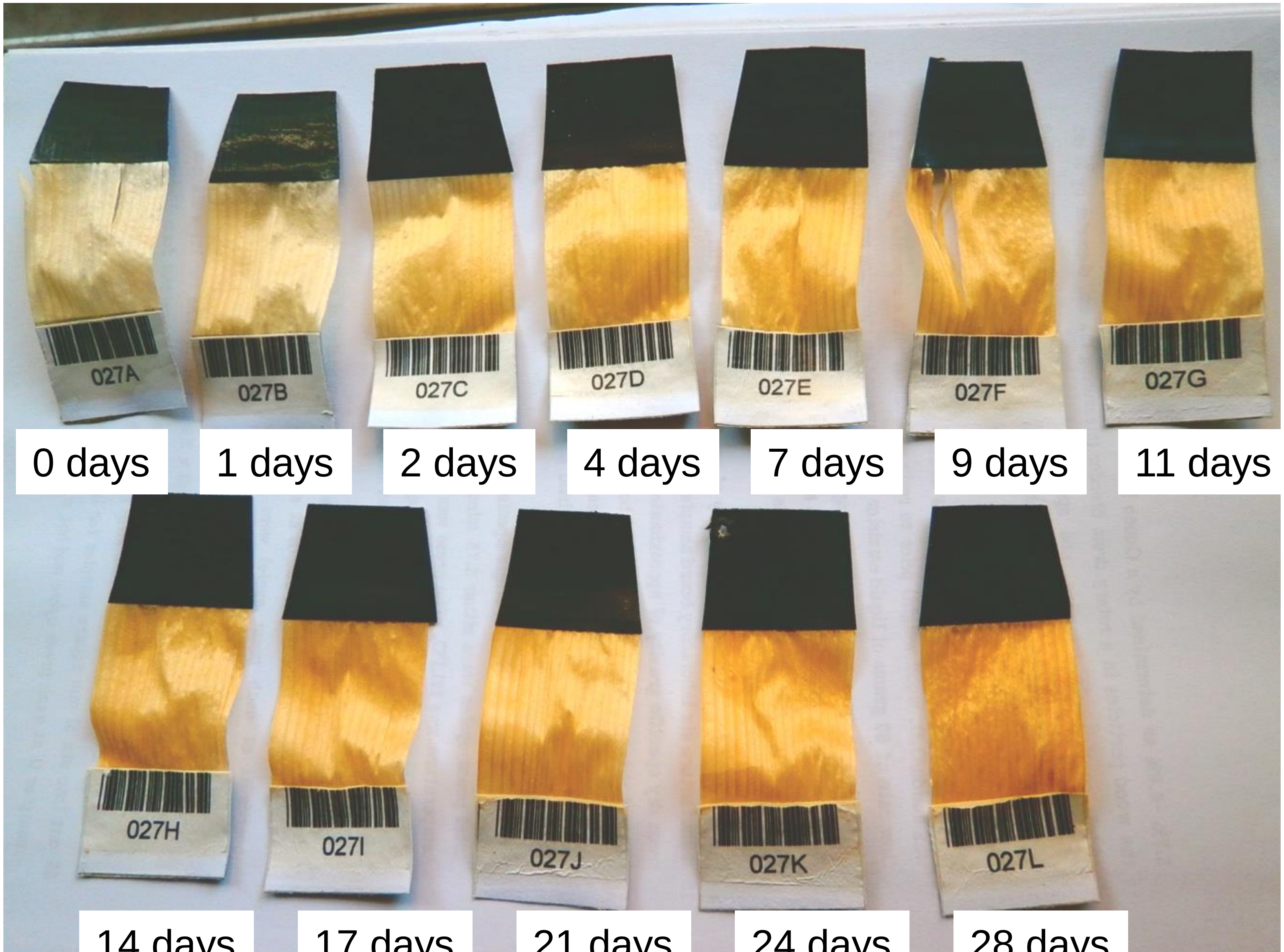
Expert person (a) and software (b) estimation of the weathering index



CASE STUDY #3: SHORT-TERM SURFACE WEATHERING

Round Robin test - COST FP1006

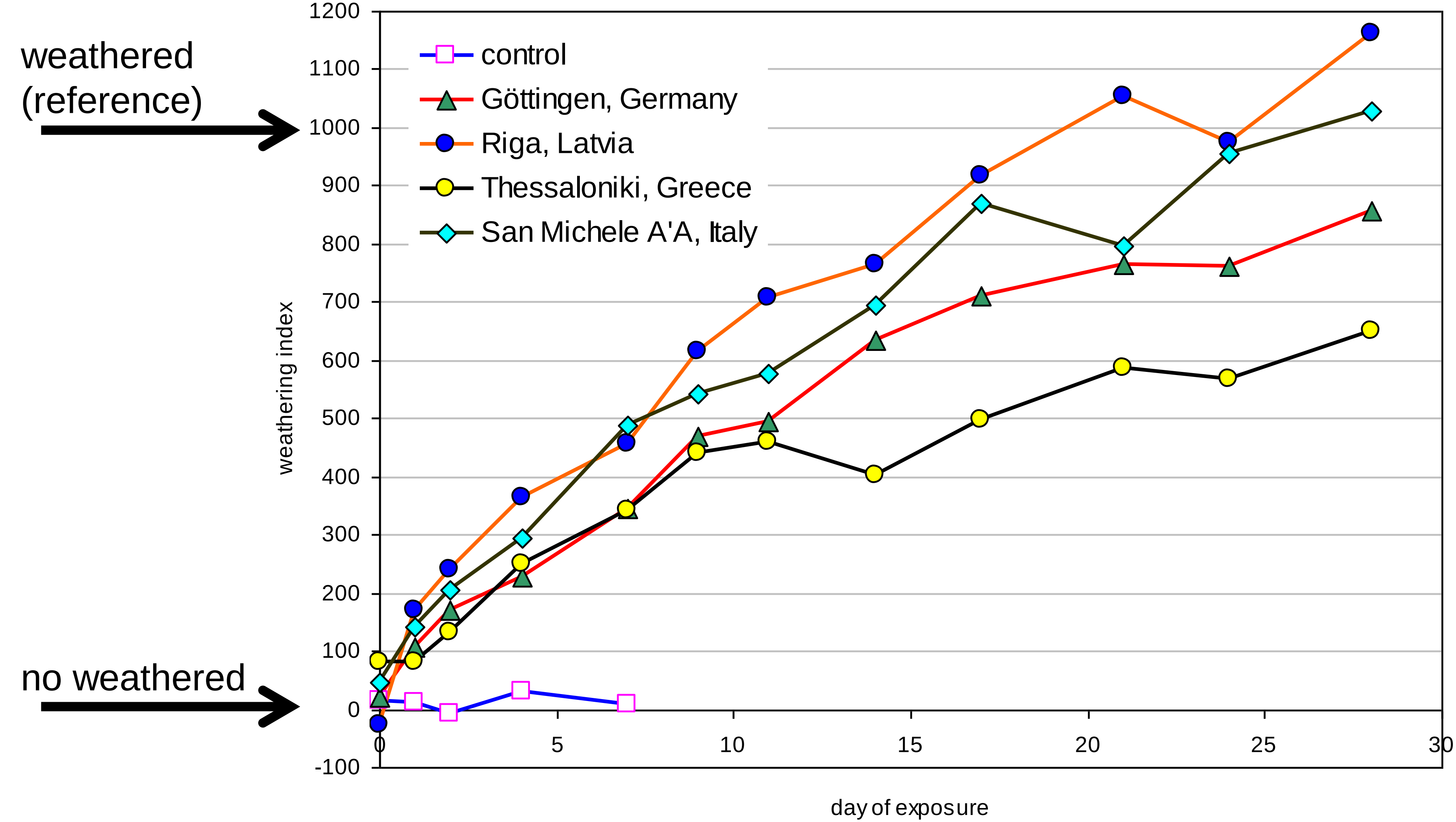
what is the degradation stage?



Weathering index estimated on the base of NIR spectra

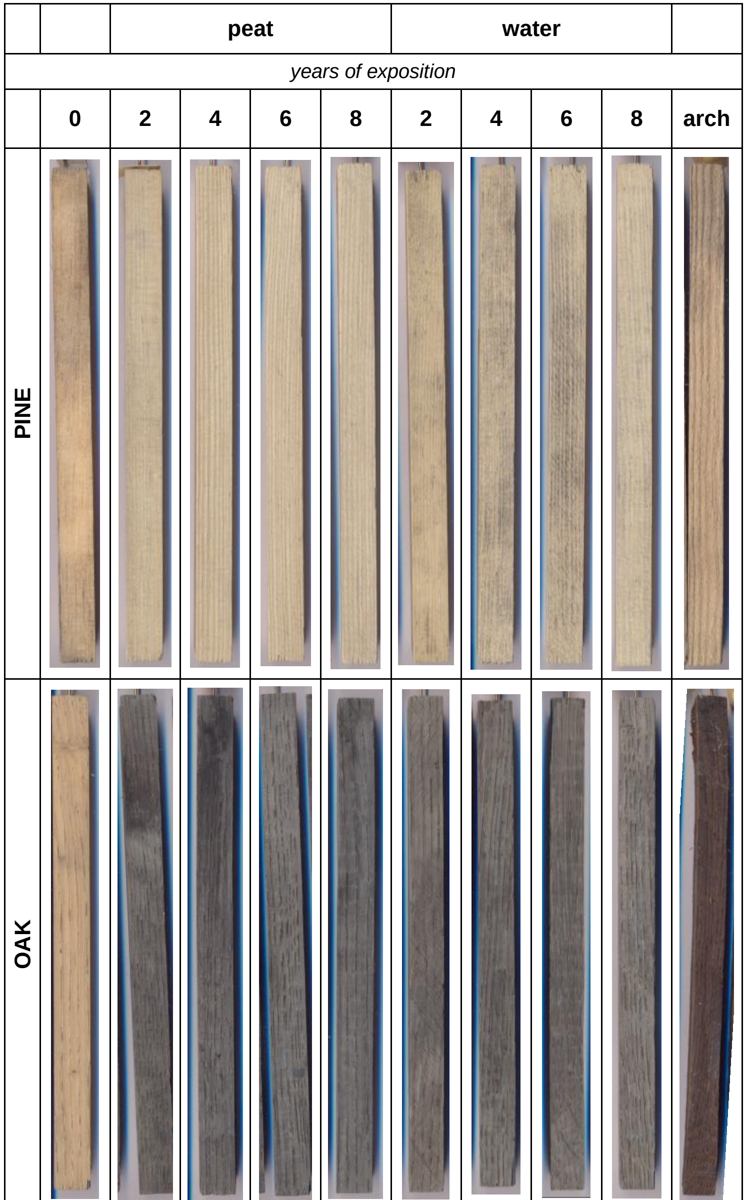
weathered (reference)

no weathered



CASE STUDY #4: SHORT TERM WATERLOGGING

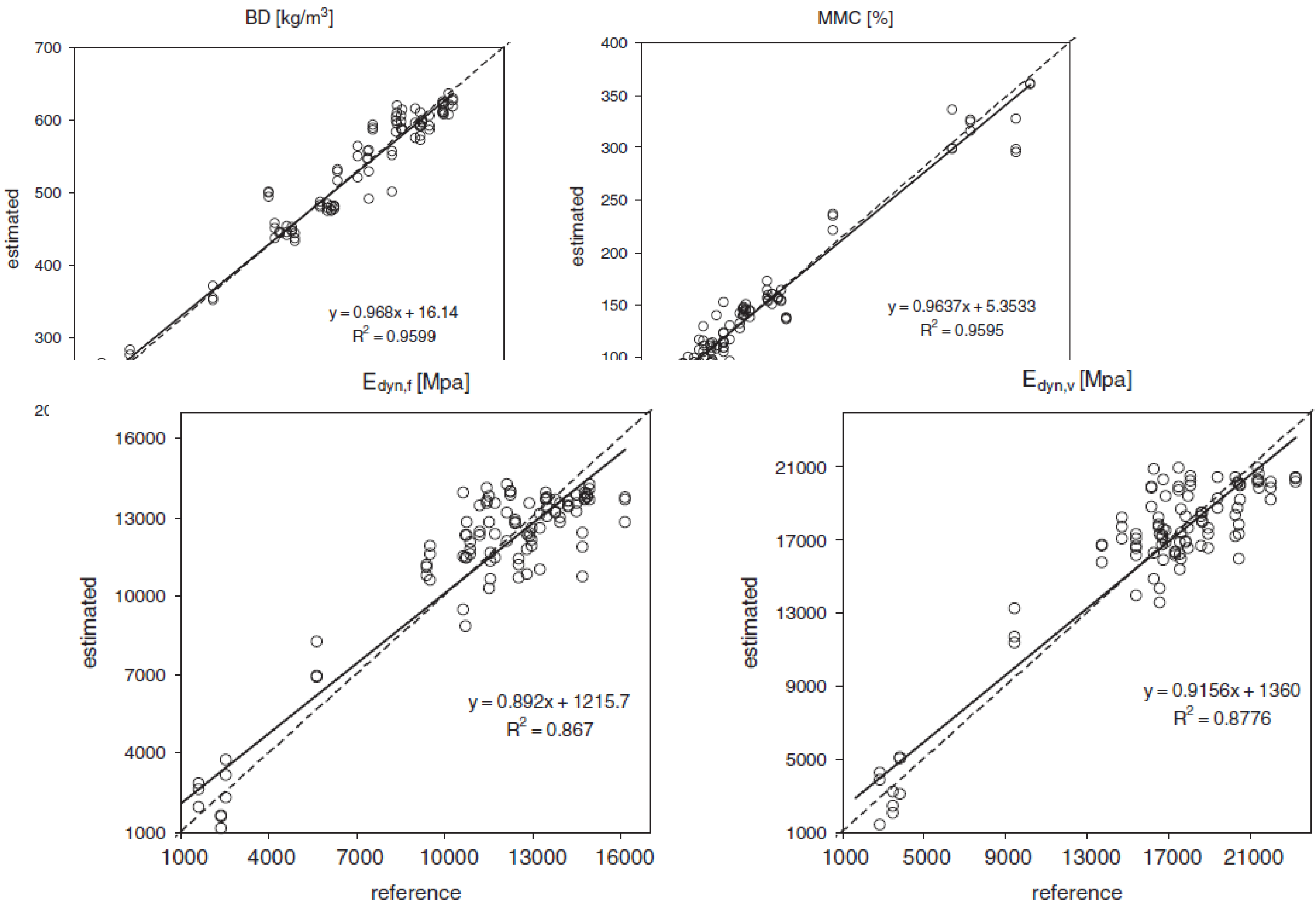
Short term waterlogging



nr	band assessment			pine		oak	
	wave number (cm^{-1})	wood component	functional group	peat	water	peat	water
1	4195	lignin	not assigned	○	○	×	∘
2	4268	cellulose	CH, CH_2	○	○	○	○
3	4401	cellulose, hemicelluloses	CH, CH_2, OH, CO	○	○	◯	○
4	4546	lignin	CH, C=O	×	×	∘	•
5	4608	cellulose, hemicelluloses	not assigned	×	×	∘	×
6	4686	hemicelluloses, lignin, extractives	CH, C=C, C=O	×	×	●	●
7	4739	cellulose	OH	○	○	○	○
8	4808	cellulose semi-crystalline and crystalline	OH, CH	○	◯	○	○
9	5051	water	OH	×	×	○	○
10	5198	water	OH center of the range	○	○	○	○
11	5245	hemicelluloses	C=O	◯	◯	◯	◯
12	5495	cellulose	OH, CO	×	×	∘	∘
13	5593	cellulose semi-crystalline and crystalline	CH	∘	○	×	∘
14	5666	not assigned	CH, CH_2	●	●	∘	○
15	5692	not assigned	CH_2	●	●	×	×
16	5800	hemicelluloses (furanose / pyranose)	CH	○	○	◯	◯
17	5865	hemicelluloses	CH	○	○	∘	○
18	5935	lignin	CH	∘	○	○	∘
19	5980	lignin	CH	◯	◯	○	○
20	6126	cellulose	OH	∘	○	×	×
21	6286	cellulose crystalline	OH	∘	∘	∘	∘
22	6334	cellulose	OH	×	×	×	×
23	6472	cellulose crystalline	OH	∘	∘	×	×
24	6715	cellulose semi-crystalline	OH	∘	∘	∘	∘
25	7003	amorphous cellulose, water	OH	∘	∘	∘	∘
26	7092	lignin, extractives	OH	◯	◯	◯	○

360 samples measured x 3 spectra/sample = **1080 spectra**

NIR-predicted material characteristics



conclusions

- the evaluation of the degradation degree of bio-materials is a challenging task
- the visual assessment, even if frequently used is (may be) very subjective
- NIR spectroscopy (as well as other analytical methods) allows indirect estimation of the material properties beside/instead of degradation degree
- it may also be used for grading

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