Origin and maturation of organic matter in thermal waters

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abstract N° 1995

25-29th September 2016
Montpellier, France
CORUM CONFERENCE CENTER
43rd IAH congress

Introduction

Research on organic matter (OM) in thermal waters (TWs)

- ~300 waters, ~500 organic compunds
- Volatile and polycyclic aromatic hydrocarbons (PAHs)
- Toxic and/or carcinogen compounds (e.g. benzene, phenols, PAHs)
- Can be the precursors of chlorophenols, chlorinated dibenzofurans, biphenyls and other halogenated hydrocarbons

Importance

- Balneology (danger vs. curative power)
- Drinking water (e.g. in SE-Hungary, dilution of arsenic waters)
- Geothermal energy: recharging wells

Aims

1) Experimental modelling of the generation of aromatic compunds in TWs, using various organic precursors

- Reactions;
- Effect of precursor OM;
- Threshold temperatures;
- Effect of ongoing OM decomposition/transformation → maturity;
- Interaction with inorganic compounds → distribution of carbon forms in TWs.

2) Assesement of the type of original precursor, based on the comparison of the quality and quantity of the compunds formed in TWs and during modell experiments, and to study

- Territorial characteristics („facies”);
- Origin and maturity (decomposition);
- Effect of temperature and depths.

Introduction

Pannonian Basin

Tertiary and Quaternary may reach 7000 m thickness

- Tectonised, fast subsidence (fast organic matter maturation)
- Subbasins formed during the middle miocene extension, sometimes in connection
- More or less similar sedimentation environments
- Chrystalline basement: folded variscian micaschist or gneiss, permian vulcanic and siliciclastic series or lower and middle triassic carbonates.

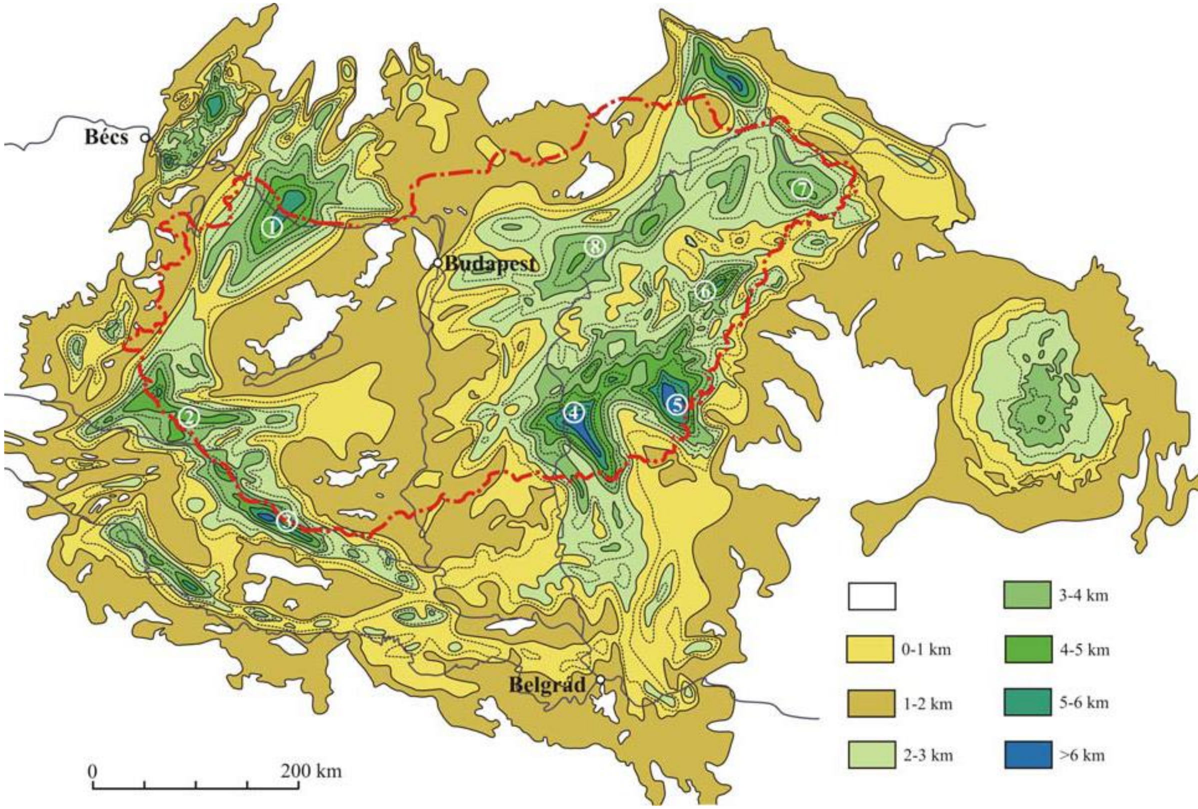
Pannonian Lake

Cca. 10-12 M years ago, continuous sedimentation:

- pelitic or abrasive conglomerate basis
- deep water turbidites
- pelitic sublitoral and slope facies
- litoral and delta facies
- alluvial plain
- swamp forest (lignite and coal)

Upper Pannonian: good aquifers, Lower Pannonian: aquitards

Pleistocene, holocene: fluvial and aeolian sediments



Organic matter in groundwater I.

Important effect on diagenetic processes and water composition. Influences

1) pH and puffer capacity;
2) solubility of inorganic and organic components;
3) redox potential;
4) **decarboxylation → CH gases, carbon dioxide →carbonate dissolution**.

Shallow groundwater

- ~mg/l OM, (up to 90% humic and fulvic acid)

Deep groundwater

- Acetate and propionate;
- g/l concentrations;
- **Considered to be oil field water**;
- Thermocatalytic decomposition or biodegradation products of kerogen, crude oil resin or asphaltene;
- Rapid appearance at around 80° C, and decreasing concentrations with increasing temperature (decarboxylation).

Aromatic compounds (mainly PAHs and phenols)

- Surface waters and recent sediments, various concentrations;
- Early stage of diagenesis may result in mg/kg PAH (perylene and phenanthrene) concentrations.

Organic matter in groundwater II.

Varsányi (1994, 1997), Varsányi et al. (2002) and Vető et al. (1998)

- Aerob and anaerob decomposition of OM (CO_2 generation) affects HCO_3^-, Na^+, NH_4^+ and I^- concentration;
- The major source of Na^+, Li^+, B^-, F^- is the decomposition of alumino-silicate minerals;
- Methane generation from acetate is not concentration-dependent;
- **Concentration and aromacity of humic acids, alkylphenols and aliphatic acids depends on temperature, organic facies and lithology.**

Increasing temperature/depth:

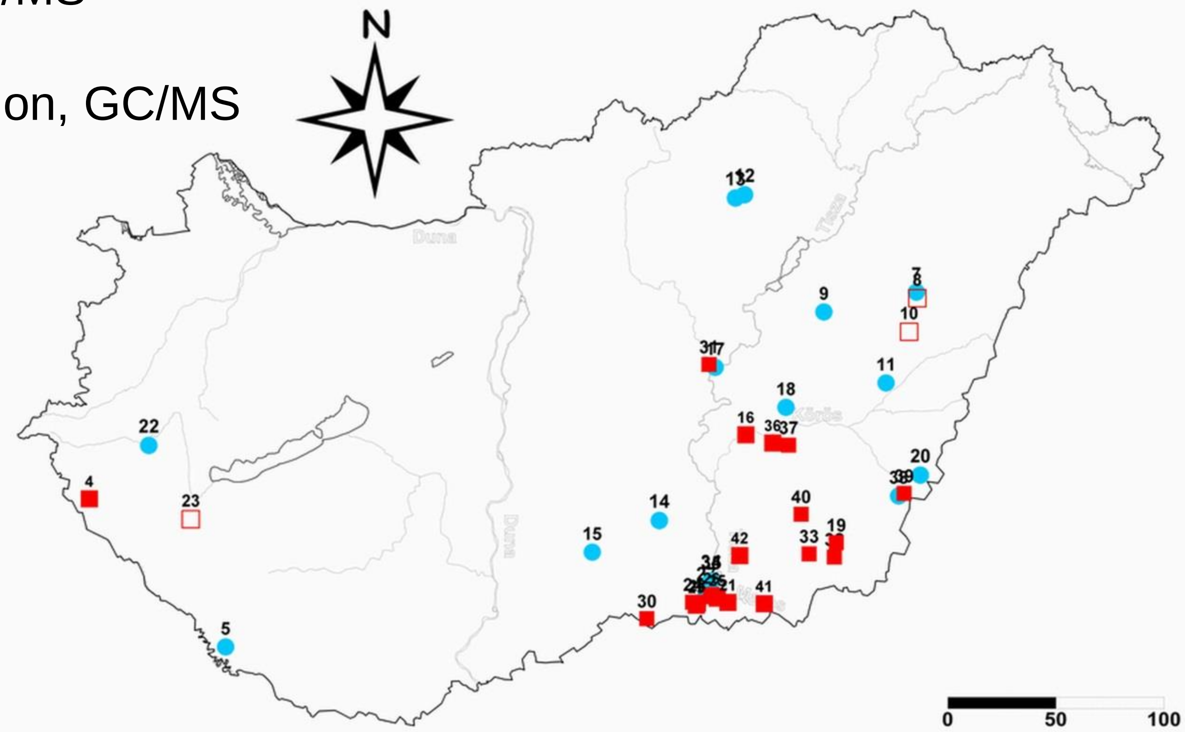
- Humic compounds show changes in concentration and composition;
- Bacterial methane generation is overprinted by thermal generation of HC gases;
- ~**80°C: mono-, di-, poliaromatic HC-s and heteroaromatic compounds, concentrations increase with temperature;**
- **~90°C: phenols, fatty acids;**
- **Relative demethylation**.

Samples and methods – TWs

Sampling: Hungarian Geological Institute (MÁFI);
Stable isotopes: MTA Institute for Nuclear Research (ATOMKI);
Routine hydrochemistry: MÁFI (ionchromatography, ICP-AES);
Trace elements: MÁFI (ICP-MS);
Organic chemical analyses: Institiute for National Health (OKI);

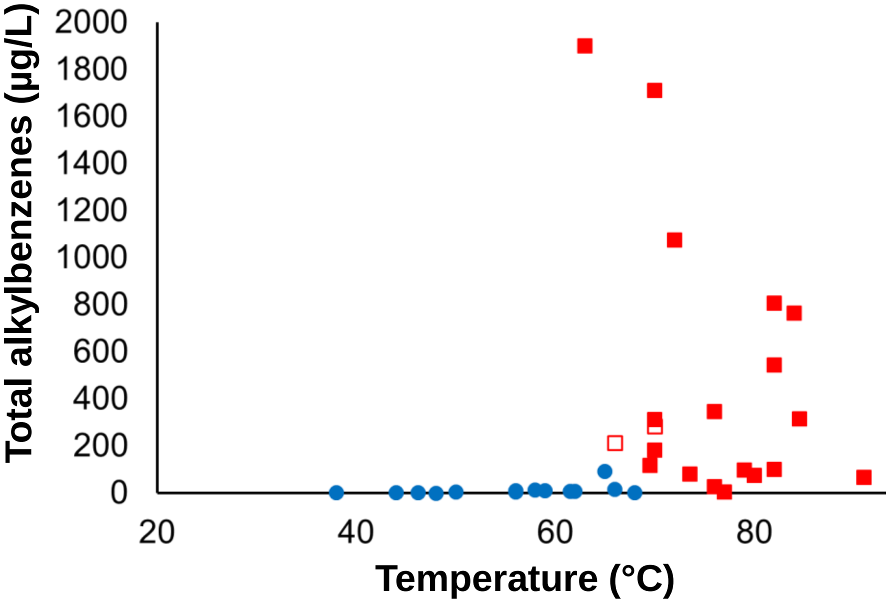
- volatiles: SPME GC/MS
- PAHs: HPLC
- phenols: derviatisation, GC/MS

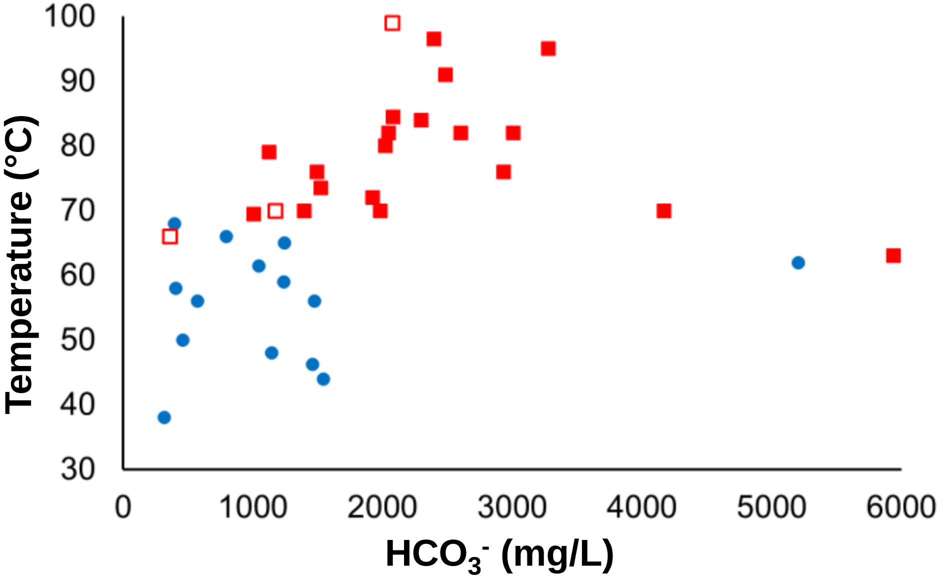
RED: phenols present
BLUE: phenols absent



Results – TWs

Temperature threshold: generation of alkylbenzenes and phenols

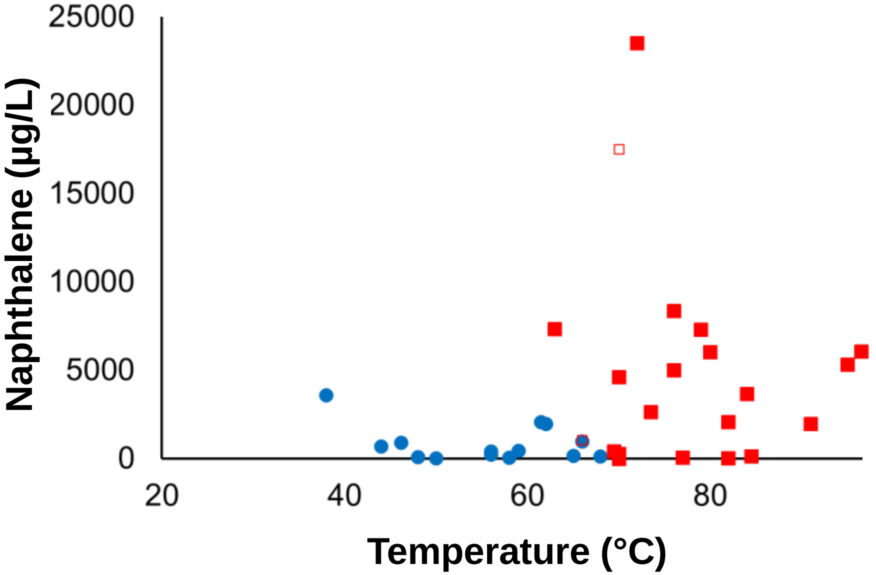




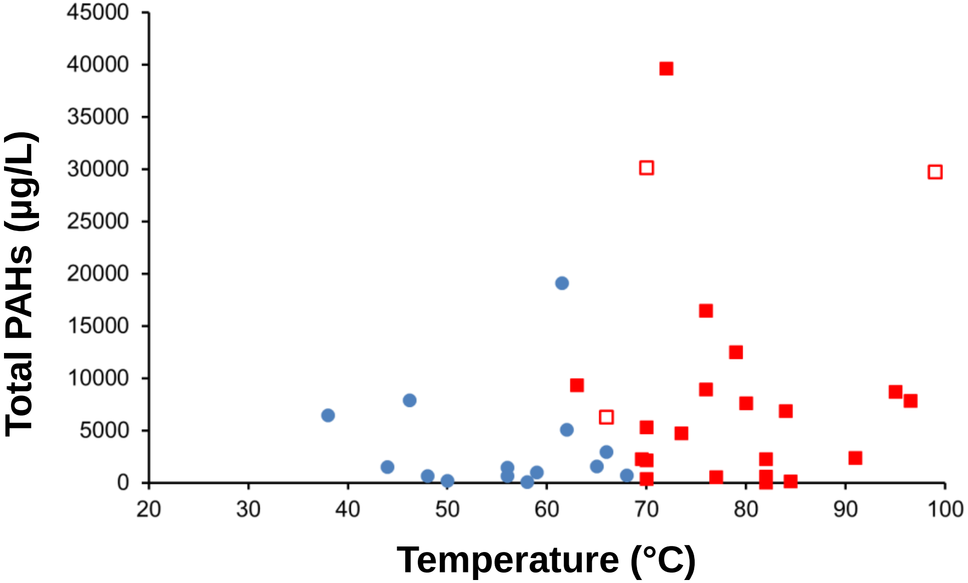
Co-generation of CO_2 and aromatic compounds

Results – TWs

Naphthalene: partly maturation product

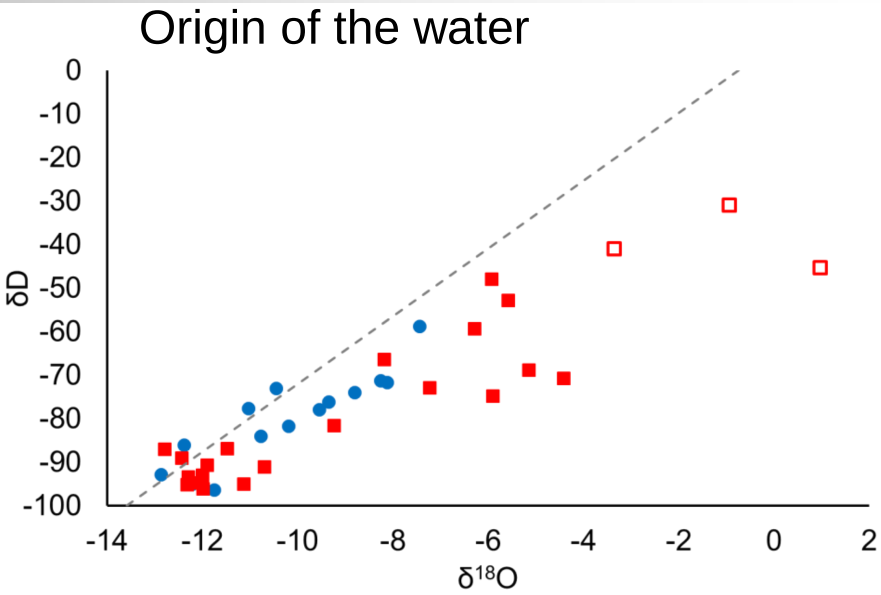


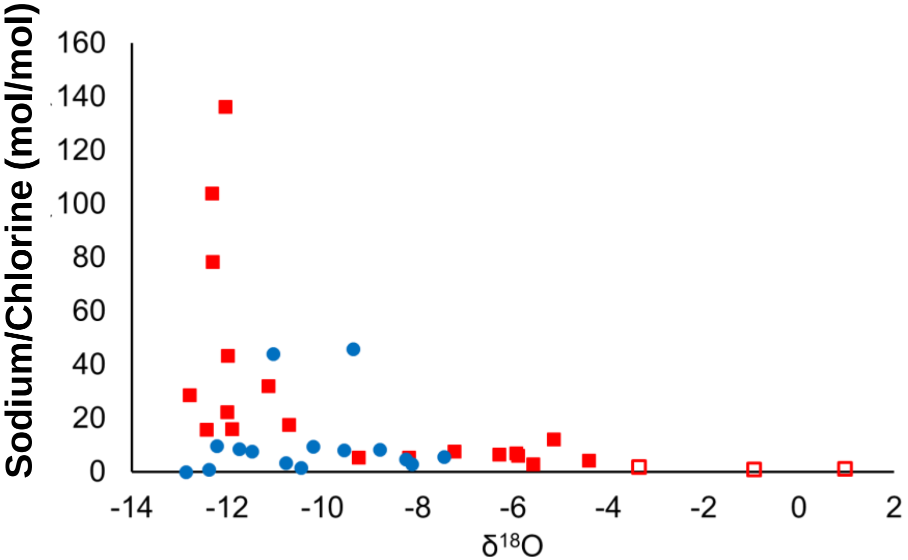
PAHs: ?

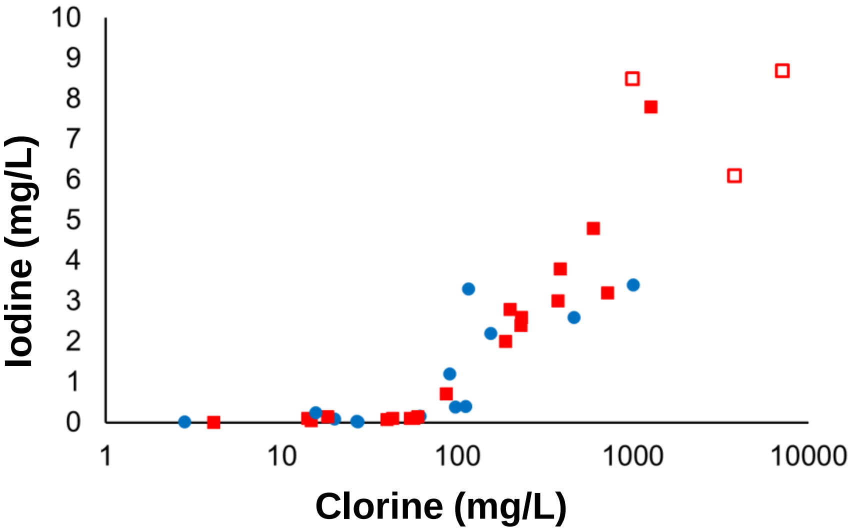


Results – TWs

- Increased hydrogencarbonate content in aromatic-rich waters;
- No correlation with mixing/age of the waters;
- PAHs are not maturity products, naphtalene partly is.







Aquathermolysis experiments

Aquathermolysis experimental

- 600 ml stainless steel Parr reactor;
- 250 ml water, 0.75 g $NaHCO_3$;
- reductive and oxidative conditions;
- 220°C, 250°C, 300°C, 320°C; 72 h; and short: FA, 24 h
- sampling: room temperature, without opening

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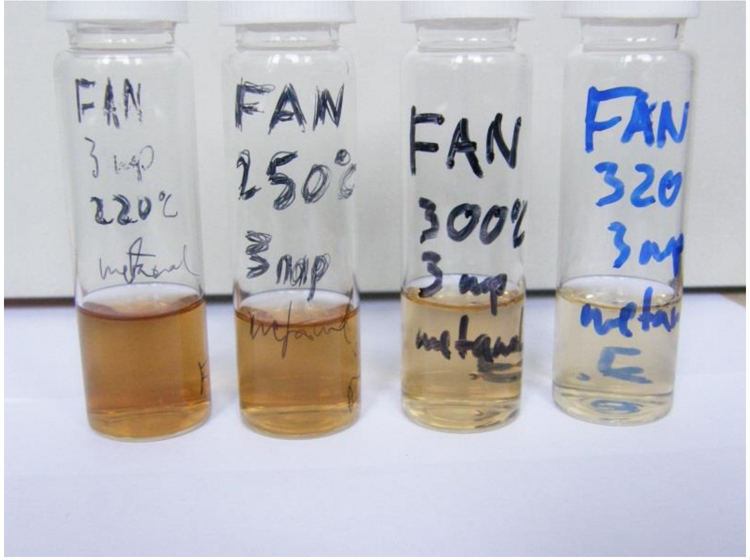
Material

FA, HA, HAFA, lignite, bitumen, organic precipitate



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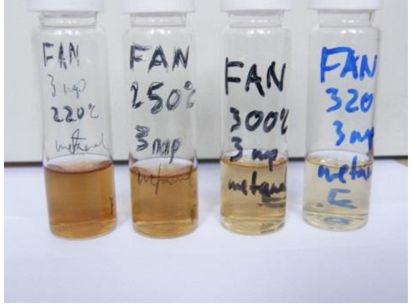


Analyses
- volatiles: static headspace GC/MS
- PAH: TWISTER, GC/MS
- phenols: liquid-liquid extraction,
  liquid injection GC/MS

Organic reactions in high temperature water

High temperature water

- Acidic and basic catalisator, solvent and reactant;
- Ionic reactions instead of radical;
- Bond clevage is enhanced;
- Intense condensation and hydrolitical reactions.

On the basis of literature, short time high temperature experiments can be applied to modell lower temperature reactions occuring on a geological timescale.

Model molecules

- C-C and C-heteroatom bond clevages;
- Aromatisation and polycondensation (cycloaddition and polymerisation reactions), heteroatom loss;
- Formation of alkylated aromatic HC-s and phenols through heteroaromatic or heterocyclic compounds

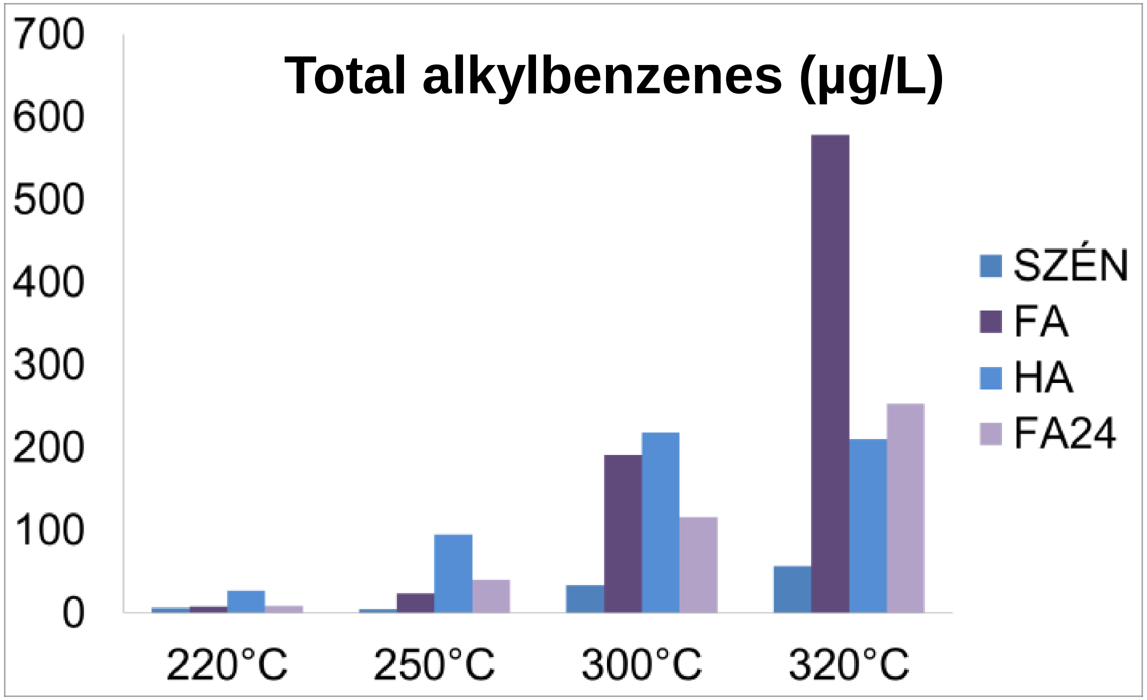
Natural OM

Mainly lignite and bitumen, fuel production

Results – Experiments

Paralell reactions, variation of relative intensities with temperature and time

C-C és C-heteroatom bond clevage: formation of benzene, alkylbenzenes, PAHs and phenols



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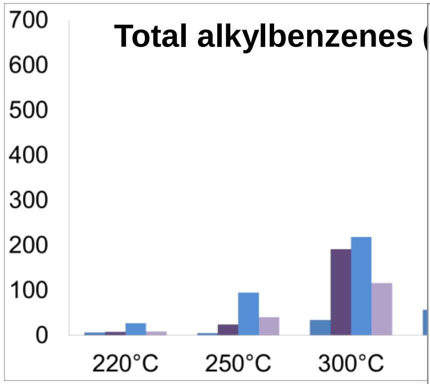

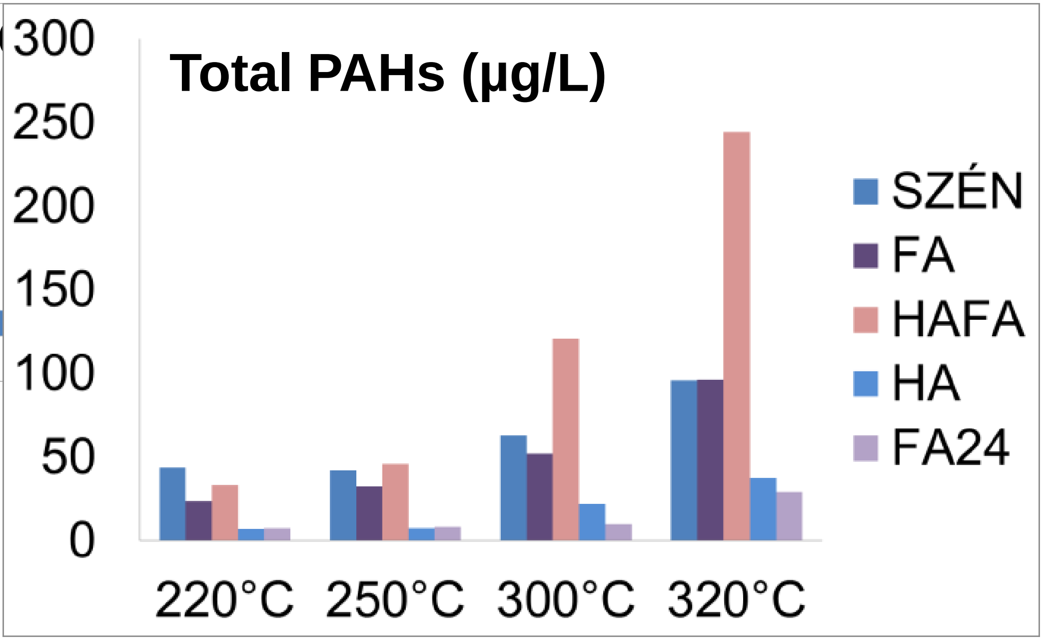

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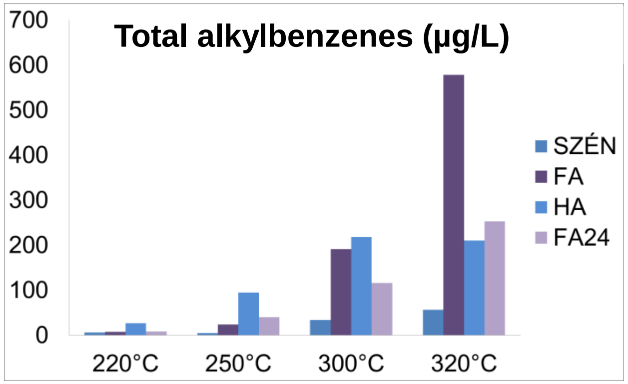
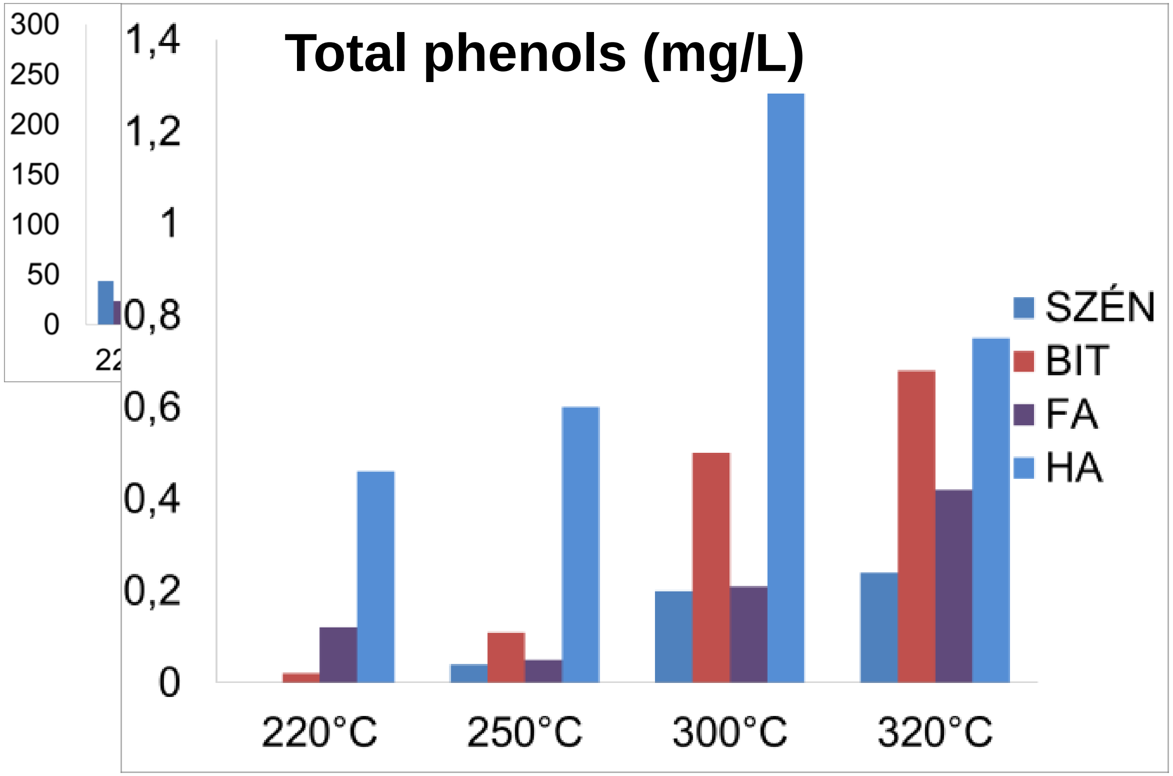
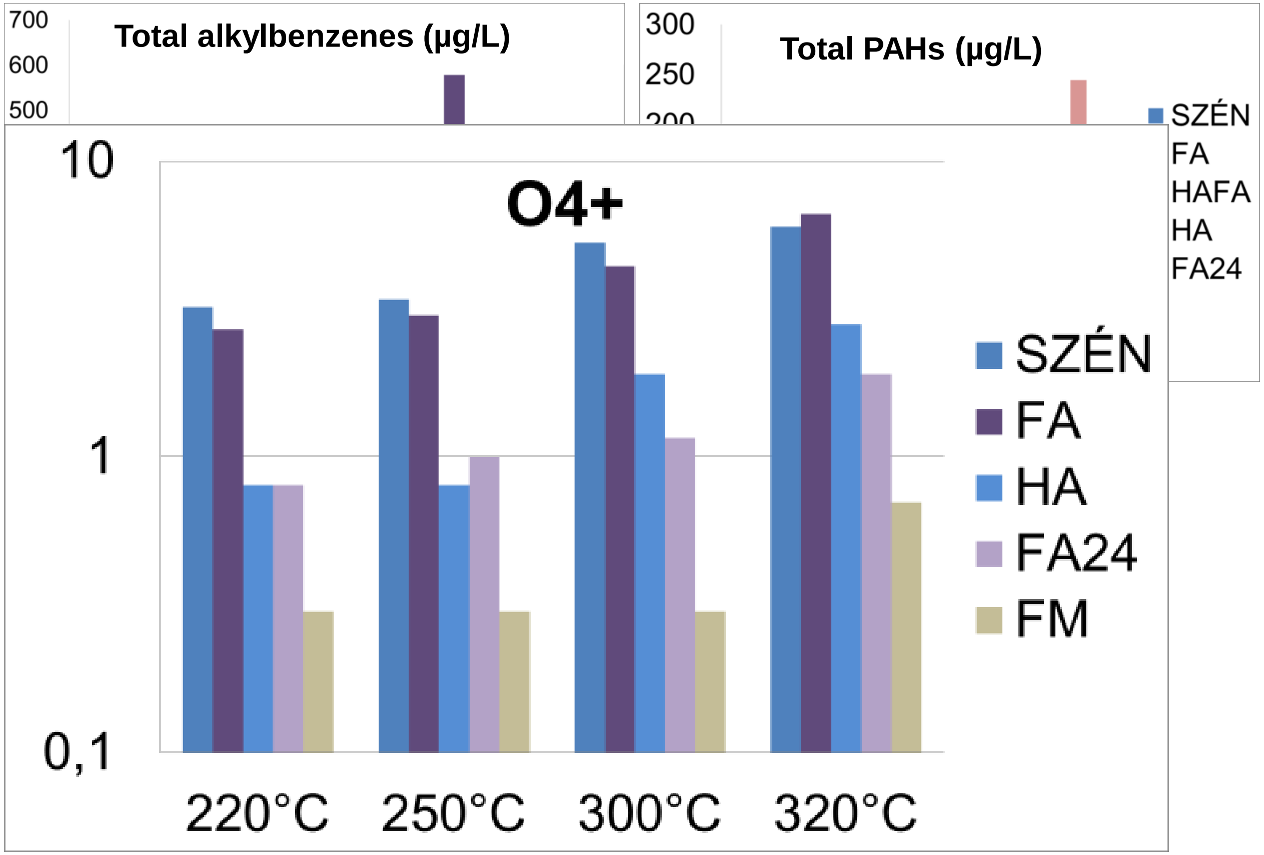


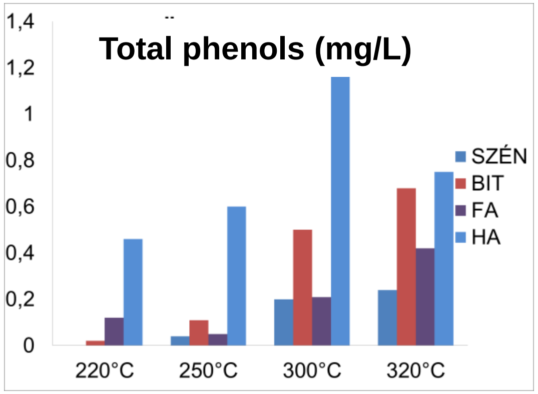


Results – Experiments

Paralell reactions, variation of relative intensities with temperature and time

Polyciclysation and aromatisation





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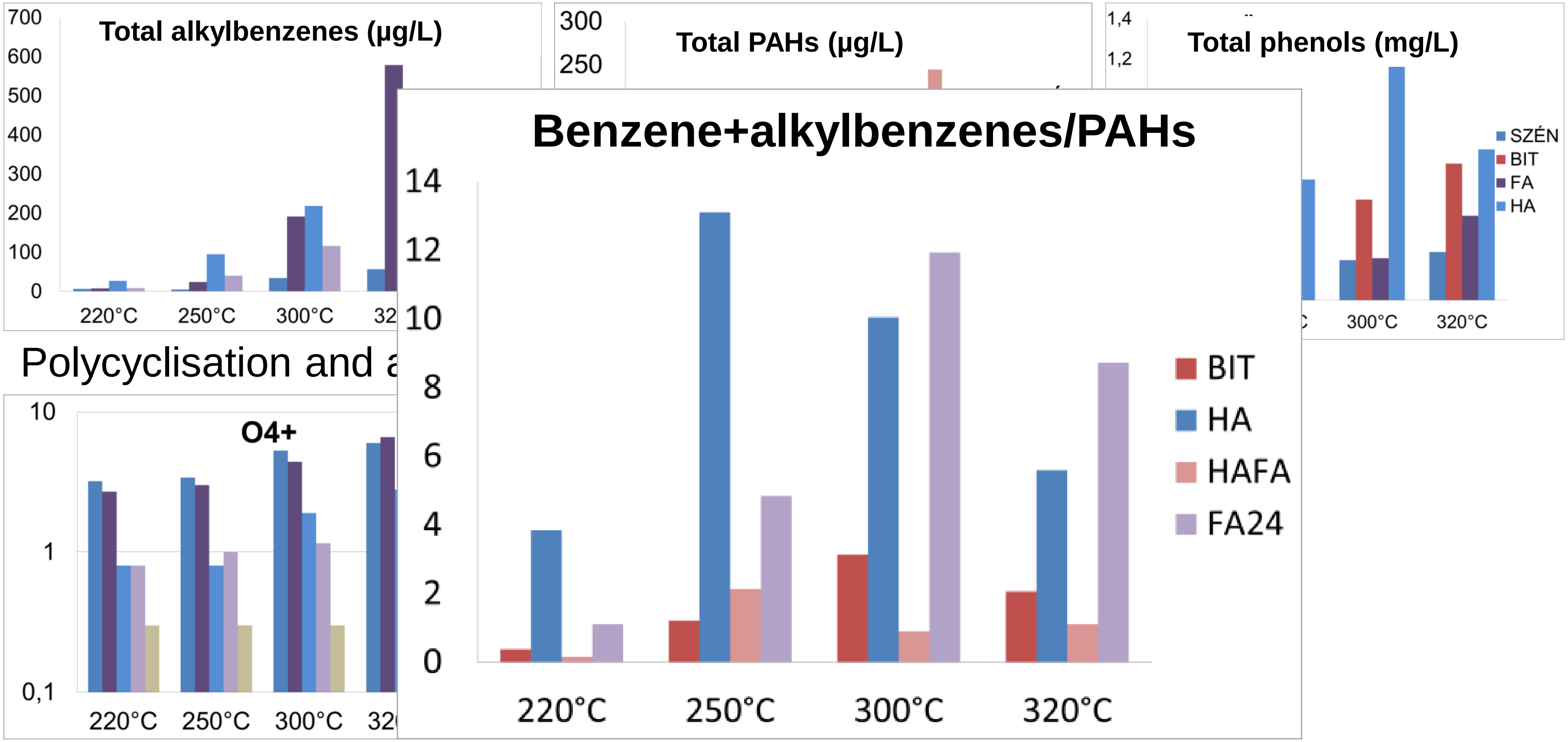

Polycyclisation and a

Results – Experiments

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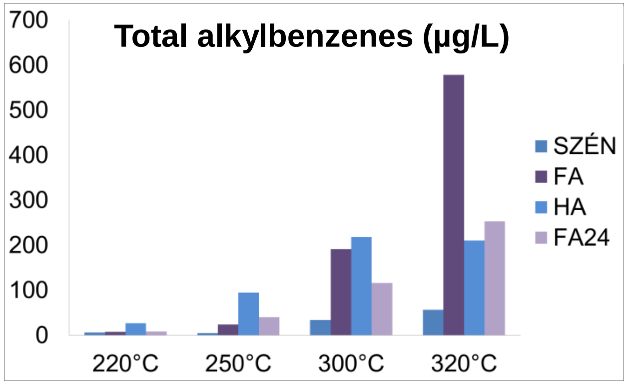
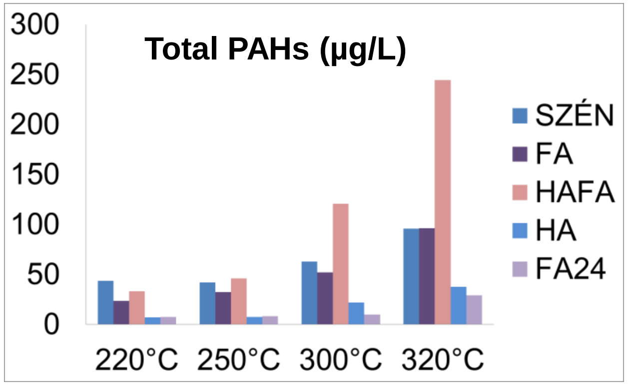
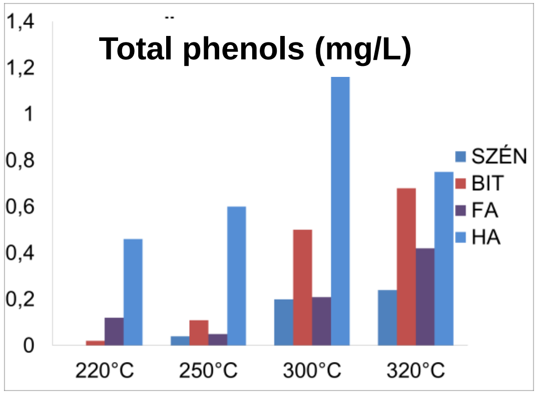
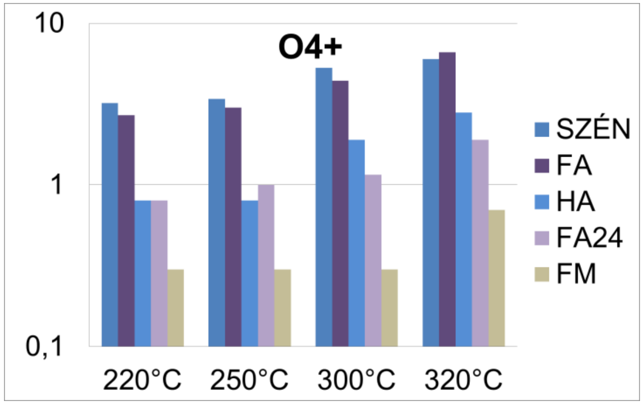
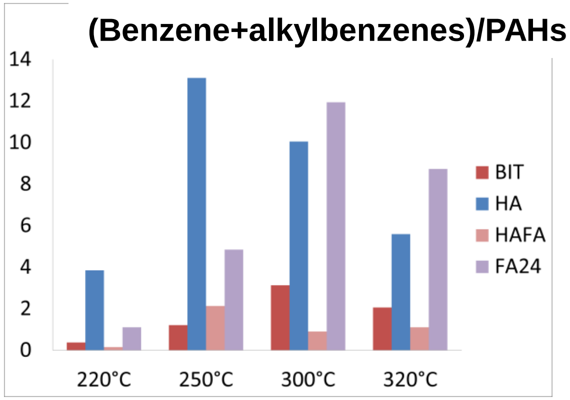






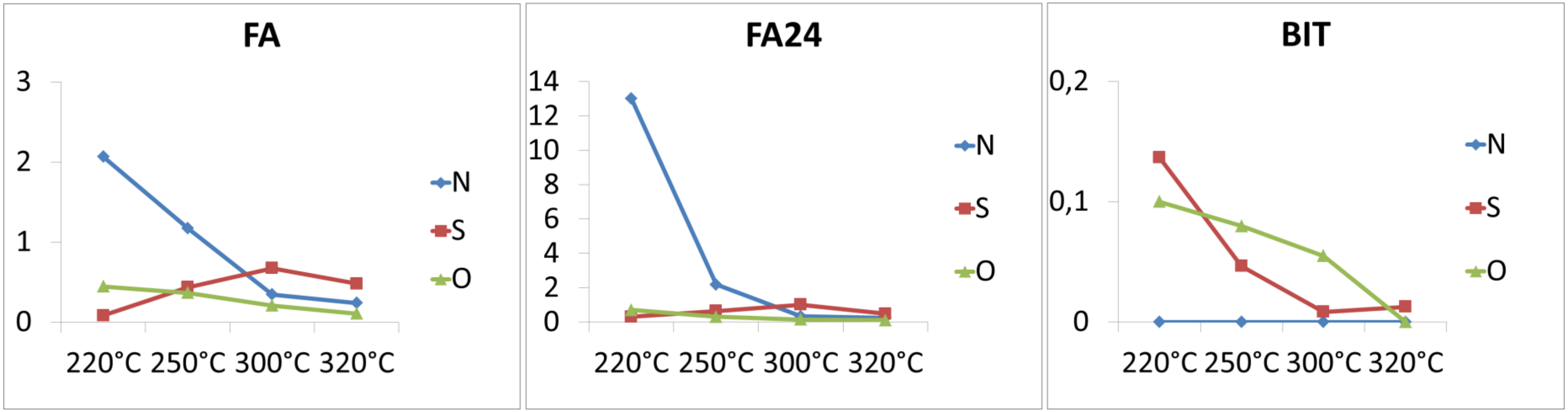
Polycyclisation and aromatisation





Results – Experiments

Decomposition of heteroaromatic compounds



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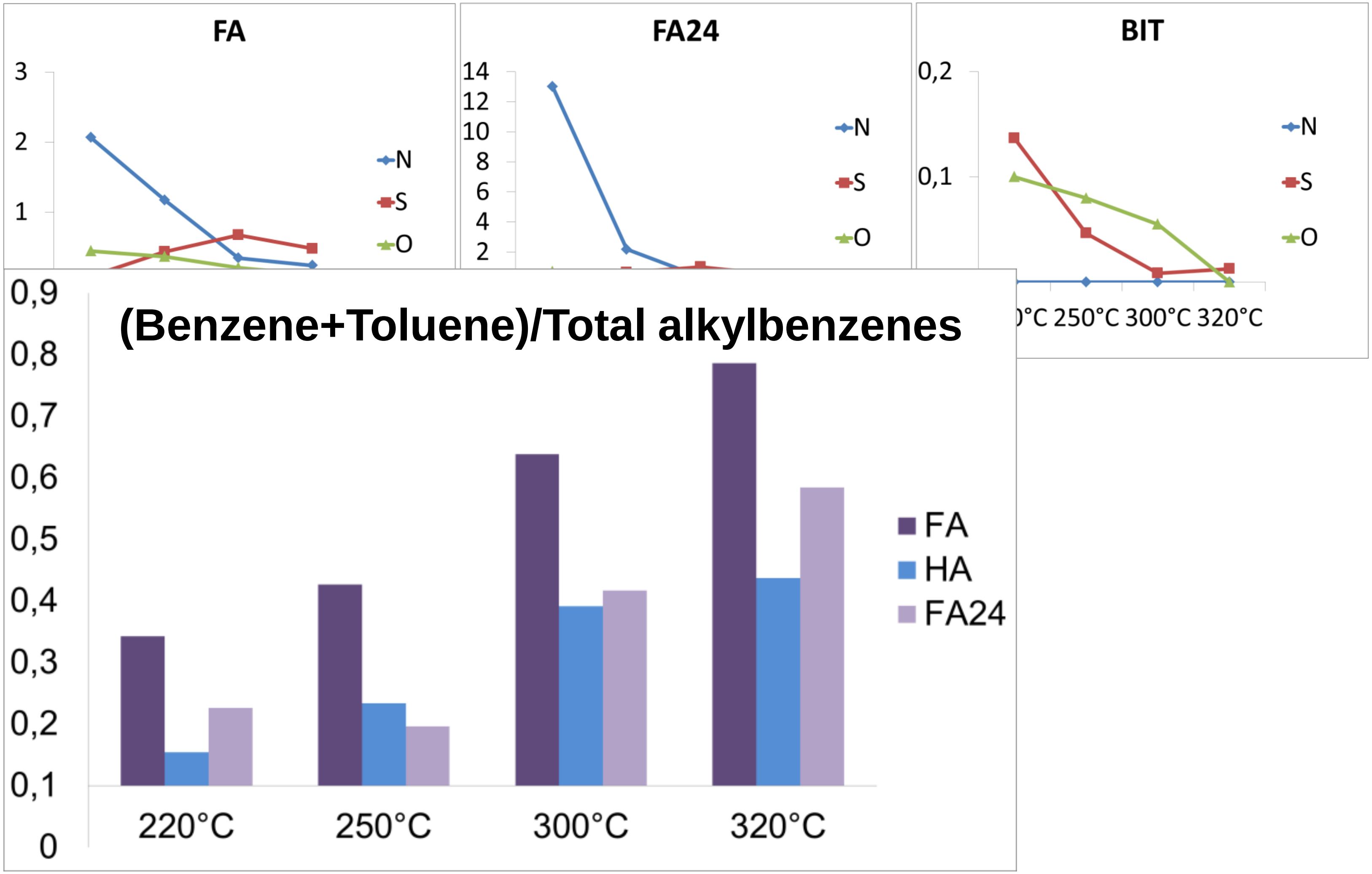

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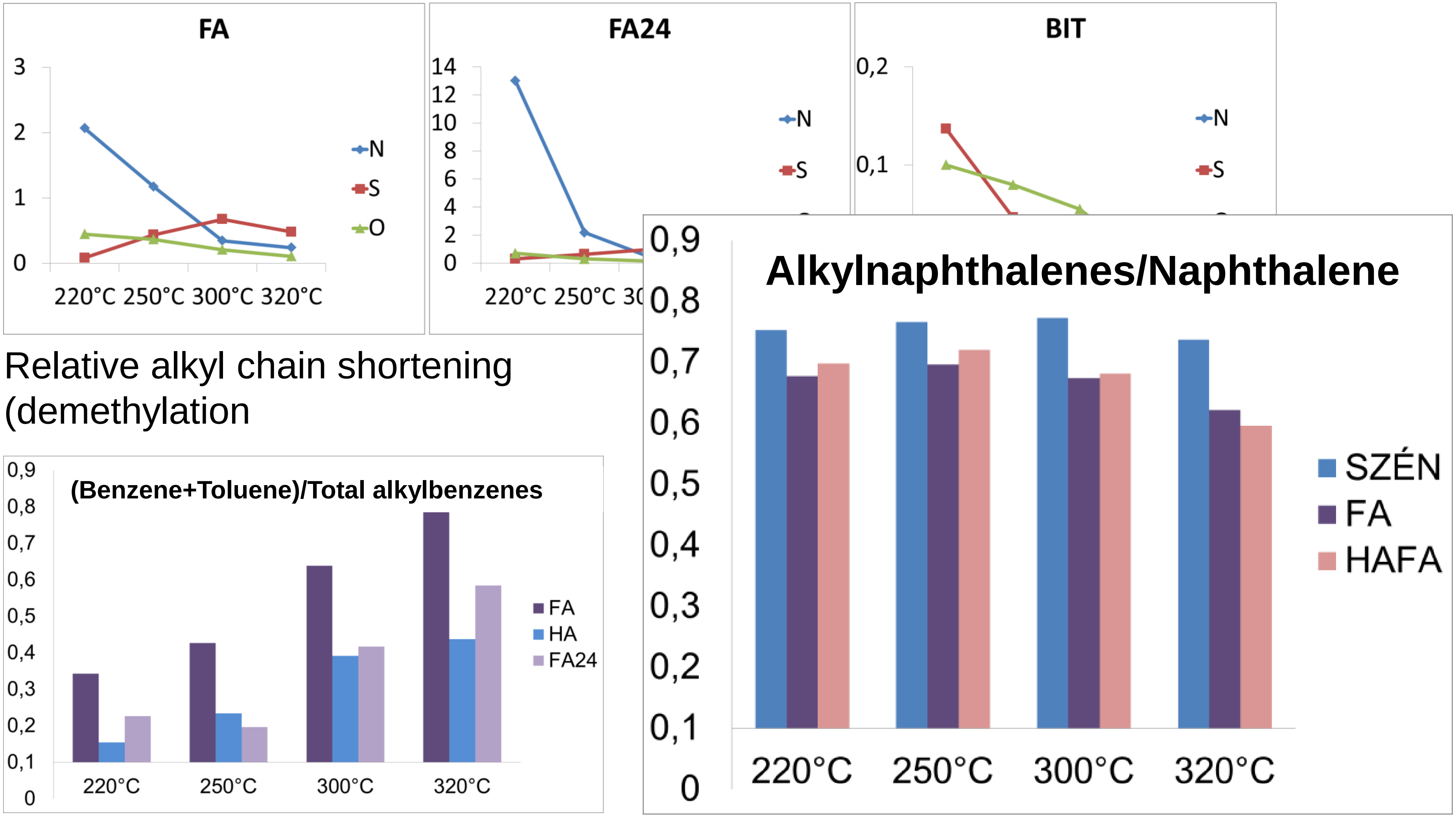
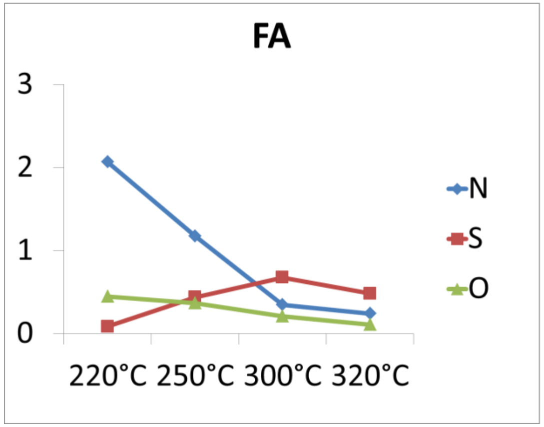


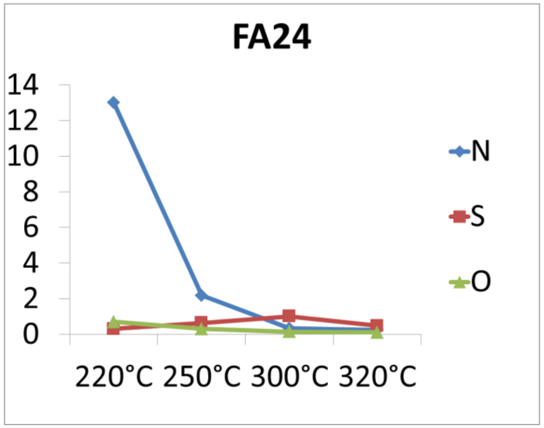
Relative alkyl chain shortening (demethylation

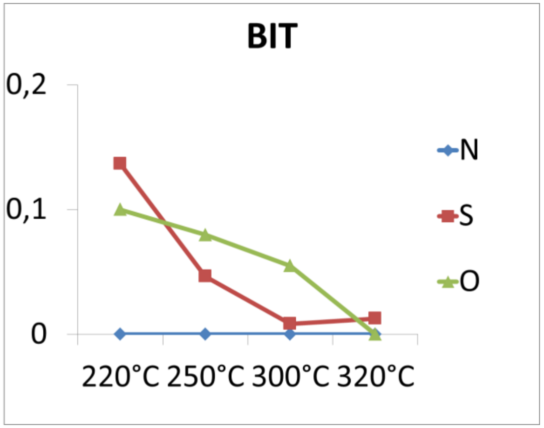
abstract N° 1995

Results – Experiments

Decomposition of heteroaromatic compounds







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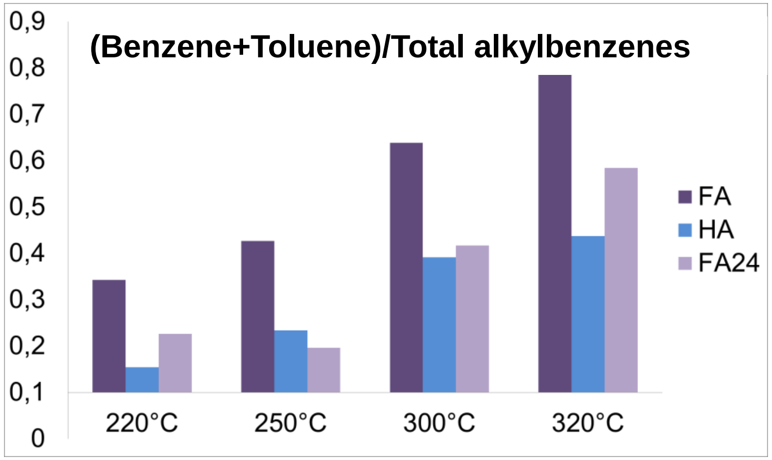
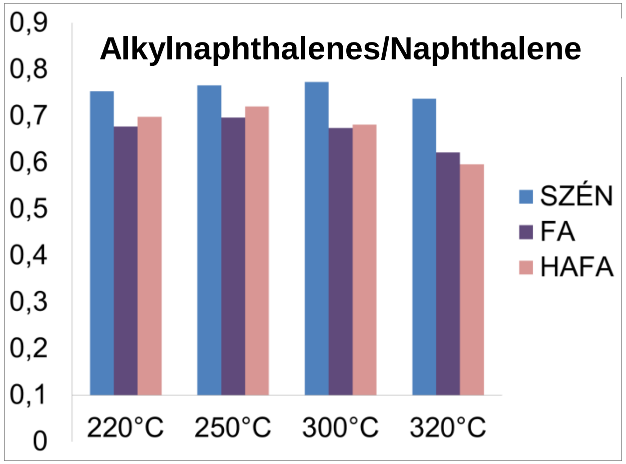


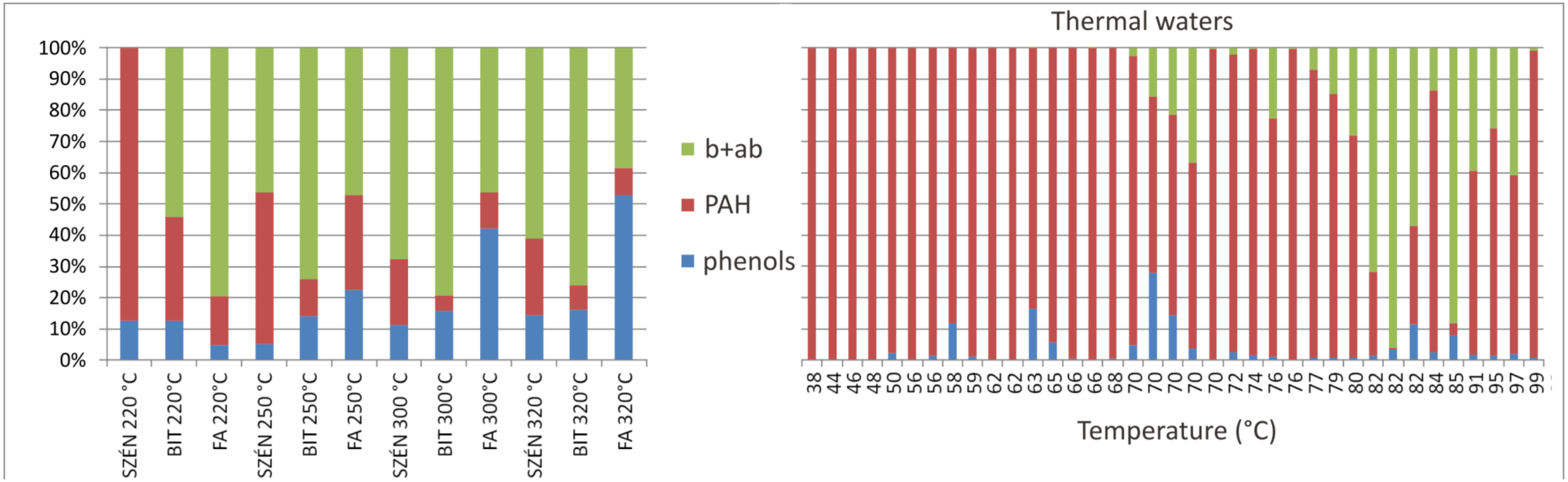


Summary - experiments

- Reactions run simultaneously (decomposition of large molecules, heteroatom loss, aromatisation, polycondensation)
- Time and temperature influences reaction intensities
- Decomposition of large molecules (aromatic generation) is faster than polycondensation
- Composition and maturity of the precursor OM is reflected by the generated aromatics
- Alkylbenzenes (and perhaps PAHs as well) undergo demethylation
- Distribution of heteroaromatics reflect their smaller thermal stability and the maturity of the precursor
- Phenols become dominant at higher temperatures

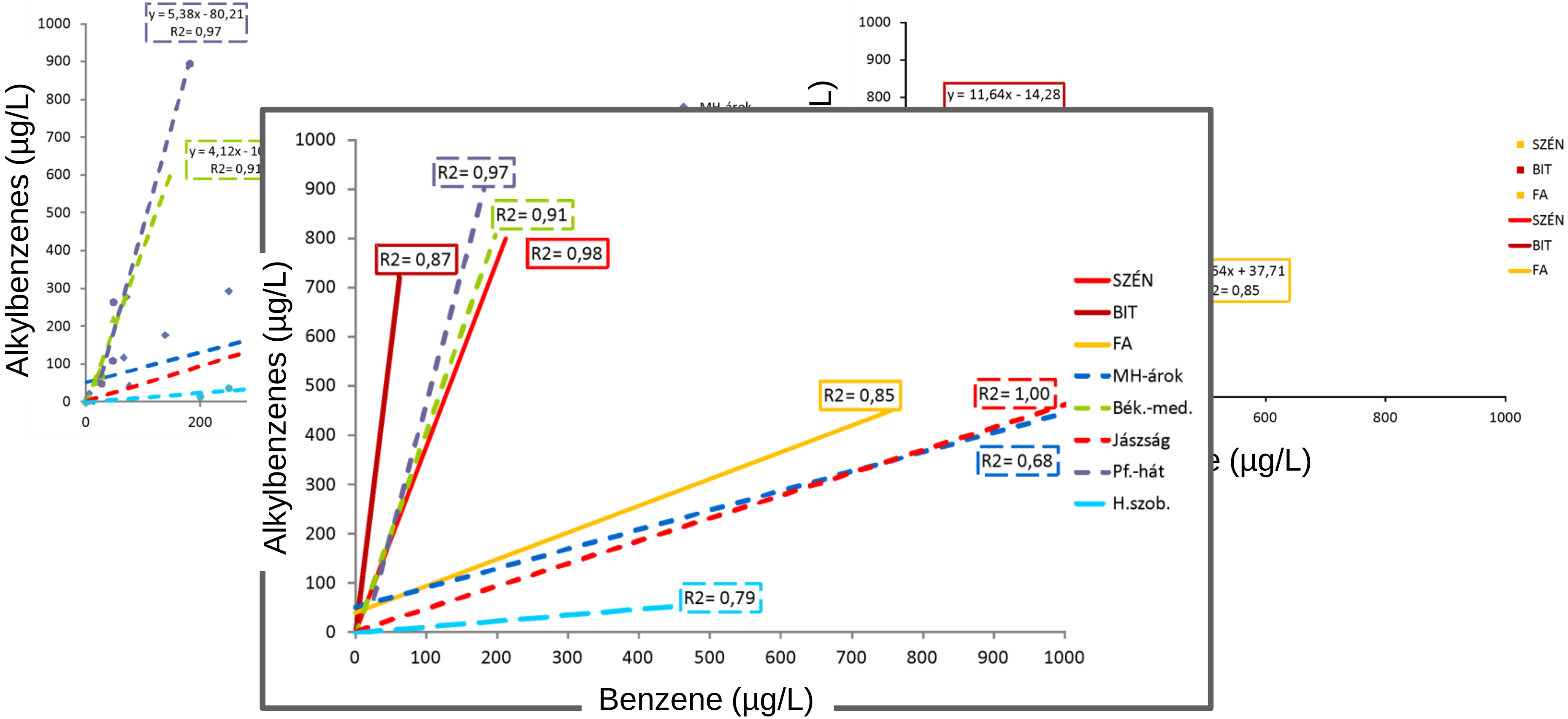
Comparison – TWs and experiments

		b+ab	PAH	phenols
Thermal waters	Max	1900	39596	5991
	Min	0	21	0
	Average	267	6850	1118
	Median	91	2934	39
	Deviation	450	9246	1765
Experiments	Max	578	354	1320
	Min	5	10	0
	Average	117	65	317
	Median	77	48	240
	Deviation	135	70	313



Comparison – TWs and experiments

Precursor OM of aromatic HCs



Conclusion

- The characteristics of the generated aromatic compounds depends on the precursor, treatment temperature and duration. Precursors can be „fresh” and more mature OM as well.
- Reactions
  - Alkylbenzene and PAH generation: C-C and C-heteroatom bond clevage of macromolecules;
  - Policyclisation and aromatisation of alkylbenzenes;
  - Formation of alkylbenzenes via heteroatom loss in heteroaromatic compounds;
  - Relative demethylation of aliphatic chains of alkylbenzenes.
- Generation of phenols and large quantities of alkylbenzenes is bound to given threshold temperatures, while PAHs appear in lukewarm waters as well. A proportion of naphthalene is also a product of thermal decomposition.
- The same compunds in the same order are formed during experiments, as in TWs (heteroaromatic compounds, alkylbenzenes, phenols), but quantities and ratios are different.
- No marker compound was found among the aromatics → the precursor of the OM in TWs can be assessed indirectly (e.g. molecular ratios).
- Origin of OM in different subbasins may be assessed on the basis of benzene and alkylbenzene concetrations, however, these assumption needs verification on a larger sample set.

Questions…

- What happened to the OM of very old connate waters?
- Where are the PAHs coming from?
- What is the contribution of microbial activity?
- What shall we see in a larger data set?

Thank you for your attention!

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