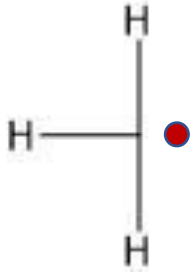
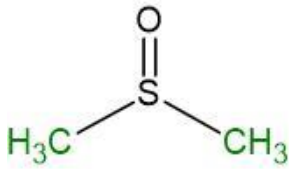


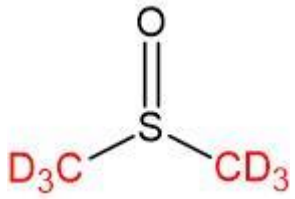
Iron catalysed formation of methyl radicals as a common source of environmentally important volatile carbon compounds

Jonas Hädeler[1], Rebekka Lauer[1], Velmurugan Gunasekaran[2], Kirsten Rheinberger[1,2], Peter Comba[2], Frank Keppler[1,3]

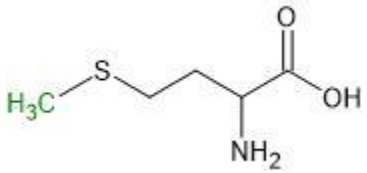
Fe^{2+}

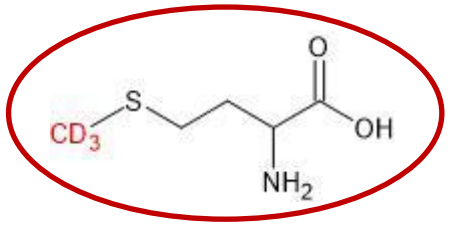
Studied substrates (ubiquitous in the environment)



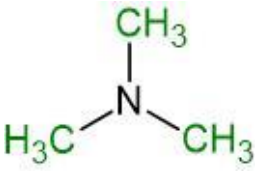


DMSO / DMSO d6

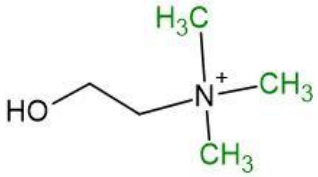


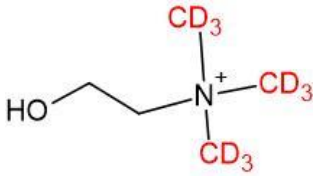


Methionine / Methionine d3 (essential amino acid)

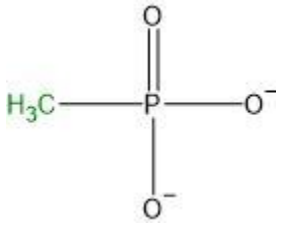


Trimethylamine / Trimethylamine d9

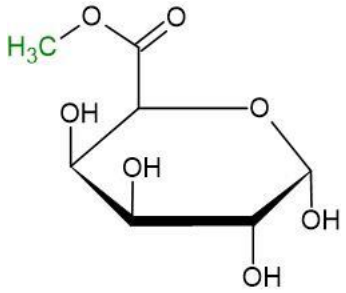




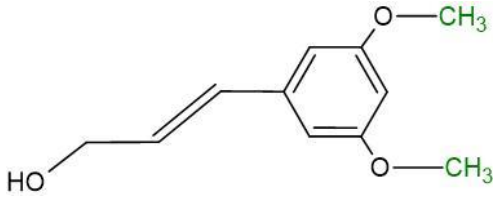
Choline/Choline d9



Methylphosphonate



Galacturonic acid methyl ester (pectin component)



Sinapyl alcohol (lignin component)

Proposed sceme for the formation of a methyl radical originated from methionine

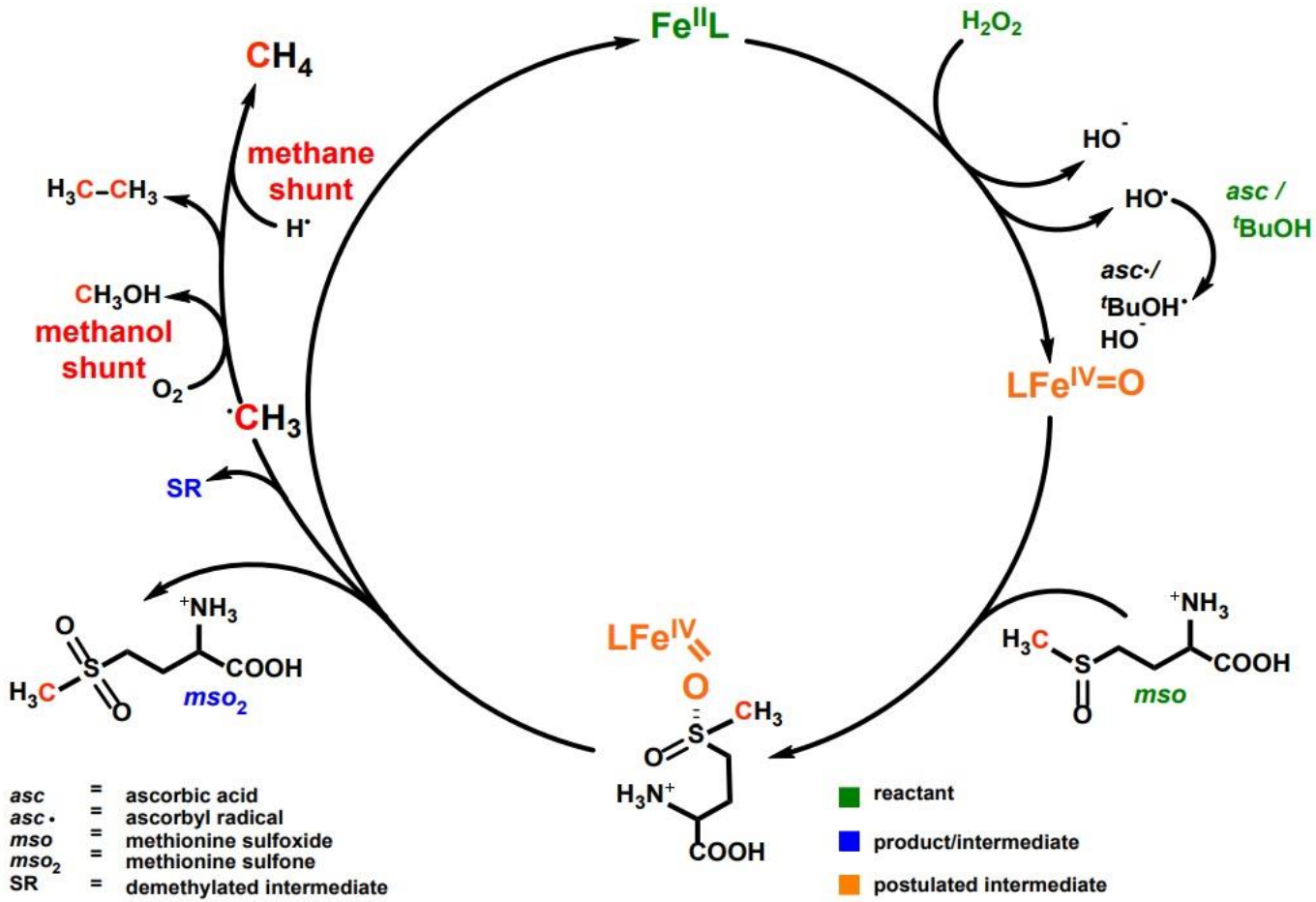
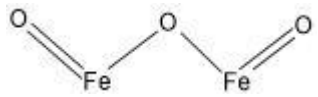
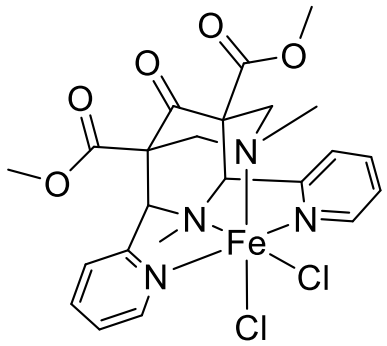


Figure modified after Althoff *et al.* 2014 and Benzing *et al*. 2017

Experimental setup

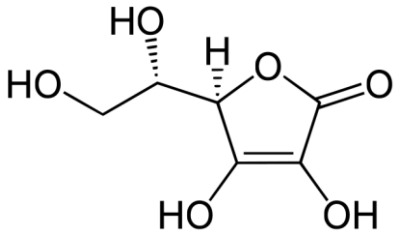


hematite



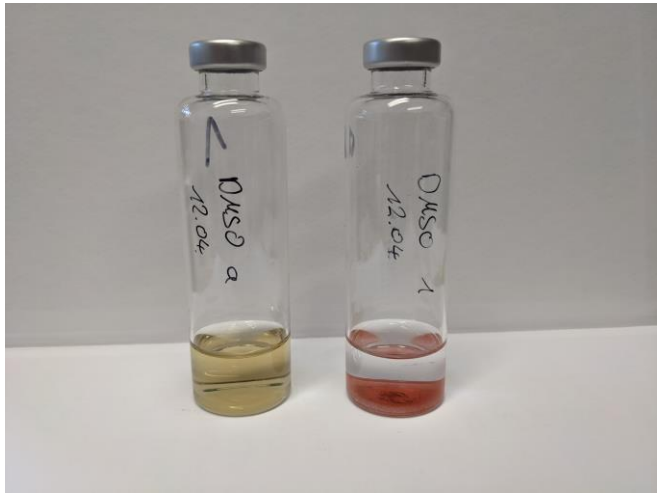
CH_3CN

artificial bispidine complex
$[Fe(N_2Py_2)Cl_2]*CH_3CN$



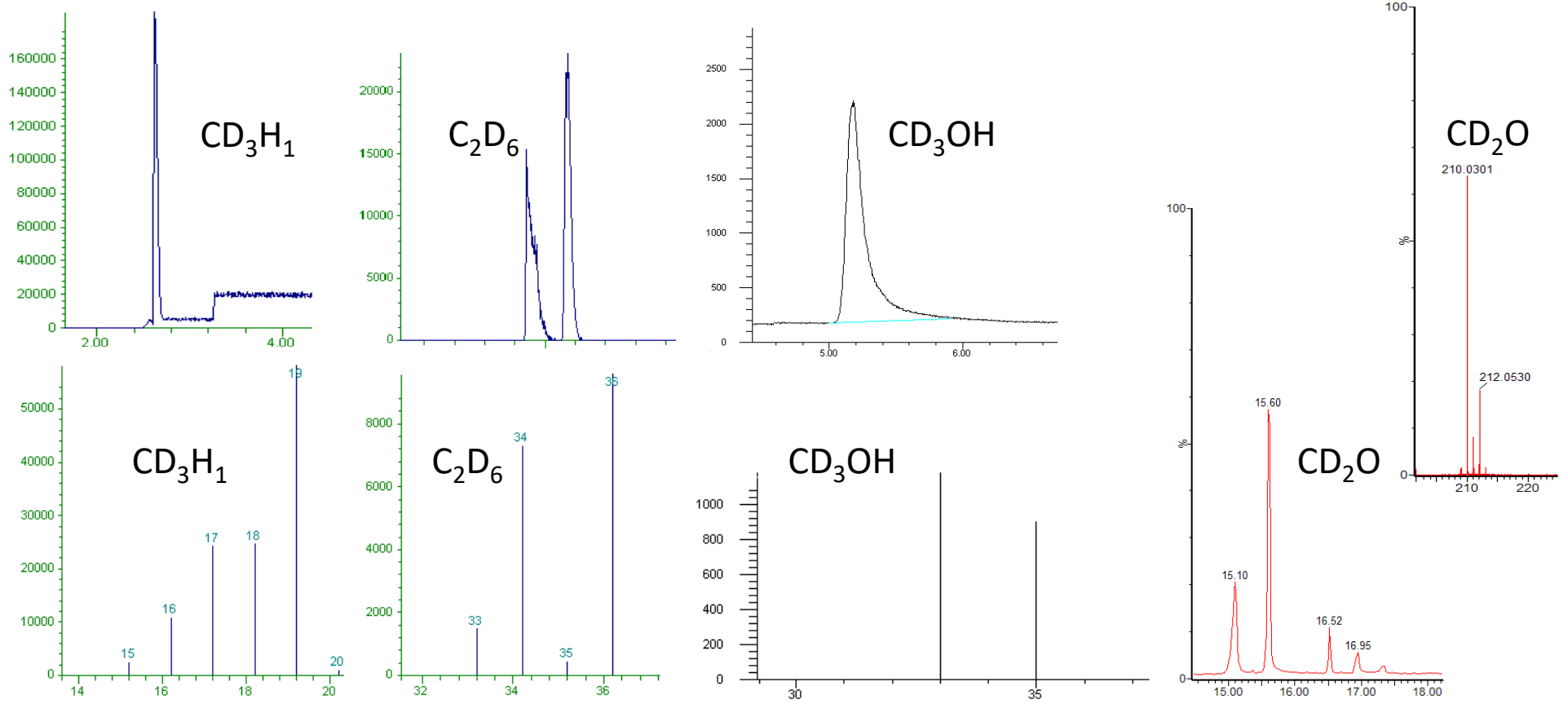
ascorbic acid

Reactant
Bispidine/Hematite
Ascorbic acid
Hydrogen peroxide (30%)
Substrate



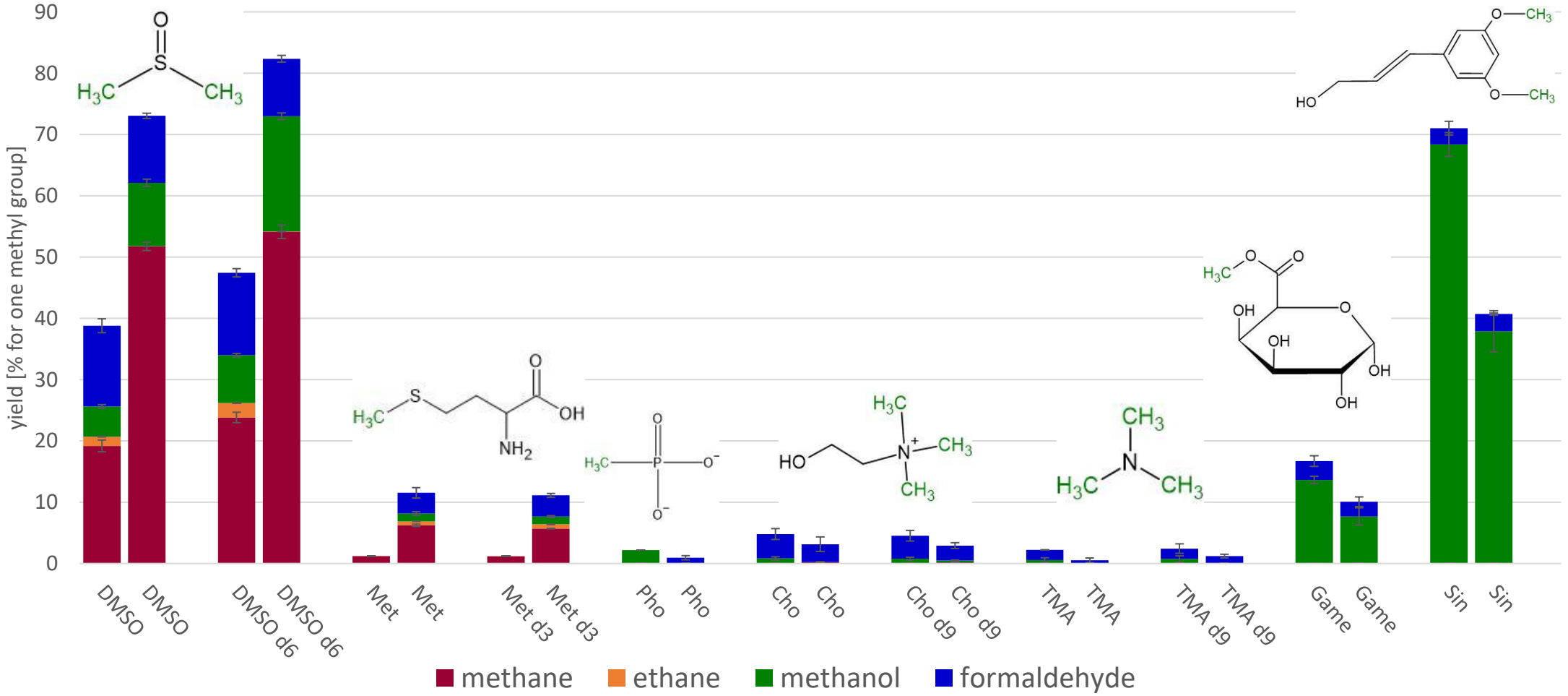
Measurement of ^{2}H-labeled methane, ethane, methanol and formaldehyde in the experiments with DMSO d6

Chromatograms and measured masses:
-CD_3H_1
-C_2D_6
-CD_3OH
-CD_2O
derivatized with pentafluorophenyl-hydrazine

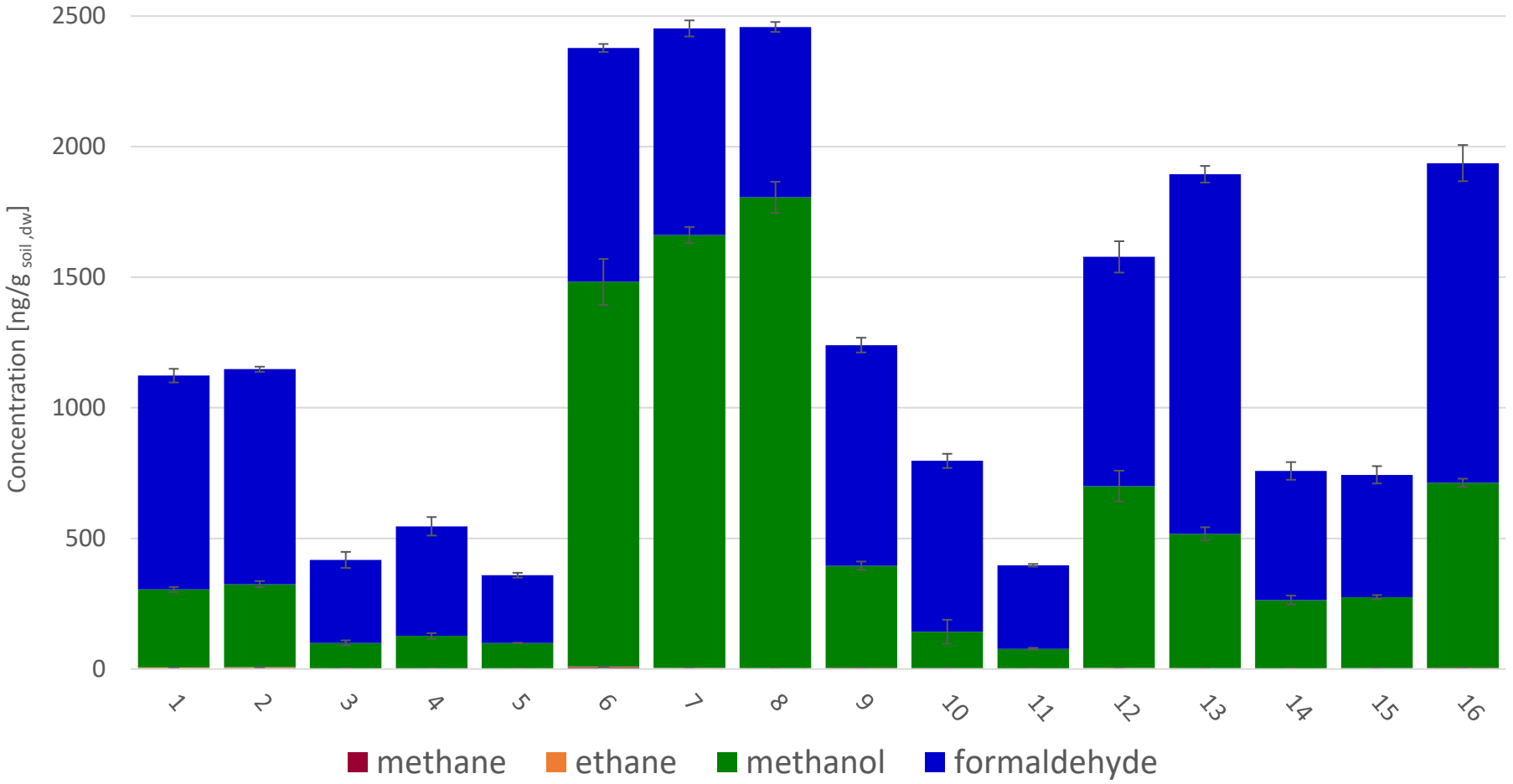


Yield of methane, ethane, methanol and formaldehyde

bispidine complex (left column) vs hematite (right column)



Experiments with different dried and sterile soils



Conclusion

- Clear evidence that the C_1-C_2-components originate from the S- N- P- and O-hetero-bonded methyl group
- Different yields of the C_1 and C_2 components depending on the precursor
- Sterile soil also has the ability to produce C_1-C_2 components

  →Mainly methanol and formaldehyde → may originate from Galacturonic acid methyl ester and sinapyl alcohol

Thank you for your attention

Please vote for me if you liked my presentation

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References

- Althoff, F., Benzing, K., Comba, P., McRoberts, C., Boyd, D. R., Greiner, S., & Keppler, F. (2014). Abiotic methanogenesis from organosulphur compounds under ambient conditions. *Nature Communications*, *5*(1), 1-9.
- Benzing, K., Comba, P., Martin, B., Pokrandt, B., & Keppler, F. (2017). Nonheme Iron-Oxo-Catalyzed Methane Formation from Methyl Thioethers: Scope, Mechanism, and Relevance for Natural Systems. Chemistry–A European Journal, 23(43), 10465-10472.