

Comparison of three methods for the analysis of lignin in soils and sediments: CuO oxidation, thermochemolysis and Derivatization Followed by Reductive Cleavage method.

Céline Estournel-Pelardy^a, Laurent Grasset^a, Leoš Doskočil^b, André Ambès^a

^aUniversité de Poitiers, SRSN, UMR-CNRS 6514, 4 rue M. Brunet, Poitiers, France

^bBrno University of Technology, Faculty of Chemistry, Purkytova 118, 612 00 Brno, Czech Republic

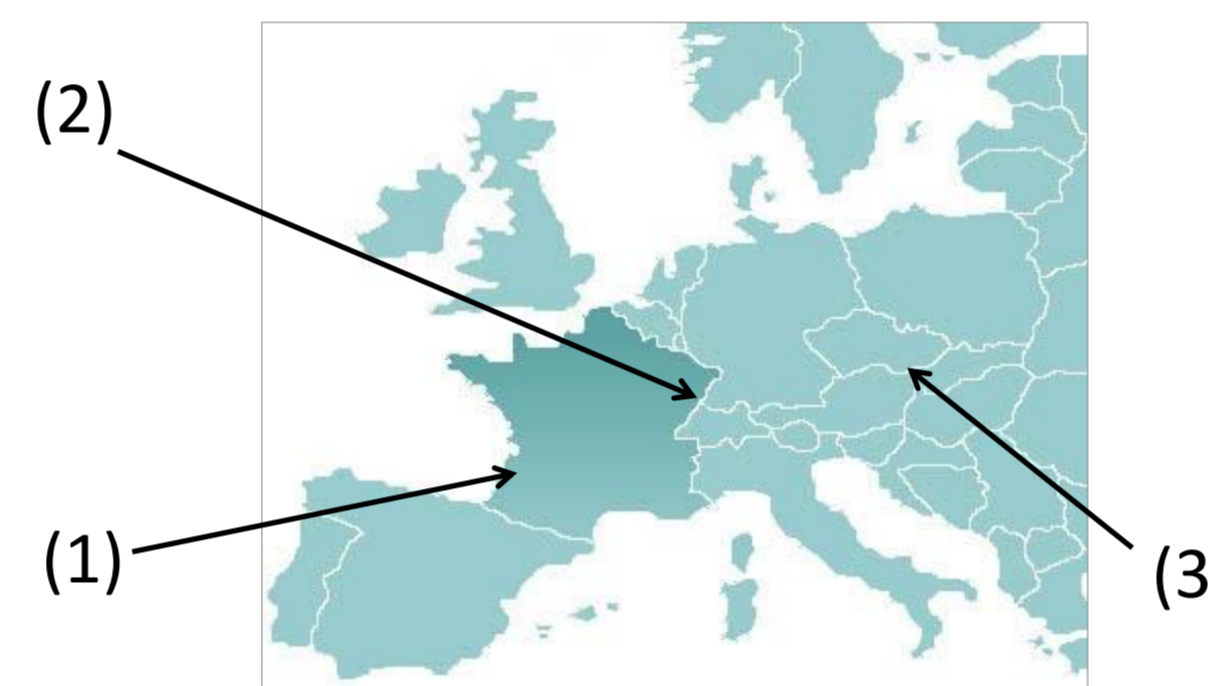
- Introduction -

Lignin monomers are among the most effective biomarkers for woody material because they provide an unambiguous fingerprint for vascular plants. Much of the work examining lignin in soils and sediments has been conducted using CuO oxidation [1] or tetramethylammonium hydroxide (TMAH) thermochemolysis [2,3]. Because they differ in the mechanism of degradation, each method results in a different suite of lignin products and compounds ratios. On the other hand, Derivatization Followed by Reductive Cleavage (DFRC) is highly efficient for cleaving lignin α - and β -aryl ethers. Commonly used in wood chemistry, it is therefore suitable for lignocellulose materials [4] but also for lignite [5]. The purpose of this study is to compare lignin analysis by CuO oxidation, TMAH thermochemolysis and DFRC procedures on a set of samples of soil and sediments.

- Samples -

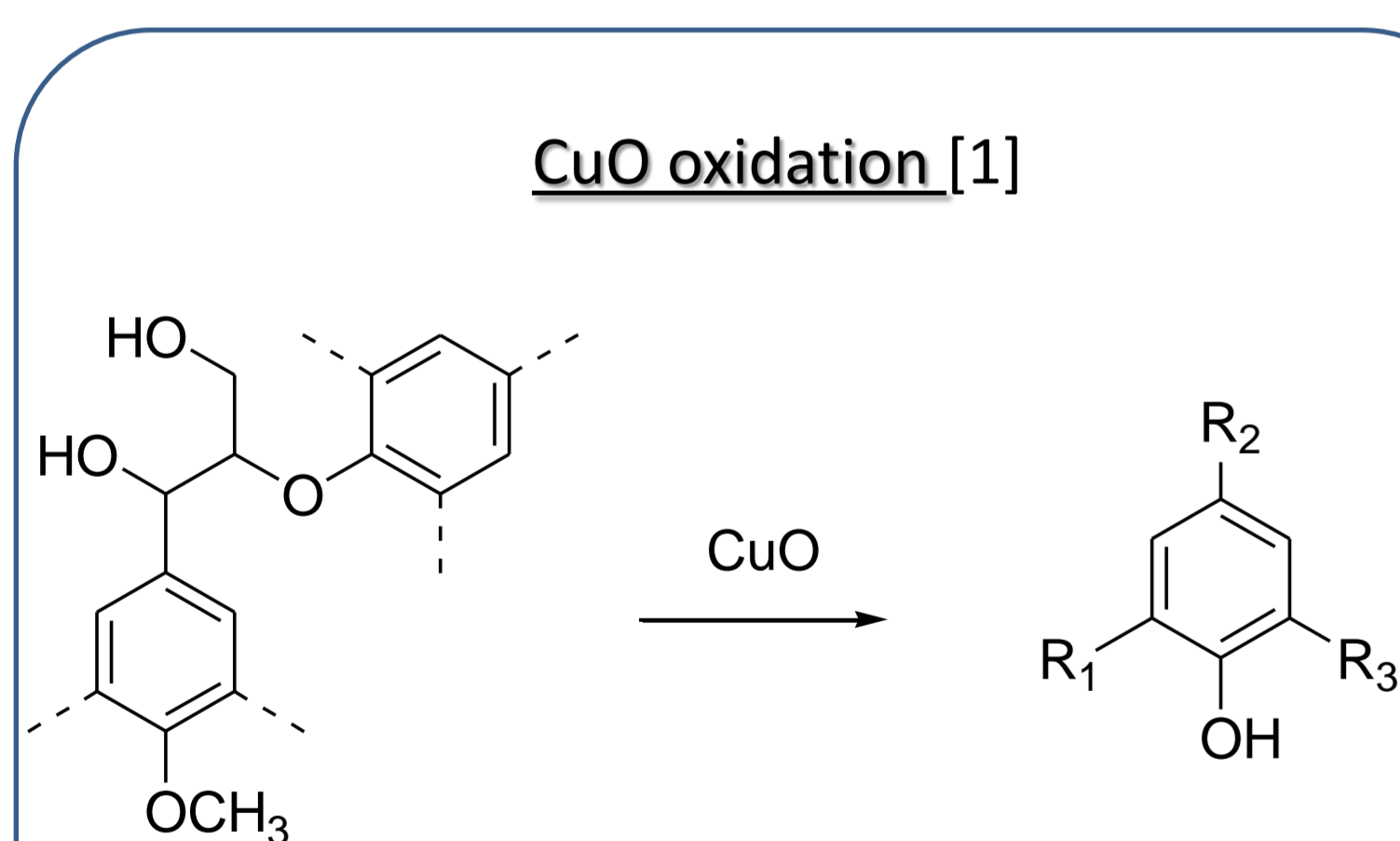
These methods were applied to three samples :

- (1) A **sandy acid forest soil sample** collected from the upper layer (0-30 cm) of a plot located in a maritime pine (*Pinus pinaster*) forest (Cestas, Landes de Gascogne, France).
- (2) A **peat sample** from a wooded Sphagnum-dominated mire (Frasne, Jura Mountains, France).
- (3) A **low rank coal lignite sample** (Hodonín, Moravia, Czech Republic).

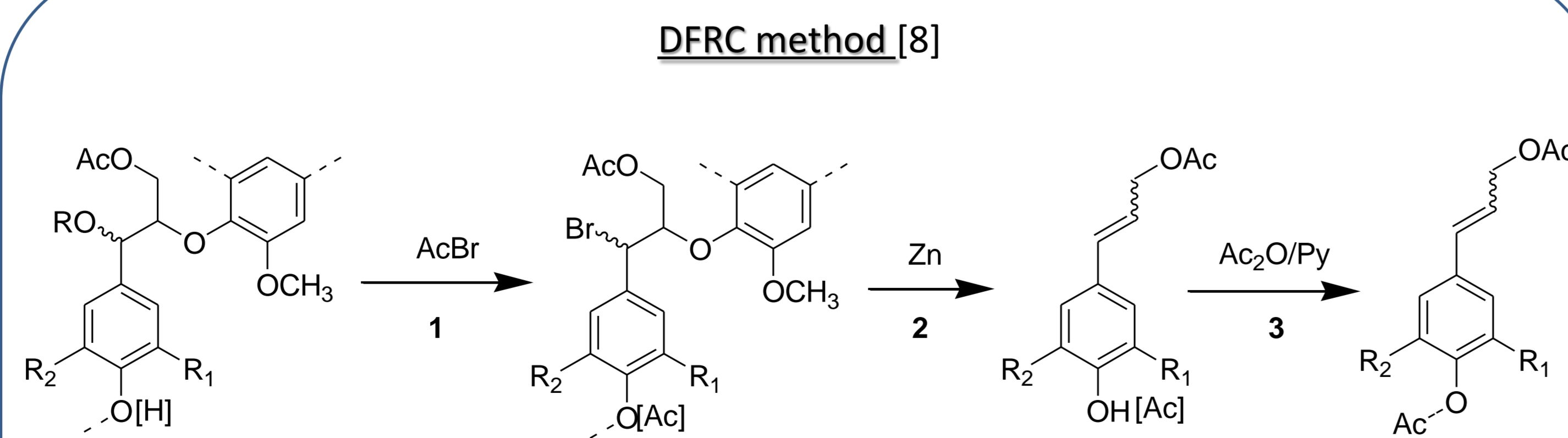
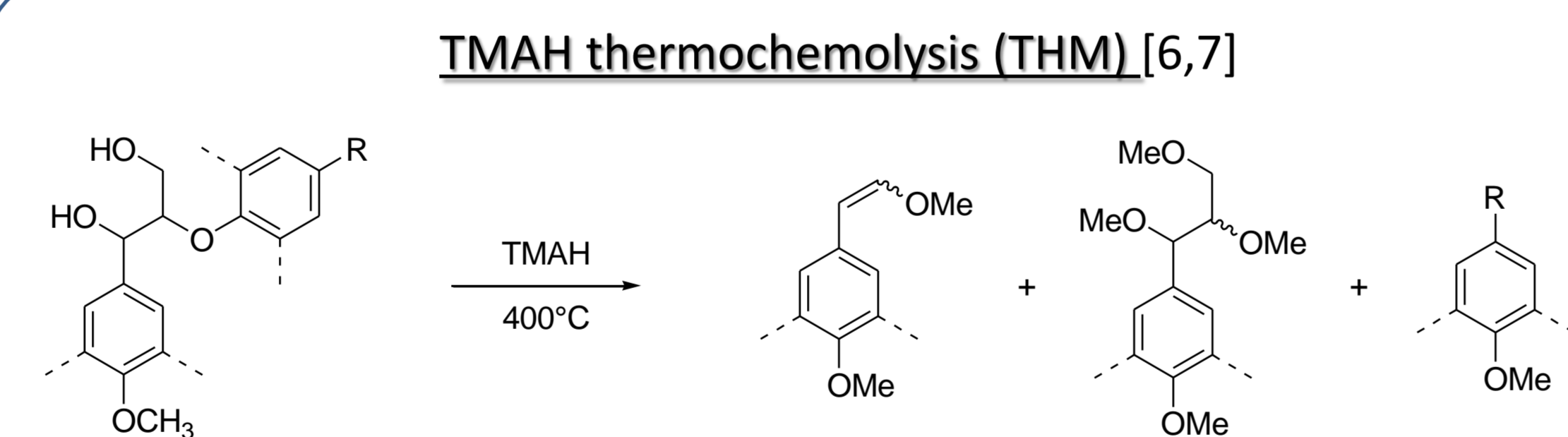


- Methods -

Different mechanisms are involved in each process: oxidation and hydrolysis with CuO, hydrolysis and methylation with TMAH, acetylation-bromination followed by reductive cleavage with zinc dust for the DFRC method.



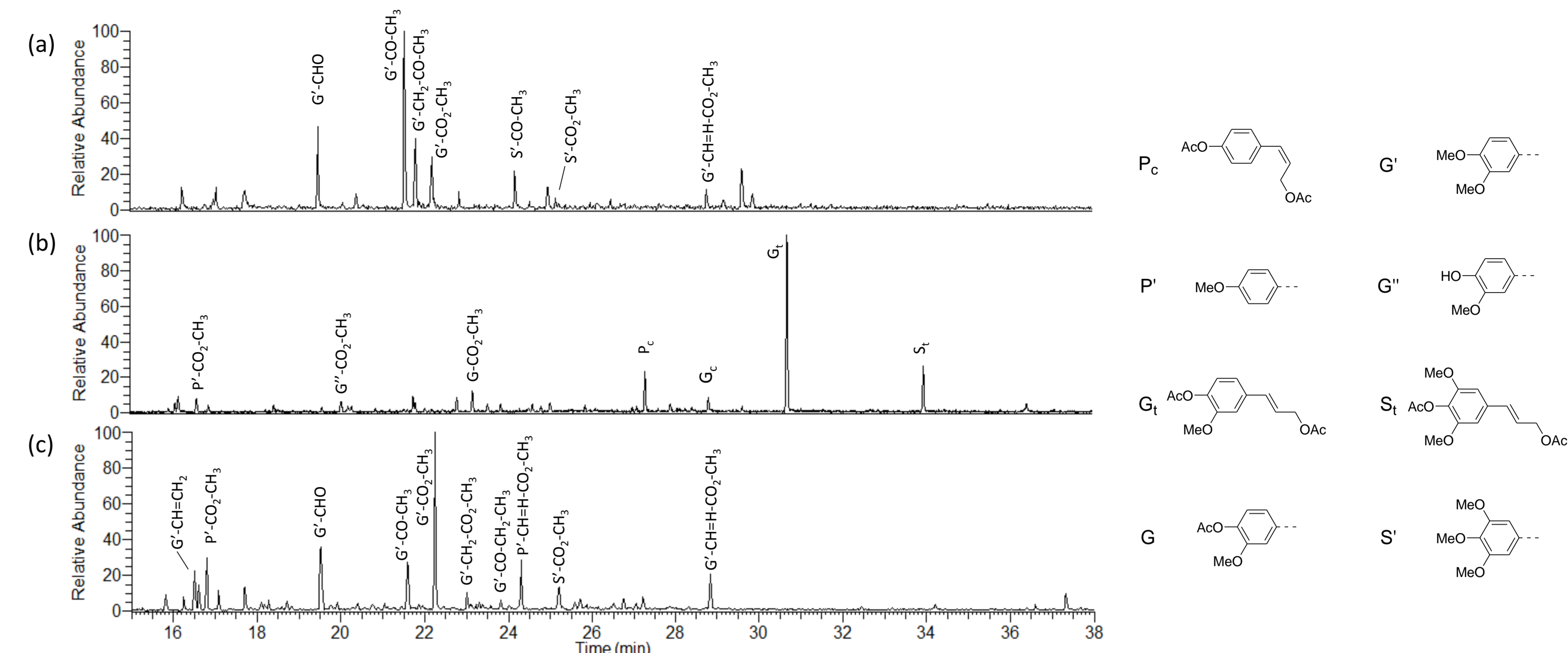
	R ₁	R ₂	R ₃
<i>p</i> -hydroxybenzaldehyde	CHO	H	H
<i>p</i> -hydroxyacetophenone	COCH ₃	H	H
<i>p</i> -hydroxy benzoic acid	CO ₂ H	H	H
vanillin	CHO	H	OCH ₃
acetovanillone	COCH ₃	H	OCH ₃
vanillic acid	CO ₂ H	H	OCH ₃
syringaldehyde	CHO	OCH ₃	OCH ₃
syringone	COCH ₃	OCH ₃	OCH ₃
syringic acid	CO ₂ H	OCH ₃	OCH ₃
<i>p</i> -coumaric acid	<i>trans</i> -CH=CH-CO ₂ H	H	H
ferulic acid	<i>trans</i> -CH=CH-CO ₂ H	H	OCH ₃



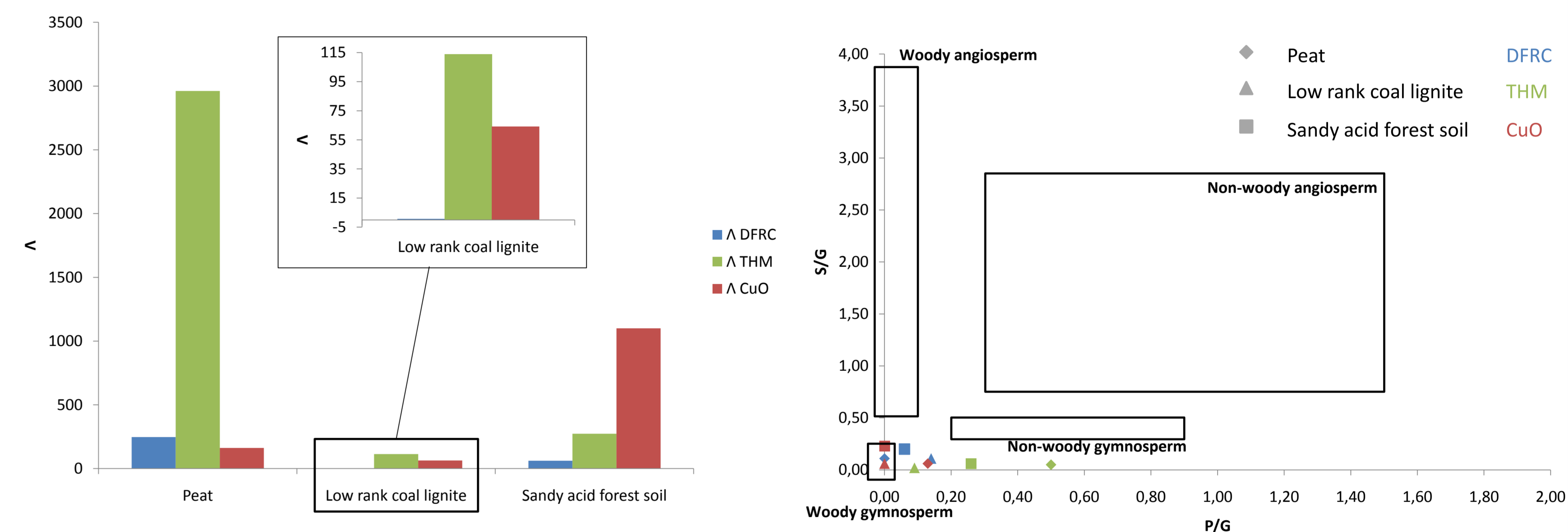
1. AcBr/Acetic acid (8/92, v/v), 50°C, 2 h
2. Zn, Dioxane/Acetic acid/Water (5/4/1, v/v/v), 50°C, 30 min
3. Acetic anhydride, Pyridine, r.t., 40 min

- Results and Discussion -

Lignin monomers obtained after CuO oxidation and TMAH thermochemolysis procedures were similar to those described in the literature [1,2]. Compounds with guaiacyl units (**G**) were predominantly identified while components with a syringyl (**S**) or *p*-hydroxyphenyl (**P**) structures were less abundant. The DFRC method released monolignols (*trans* coniferyl diacetate and *trans* sinapyl diacetate) that arose from β -ether cleavage and minor components with predominantly guaiacyl units originating from other structures.



m/z 77 ion mass fragmentogram of ligneous compounds released after (a) CuO oxidation, (b) DFRC method and (c) TMAH thermochemolysis on the sandy acid forest soil sample



Total lignin yields, reported as Λ , were calculated as the sum of the concentrations of all lignin-derived compounds normalized to 100 mg of organic carbon. For the three samples, results showed that Λ_{CuO} and Λ_{TMAH} are higher than Λ_{DFRC} (between twenty and one hundred times).

Because the DFRC method is the most specific one to analyse intact monolignols, it will be interesting to use it to follow lignin degradation in environment.

The regions representing compound ratios typical of the defined plant and tissue type are the traditional delineations used in CuO analysis [3].

The three procedures show similar distributions. S/G and P/G ratios, near to zero, confirm the woody gymnosperm origin of our three samples. Small differences observed for TMAH thermochemolysis could be explained by the incapacity of unlabeled TMAH thermochemolysis to distinguish monomers produced from intact lignin and those from non lignin sources.

- Conclusion -

Because the three methods do not react with the same lignin pools (differences are due to chemical and/or physical arrangements), direct comparisons should be made carefully but could be viewed rather than complementary methods for a fine characterization of lignin in soils and sediments.

- References -

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