

Ph. D. Thesis

**CHARACTERISATION OF AROMATIC COMPOUNDS  
IN THERMAL WATERS AND EXPERIMENTAL  
MODELLING OF THEIR GENERATION**

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# 1. Introduction

Thermal waters in the Pannonian Basin may contain high amounts of dissolved organic matter that may exert positive and negative effects on their use. Thermal waters are used for balneologic purposes and organic compounds may contribute to the curative power. In Hungary thermal waters are mixed to drinking water (mostly in those areas where natural arsenic content is increased in groundwater). In case of geothermal use, the coagulating organic matter greatly decreases the efficiency of re-injecting wells (by two orders of magnitude) causing an additional cost. However, according to the legal regulations the detailed analysis of organic compounds is not obligatory. For these reasons research on origin and behaviour of organic compounds in thermal waters has a great importance.

During the last two decades mono- and polyaromatic compounds were found at hundreds of water localities studied. Among these were benzene and alkylbenzene homologues, polycyclic aromatic hydrocarbons (PAH), phenol homologues, mono- and polycyclic heteroaromatic compounds. Some of these are toxic and/or carcinogen (e. g. benzene, phenols, PAH-s), or act as precursors of chlorinated hydrocarbons.

The aims of my research was to study the decomposition of organic matter as the source of aromatic compounds, the temperature dependency of the concentrations and qualities of the aromatic products and their relationship with the origin of the water.

I also carried out hydrous pyrolysis (aquathermolysis) experiments on different precursor candidates (humic and fulvic acid, bitumen, lignite and a precipitate from a geothermal well) to model the generation of aromatic compounds in water.

I compared the results of the experiments with the observations on thermal waters to describe the effect of temperature and precursor material and thus, assess the type of the major contributing organic matter.

On the basis of the literature, description of the reactions by exact chemical equations is not possible because of the very complex chemical structures and the presence of several simultaneous and competitive chemical reactions; however, it is possible to examine the temperature dependent trends.

## 2. Samples and methods

### 2.1 Thermal waters

Thermal water samples were taken in representative localities in Hungary with different watershed lithologies. The aquifers are mostly of Late Pannonian (Late Miocene) age; the depths of screened intervals vary between 411 and 2264 meters. Outflow temperatures (from 38°C to 99°C) do not show strict correlation with depth, which can be explained by the different geologic settings and geothermal gradient values. Most of the water samples are of sodium-hydrogen-carbonate type, three samples, characterised by  $\delta^{18}\text{O}_{\text{SMOW}}$  values close to 0‰, are of sodium-chloride type. Most of the samples originate from southeastern Hungary.

In the Pannonian Basin the Quaternary and Tertiary sediments can reach a thickness of 7000 m, depending on the bedrock morphology. The Upper Pannonian and younger formations differ from the Lower Pannonian both in petrological and hydrogeologic features. The gravelly, sandy delta sediments of the Upper Pannonian are characterized by good permeability. The meteoric (and paleometeoric) waters reach a great depth in a short time. The top of the Lower Pannonian mostly consists of siliciclastic, fine grained brackish and lacustrine sediments characterized by extremely low porosity and permeability.

Thermal water samples were taken by the Geological Institute of Hungary from operating wells between 2001 and 2002. Several litres of water were put into clean polyethylene sampling bottles and closed hermetically. The analyses were performed within a few days while samples were stored below 4°C. For organic chemical analyses water samples were collected in 2.5-liter, solvent washed, dried (200°C) glass bottles with glass stoppers. Samples were cooled during transport and stored at 4 °C till extraction within 2–3 days. The stable isotope ratio analyses were carried out in the Institute of Nuclear Research of the Hungarian Academy of Sciences. The results are given in the conventional  $\delta$  notation as the per mil (‰) deviation of the isotope relative to known standards ( $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000$ , where  $R_{\text{sample}}$  and  $R_{\text{standard}}$  are the D/H and  $^{18}\text{O}/^{16}\text{O}$  ratios in the sample and in the standard, respectively). The standard water for hydrogen and oxygen isotopes is Vienna Standard Mean Ocean Water (VSMOW).

The inorganic chemical analyses were carried out in the Geological Institute of Hungary. Dissolved inorganic compounds ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ) were determined by ion chromatography and ICP-AES (Jobin Yvon ULTIMA 2C) spectrometry, while for trace

elements ICP-MS (VG PlasmaQuad II STE) was used. The organic chemical analyses were performed in the National Institute of Environmental Health. The organic compounds of waters were separated by chromatography and were measured from their dissolution in hexane. Identification was carried out on the basis of their mass spectra and retention times. The relative concentrations of the individual compounds were determined from the area of the peaks. Quantitative measurements were performed for the following compound groups: volatile compounds (halogenated hydrocarbons, alkylbenzenes and naphthalene), polyaromatic hydrocarbons (PAHs) and phenols. Thirty-two halogenated hydrocarbon, 14 alkylbenzene, 15 PAH and 16 phenol standards were quantified. The volatile compounds were measured by solid phase microextraction (SPME) method with an HP 5890 GCMS on the basis of EPA 524.2. and EPA 8260 (He carrier gas; 250°C splitless injector; oven heating: 40°C, 6°C/min to 230°C, 10 min delay). The amounts of polyaromatic hydrocarbons (containing 2, 3, 4 or 5 rings) were measured with high-pressure liquid chromatography (HPLC) on the basis of EPA-550.1. (Guard column: Phenomenex Security Guard 4×3.0 mm 5 μ C18; analytical column: Supelcosil LC-PAH 250×4.6 mm 5 μ C18; T=35°C; ACN/water: 0 min=50/50, 5 min=50/50, 25 min=90/10, 45 min=100/0, 50 min=100/0, 55 min=50/50, 60 min=50/50.) Naphthalene was measured in two different groups with different techniques (among volatiles and PAHs, by SPME GCMS and HPLC, respectively). Phenols were determined by extraction and by acetate derivation (and extraction) methods with gas chromatography.

## ***2.2 Aquathermolysis experiments***

HA and FA samples were prepared from Keszthely Peat (W-Hungary) using the recommended IHSS method (<http://www.ihss.gatech.edu/soilhafa.html>). Sample HAFa is a humic and fulvic acid mixture gained from deep, warm thermal water (2103 m, 92°C) from SE-Hungary, extracted with the recommended IHSS method (<http://www.ihss.gatech.edu/soilhafa.html>), but without the final separation of humic and fulvic acids. The extraction of humic substances was carried out at University of Szeged.

SZÉN sample was taken from Dudar Lignite, without any pretreatment.

Bitumen (BIT) sample was pulverized and extracted with chloroform from the 1591,2–1591,4 m section of Tiszapalkonya-I borehole in the Institute for Geochemical Research, Hungarian Academy of Sciences.

The precipitated material (CSAP) originates from the filter of an active geothermal well at Hódmezővásárhely. The organic matter was gained through liofilization at the Department of Microbiology, Eötvös Loránd University.

Aquathermolysis experiments were carried out under oxidative and reductive conditions. The experimental temperatures were generally as follows: 220°C, 250°C, 300°C, 320°C with treatment time of 72 hours. The fulvic acid sample was also treated for 24 hours at the same temperatures to study the effect of the duration of thermal treatment.

The experiments were carried out in a 600 ml stainless steel reactor vessel (Parr Instruments). The amounts of the samples were 25 mg and 100 mg for oxidative and reductive treatments, respectively. Samples were treated in distilled water containing 3 g/l NaHCO<sub>3</sub>. The water was previously heated over 250°C then cooled down close to room temperature. For heating under oxidative conditions the sample was put into the 250 ml of pre-treated water, the vessel was closed and the heating started.

To achieve reductive conditions (closer to natural environment), 50 mg of ascorbic acid was added to the sample as a reducing reagent and before heating, N<sub>2</sub> gas was purged through the vessel and the water to eliminate as much oxygen as possible, and to exchange the headspace gas to nitrogen. The initial overpressure was 2 bars in the vessel. Sampling was carried out at room temperature, through a sampling valve, without opening the vessel. For GC-MS analyses in all cases an Agilent 7890 gas chromatograph and an Agilent 5975C inert XL mass spectrometer (MS) (Agilent Technologies, Germany) equipped with GERSTEL MPS2-XL autosampler and GERSTEL CIS4 programmable temperature vaporizer (PTV) inlet (GERSTEL GmbH, Germany) were used. The temperature of the transfer line, ion source and quadrupole were set at 250°C, 230°C, 150°C, respectively. The MS was used in simultaneous SCAN/SIM mode. The concentration of target compounds was determined from selected ion monitoring (SIM) data. SCAN mode was used to investigate presence of any other compounds. For every analyte one target ion and two qualifiers were measured. External standard calibration was used in every case.

Benzene and alkylbenzene content was determined with a static headspace method in accordance with the Hungarian Standard for the determination of volatile aromatic hydrocarbons (MSZ 1484-4:1998). Ten ml sample was transferred to a 20 ml crimp cap vial. Anhydrous sodium sulfate (5 g) was added just before crimping. The sample was held for 15 min at 80°C and agitated with 600 rpm. Sample (2.5 ml) was collected from the headspace with a 2.5 ml headspace syringe which was thermostated at 105°C. The sample was injected to the PTV injector equipped with a Tenax TA filled inlet liner. The injector was operated in

split mode with a 10:1 split ratio. The injector temperature was set at 10°C, it was rapidly elevated to 260°C at 12°C/s and was kept hot during the analysis. An RTX-VMS (20 m x 180 µm x 1 µm) column was used to separate the analytes with a constant 1 ml/min flow of helium (5.0). The oven program was 40°C (2 min), 40°C/min, 100°C (0 min), 20°C/min, 160°C (0 min), 50°C/min, 240°C (1 min) and the scan range was 40–300 Da.

Polycyclic aromatic hydrocarbon content was determined with a stir bar sorptive extraction method based on the work of Kolahgar et al. (2002). Ten ml of sample was transferred to a 40 ml vial and 2 ml methanol was added. A 10 mm Twister bar (GERSTEL, 0.5 mm phase thickness) was placed in it. The sample was agitated for 2 h at 1200 rpm. Initial temperature of the thermal desorption unit (TDU) was 50°C, after 0.5 min this was elevated to 280°C and held for 6 min. In order to thermally desorb the analytes a higher desorption flow, 50 ml/min was used. The temperature of the TDU transfer was 280°C and the TDU was operated in splitless mode. During the desorption analytes were collected in the cooled PTV inlet with an empty baffled inlet liner. Injector temperature was set at 10°C and after removing the sample and setting the head pressure, it was rapidly elevated to 300°C at 12°C/s. This final temperature was held during the analysis. Analytes were transferred to the column in split injection mode with a 10:1 split ratio. A HP-5MS (30 m x 250 µm x 0.25 µm) column with a constant 1 ml/min flow of helium (5.0) was used to separate the analytes. The oven program was 50°C (1.5 min), 20°C/min, 180°C (0 min), 15°C/min, 250°C (0 min), 3°C/min, 275°C (0 min), 5°C/min, 305°C (0 min), 40°C/min, 320°C (5 min) and the scan range was 50–550 Da.

The concentrations of the phenol homologues was carried out on the basis of 8040 EPA method by liquid-liquid extraction and liquid injection. 10 ml sample was acidified with hydrochloric acid and then extracted with 1 ml hexane. 1 µl of the water-free extract was injected into the PVT injector (cold, splitless mode, quartz wool liner). The 40°C injector was heated to 280°C with 720°C/min rate after 0.2 minutes delay and was kept at 280°C until the end of the analysis. The components were separated on a HP-5MS (30 m x 250 µm x 0.25 µm) column. He (5.0) carrier gas flow rate was 1 ml/min. The oven program was 40°C (1 min), 40°C/min, 80°C (17 min), 50°C/min, 300°C (2 min). SCAN range was 50-550 Da.

### 3. Summary of new scientific results

1. I have elaborated an experimental method to model the organic reactions that occur in thermal waters. I carried out hydrous pyrolysis (aquathermolysis) experiments on different precursor materials. On the basis of the results I have quantitatively characterised the aromatic compounds generated from natural precursors and the effect of treatment temperature and duration on these reactions.

2. I suggest that the following reactions occur during hydrous pyrolysis of different organic precursors:

- Alkylbenzene and PAH generation through the splitting of C-C and C-heteroatom bonds of macromolecules;
- Polycyclisation and aromatisation of alkylbenzenes;
- Formation of alkylbenzenes through the splitting of heteroatomic bonds and heteroatom loss in heteroaromatic compounds;
- Relative demethylation of aliphatic chains of alkylbenzenes.

3. I corroborated that phenols, benzene and alkylbenzenes found in thermal waters are generated from the thermal decomposition of organic matter, and their generation is related to that of carbon dioxide and hydrocarbon gases.

4. I showed that organic matter precursors of different types and maturities generate aromatic compounds (alkylbenzenes, phenols, polycyclic aromatic hydrocarbons and heteroaromatic compounds) in different concentrations and ratios. These results indicate that aromatic compounds in thermal waters are not necessarily related to oil fields. However, hydrocarbon generation occurs in the sub-basins.

5. Comparing the aromatic compounds of thermal waters with those generated during aquathermolysis experiments I demonstrated that 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.

6. I concluded that the concentrations of aromatic compounds in thermal waters do not show correlation with the outflow temperatures above the required threshold temperature. The aromatic concentrations and the compound classes are similar in waters of meteoric origin and in waters characterised by less negative  $\delta^{18}\text{O}$  values and higher chlorine and iodine concentrations, thus, organic compound characteristics are independent of water origin.

7. I concluded that the concentrations of benzene and alkylbenzenes show excellent correlation in waters originating from different sub-basins and also in the experiments. In this case the slope of the trend line is determined by the precursor material. Trend lines of the waters originating from a given sub-basin overlap with the trend lines set up by experimental data. On the basis of these results I suggest that the major precursor of the aromatic compounds of thermal waters originating from a given sub-basin can be assessed. However, these assumptions were made on a limited database and further studies are needed to verify the observed relationships.



## 4. Publications and abstracts

### Related to the Thesis

- Fekete J., Sajgó Cs., Kramarics Á., Eke Zs., Kovács K., Kárpáti Z. (2012) Aquathermolysis of humic and fulvic acids: Simulation of organic matter maturation in hot thermal waters. *ORGANIC GEOCHEMISTRY* 53, pp. 109–118. **IF: 2.785**
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### **Other publications**

Kern Z., Patkó M., Kázmér M., Fekete J., Kele S., Pályi Z. (2012) Multiple tree-ring proxies (earlywood width, latewood width and  $\delta^{13}\text{C}$ ) from pedunculate oak (*Quercus robur* L.), Nyírség, NE Hungary. QUATERNARY INTERNATIONAL In Press. **IF: 1.874**

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