

Ph.D. thesis

**Characterization of humic substances isolated from thermal
waters of south-east Great Plain**

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1. Introduction

Humic substances are considered an assemblage of high molecular weight organic molecules with acidic character originating from the decomposition of plant and animal residuals by the process of humification involving physical, chemical, as well as enzymatic, and microbiological reactions. This part of natural organic matter in dissolved, precipitated form, and chemically bound to inorganic constituents can be found in all environmental systems. Humic substances exist in the colloidal size range. Their aqueous solutions equally show properties of association colloids and polyelectrolytes, as well as those of colloidal dispersions by the relatively less change of the conditions. Fractions of humic substances are operationally defined; the procedure is based on their pH-dependent solubility. Fulvic acids are soluble in water under all pH conditions, humic acids precipitate in acids, but dissolve at alkali pHs. Humic substances have many favourable effects, for example they increase soil fertility, and moreover human use of their metal complexes is known, too. A disadvantageous feature, however, is that their interactions with organic and heavy metal pollutant can increase solubility of these contaminants, thus causing serious environmental problems.

During the history of more than two hundred years of humus-related research mainly soil derived humic substances have been investigated. Aquatic humic substances have been in the forefront of public attention for few decades after it was recognized that the potential source materials for trihalomethanes, which appear due to chlorination of drinking water, were humic substances naturally present in waters. In the isolation of aquatic humic substances it presents difficulties that their concentration in natural waters mostly very low. However, in recent decades considerable progress has been made in the technological implementation of the isolation procedure, but with some exceptions, the groundwater research is still slowly started.

Thermal waters have been traditionally used as drinking and spa water for centuries. Groundwaters often have significant organic matter content, of which a part may consist of humus fractions. This is even more remarkable, since the humic substances are proven anti-inflammatory and antiviral effects. Therapeutic effect of organic materials present in bath waters has recently begun to investigate. Heat of thermal water can be extracted, thus it provides local, import independent, renewable energy, which is free from pollution emission and unaffected by diurnal and seasonal weather conditions. Essential points in the practical and legal regulation of thermal water utilization are to preserve the sustainability of geothermal energy, and to solve the disposal after utilization. Only after energy exploitation the injection of cooled thermal water back into the aquifer is permitted or required. However,

precipitations observed on the filters of the injection wells significantly increase operating costs of wells due to fouling of filters. The origin of these dark precipitations is still unclear, but presumably higher molecular weight organic materials of thermal water also contribute to them. It is obvious that the quantity and quality of humic substances essentially influence the usability of thermal waters.

My aims were

To sample and preserve thermal waters of south-east Great Plain in Hungary, as well as to perform routine analytical tests and compare results with previous ones. To study organic matter of thermal waters that can be adsorb on C18-SPE column directly by ESI-FT-ICR mass spectrometry.

To isolate operationally defined humic and fulvic acids from thermal waters of south-east Great Plain in Hungary. To compare the characteristics of the obtained fractions with those of some members of the collection consisting of standard and reference samples established by International Humic Substances Society.

To study the effect of the water sample preservation by acidification applied in different time after water sampling on the properties of isolated humic fractions.

To characterize the elemental composition of isolated humic substances by elemental analysis, as well as the diversity of functional group content by FTIR and ¹H-NMR spectroscopy, and to determine the amount of mainly acidic groups by potentiometric acid-base titration.

To identify amino acids and carbohydrates liberated after hydrolysis of humic substances, and to determine the contribution of these molecules to the elemental composition of humic substances.

To investigate the fluorescence of dilute aqueous solution of humic and fulvic acid samples.

To develop reproducible measurement conditions for the analysis of humic fractions by ESI-FT-ICR mass spectrometry. To identify compounds involved in samples based on molecular masses determined from the observed mass spectra, then to evaluate the differences between the samples based on illustration on the Kereven diagram and grouping according to aromaticity index. In addition, to develop a new method for comparing compositional changes of molecules.

2. Materials and methods

I sampled thermal water in quantities of 30-100 litres from wells of south-east Hungary in February 2006, January 2007 and February 2008. I studied thermal waters from three wells in Makó and three wells in Szeged. I isolated operationally defined humic and fulvic acids from thermal waters tapped from Upper Pannonian layers of Pannonian Basin (depth range between 750 and 2100 meters) according to the procedure concerning aquatic humic substances recommended by International Humic Substances Society. Preparative quantities of low-ash (<1.0 weight %) aquatic humic substances can be obtained by adsorption chromatography on XAD-8 resin (Amberlite), ion exchange (Varion KSM) and freeze-drying. The isolation procedure started with the acidification of the water samples. The acidification was performed after cooling down water samples in the laboratory in the sampling of 2006 and 2007. However, water samples were acidified immediately after outcropping thermal water in the field in the sampling of 2008. By the modification it was possible to study the effect of changed conditions such as decreasing temperature, and presence of oxygen. By comparison I also investigated characteristics of humic and fulvic acid (SRHA, SRFA) samples isolated from surface water (Suwannee River), which are members of the collection consisting of standard and reference samples, established by International Humic Substances Society.

The characteristics of the wells and tapped thermal waters (borehole depth, perforated depth, tapped water temperature), as well as data concerning the organic matter content (total organic carbon, permanganate and chromate chemical oxygen demand) and inorganic content (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Cl^- , Br^- , I^- , F^- , SO_4^{2-} , HCO_3^- , S^{2-} , PO_4^{3-} , CO_3^{2-} , HBO_2 , H_2SiO_3 , total and phenolphthalein alkalinity, total and carbonate hardness, specific conductivity, total dissolved solids) were provided by Zoltán Kárpáti (National Institute of Environmental Health, later Budapest Sewage Works Ltd.) and István Horváth (Geological Institute of Hungary). The staff of Geological Institute of Hungary conducted on-site and laboratory tests in the sampling of 2007.

I carried out the spectrophotometric analysis of water samples by Uvikon 930 dual-beam UV-Vis spectrophotometer and Ocean Optics USB2000 spectrophotometer using 1 cm optical path-length quartz cuvette over the 200-800 nm. I determined the p- and m-alkalinity values from titration curves of water samples obtained by potentiometric acid-base titration. I investigated directly the organic matter content of water samples from shallowest and deepest wells in the sampling of 2008 using C18-SPE column (Varian) by ESI-FT-ICR mass

spectrometry. I acidified the thermal water samples immediately after outcropping thermal water in the field, and one day following, too.

The elemental composition of the isolated humic substances as weight percent (N, C, S, H content) was determined by Fisons NA1500 NCS analyzer in the Geological Institute of Hungary (at 1010°C, $O\% = 100\% - (N\% + C\% + S\% + H\%)$). Elemental analysis was also carried out during the carbohydrate and amino acid analysis, the C and N content were measured by Carlo Erba 1108 CHN analyzer (Columbia, USA).

I performed potentiometric acid-base titration of the isolated humic and fulvic acid fractions (like the titration of the water samples) by a home made computer-controlled titrator system (GIMET1). I studied the amount of charged groups formed by deprotonation process of acidic functional groups.

I investigated the isolated humic fractions by various spectroscopic methods. The infrared spectra were acquired by Perkin Elmer 1600 FTIR spectrophotometer in Geological Institute of Hungary. The measurements on the pellets produced from the mixture of the samples and potassium bromide were carried out. I performed the $^1\text{H-NMR}$ measurements by Bruker AV 500 MHz device in the lab of Neurobiological Knowledge Center of South Plain in Hungary. I dissolved the samples in NaOD of 40 weight percent and D_2O (Sigma-Aldrich). I investigated the fluorescence of humic samples by Horiba Jobin Yvon Fluoromax-4 spectrofluorometer with Xenon lamp of 150 Watt using 1 cm optical path-length quartz cuvette. I chose the 3-nm slit of the excitation and emission monochromator in any case.

The carbohydrate and amino acid analysis was carried out at the University of South Carolina (Columbia, USA). Prior to the carbohydrate analysis the humic samples were hydrolyzed with 1.2 M H_2SO_4 , and then neutralized by passing cation exchange resin. After desalting neutral aldoses were isocratically separated with 25 mM NaOH on PA 1 column, then were measured with Dionex 500 system equipped with an amperometric detector. Before the amino acid analysis samples were hydrolyzed with 6 M hydrochloric acid for 20 hours at 110 °C. Enantiomeric amino acids were separated on a Licrospher 100 RP18 with Agilent HP 1100 apparatus after in-line derivation with OPA/IBLC or OPA/IBDC reagents at 20 °C.

I performed the FT-ICR/MS measurements at the Helmholtz Zentrum München (Neuherberg, Germany) with a Bruker APEX Qe Fourier transform mass spectrometer equipped with a 12 Tesla superconducting magnet and an Apollo II electrospray source in negative mode ionization. After the exact masses of molecules had been determined, I calculated the molecular formulas by a software tool, written in-house according to the

following criteria: the maximum number of elements in case of C is 100, for O is 80, for N is 5, for S is 2 and H unlimited, the atomic ratios of values, $0 < H/C < 2.5$ and $0 < O/C < 1$, and the N-rule. The calculations were concerned only single-charged molecular ions. The given molecular formula was accepted only if the peak corresponding molecule containing ^{13}C isotope was found in the spectrum, too. In case of molecular formula assignment and ^{13}C isotope search less than 1 ppm difference was allowed.

3. Summary of new scientific results

T1. *The concentration of humic acid and fulvic acid fractions isolated from thermal water and their ratio*

I determined humic and fulvic acid (HA and FA) concentration of deep thermal waters on the basis of the mass of the humus fractions isolated according to IHSS procedure and the volume of the water samples; which resulted in significantly different values, 0.7 to 6.9 mg L⁻¹ for HA and 0.5 to 2.6 mg L⁻¹ for FA, respectively. The humic acid concentration is typically higher than the fulvic acid concentration; their ratio (HA: FA) is usually 2:1, which appreciably different from 1:3 ratio found in surface water environment. I concluded that humic content decomposes into smaller organic compounds and molecules of fulvic acid fraction decay in higher degree than those of humic acid fraction based on the decrease of the humic substances concentration relative to total organic carbon (from 0.4 to 0.1) as well as that of fulvic acid content relative to humic acid content with increasing depth of thermal waters in accordance with the results of **T5**. Other possible reason for the relative small fulvic acid content may be that compounds originating from interaction between kerogen and groundwater are mainly in the humic acid fraction.

T2. *The origin of humic substances isolated from thermal water*

I deduced the origin of humic substances isolated from thermal water on the basis of the organic matter content of thermal waters and characteristics of isolated humic and fulvic acids, respectively. I concluded that humic substances also originate from either kerogen containing sediment or groundwater recharge of organic matter content, but their source is not related to oil field on the basis of total organic carbon content of thermal waters (6.1 to 138.8 mg L⁻¹) taking into account geological and hydrogeological analogy, too. Humic substances isolated from thermal water are related not to aquatic, but terrestrial humic fractions according

to the values of dissociated acidic functional groups determined by potentiometric acid-base titration (8.3 to 11.1 mmol gC⁻¹ for HA and 14.7 to 16.6 mmol gC⁻¹ for FA, pH=10). The patterns of infrared spectra of humic acids isolated from thermal water support the relationship with sedimentary organic matter. As they show strong absorption at wavenumbers of 3400, 2900, 1720, 1600 and 1200 cm⁻¹ as well as the intensity of absorption bands at 1720 and 1600 cm⁻¹ is nearly the same, but it is no absorption at 1640 cm⁻¹. Infrared spectra of fulvic acids isolated from thermal water are similar to these, but they show typically strong absorption at wavenumber of 1720 cm⁻¹, as well as the intensity of the peak is lower at 1600 cm⁻¹.

T3. *The permanency of the characteristics of isolable humic substances after outcropping of thermal water*

I could conclude the permanency of isolable humic substances by studying the effect of changing conditions (decreasing temperature and the presence of oxygen) by means of acidification preserving the state at different times after outcropping. Based on the results of elemental analysis, I found that humic substances are not enriched in oxygen, the amount of their oxygen containing functional groups does not increase after outcropping of thermal water. Infrared, ¹H-NMR and fluorescence spectra of humic substances from different samplings and their parameters derived from those spectra ($A_{2925\text{cm}^{-1}} / A_{1620\text{cm}^{-1}}$, $A_{1710\text{cm}^{-1}} / A_{1620\text{cm}^{-1}}$ és $A_{2925\text{cm}^{-1}} / A_{1710\text{cm}^{-1}}$, relative abundance of aliphatic I, aliphatic II, heteroatomic and aromatic protons, excitation and emission wavelength), as well as carboxyl and phenolic hydroxyl group content estimated from dissociation curves measured by potentiometric acid-base titration do not show difference. The pattern of atomic ratios, which were calculated from molecular formulas determined by ESI-FT-ICR mass spectrometry, occupied on the van Krevelen diagram does not change depending on the time of the acidification, too.

T4. *Comparison of the elemental composition of humic substances isolated from thermal water with that of humic substances extracted from other sources, as well as comparison of their elemental and functional group composition, carbohydrate and amino acid content, fluorescence and mass spectrometric characteristics with those properties of humic substances isolated from surface water*

4a. H/C and O/C atomic ratios determined by elemental analysis for HA and FA samples derived from thermal water are located in the van Krevelen diagram within the range

defined for the humic substances extracted from other sources, thus the studied humic substances isolated from thermal water exist in preferred composition range in nature, too.

4b. On the basis of elemental analysis, I concluded that humic and fulvic acids originating from thermal water differ mainly in carbon and oxygen content from the corresponding fractions isolated from surface water. The features of humic and fulvic acids derived from thermal water were compared with those of SRHA (Suwannee River humic acid) and SRFA (Suwannee River fulvic acid) which are the members of collection containing standard and reference samples established by IHSS; their carbon content is higher, but oxygen content is lower than that of SRHA and SRFA. The existence of humus fractions with high nitrogen (5.89%) and sulfur (3.95 and 4.00%) content denotes such organic matter sources and geochemical circumstances, which differ from those of other humic substances. Basing on the results of elemental analysis and potentiometric acid-base titration, I found that the largest proportion of oxygen in fulvic acids from thermal water is present in carboxyl group ($63.6 \pm 7.3\%$), however humic acids contain the latter in smaller proportion ($51.3 \pm 12.1\%$). While SRFA has higher oxygen content, but it has lower oxygen content present in carboxyl group (39.8%) than that in the corresponding fractions isolated from thermal water. On the basis of this observation, I concluded that oxygen content of humic fractions isolated from thermal water is chemically more uniform than that in the fractions from surface water. Based on the relative abundance values of structural protons determined by $^1\text{H-NMR}$ spectroscopy, I established that humic samples from thermal water are much more depleted in heteroatomic protons (12.2 to 5.5%) than that of the corresponding fractions from surface water. This fact is in good agreement with the results of carbohydrate and amino acid analysis, as humic substances from thermal water have typically smaller hydrolysable carbohydrate and amino acid content (1.1 to 6.1 and 5.2 to 20.5 $\mu\text{mol g}^{-1}$ sample). Exceptions are humic fractions with higher nitrogen content, in which nitrogen is present mostly in amino acid (15 or even more than 60%), but sulfur content is not related to the presence of cysteine or methionine in humic fractions with high sulfur content. I inferred that fluorophores are qualitatively different in humic substances isolated from thermal water on the basis the specific differences in the values of fluorescence excitation (λ_{ex}) and emission wavelength (λ_{em}) of humic and fulvic acids from thermal water (HA, λ_{ex} : 355 to 305 nm; HA, λ_{em} : 440 to 385 nm; FA, λ_{ex} : 350 to 305 nm; FA, λ_{em} : 440 to 400 nm) related to that of the sample from surface water (SRFA, λ_{ex} : 340 nm; SRFA, λ_{em} : 450 nm).

T5. *The change of the characteristics (heteroatom composition, especially oxygen content, and aliphatic/aromatic character) of humic substances isolated from thermal water with increasing depth of wells*

O/C atomic ratio of humic substances determined by elemental analysis decreases (from 0.42 to 0.33 for HA and from 0.56 to 0.49 for FA), but their H/C atomic ratio increases (from 0.87 to 0.99 for HA and from 0.93 to 1.13 for FA) with increasing depth of wells. On the basis of potentiometric acid-base titration the percentage of oxygen involved in carboxyl group content related to the whole oxygen increases (from 47.3 to 60.4 % for HA and from 58.4 to 74.3 % for FA) with increasing depth. Absorbance ratios derived from FT-IR spectra also change depending on the depth; the ratios of aliphatic to aromatic ($A_{2925\text{cm}^{-1}} / A_{1620\text{cm}^{-1}}$) and that of carboxyl to aromatic ($A_{1710\text{cm}^{-1}} / A_{1620\text{cm}^{-1}}$) increase, but the ratio of aliphatic to carboxyl ($A_{2925\text{cm}^{-1}} / A_{1710\text{cm}^{-1}}$) is unchanged in a function of the depth of wells. On the basis of the change in the ratios, I deduced that humic and fulvic acid fractions isolated from thermal water become more aliphatic and/or less aromatic character gradually with increasing depth while the carboxyl contents of the samples increase or not change at all. In summary I concluded that the reason of decreasing oxygen content with increasing depth of thermal water source is the decrease of oxygen containing functional groups other than carboxyl group. On the basis of $^1\text{H-NMR}$ spectra the amount of heteroatomic protons unambiguously decreases with increasing depth of thermal water exploitation, as well as the relative abundance of aromatic protons increases to some extent and that of aliphatic protons I in higher degree, but the change of aliphatic protons II is not obvious.

Fluorescence excitation and emission wavelength values of dilute aqueous solutions of humic and fulvic acid samples isolated from thermal water decrease in a function of the depth of wells, i.e., this relation shows blue shift. Based on this observation I stated that the degree of aromatic polycondensation and conjugation decreases with increasing depth.

I developed a data processing method for investigation of compositional changes of molecules identified by ESI-FT-ICR mass spectrometry, which the members of compound classes sorted by heteroatoms classify further according to their hydrogen deficiency expressed by Z value. On the one hand molecules containing less oxygen atoms of compound classes are present in higher relative abundance with increasing depth. On the other hand, the Z value, which changes along with the number of oxygen atoms, is less negative than that expected. This denotes that the identified part of the samples becomes less unsaturated, less aromatic character.

Furthermore, based on the available indirect facts I drew a conclusion that the average molecular weight of humic substances changes in a function of the depth of thermal water source. First, based on the decrease of the humic substances concentration relative to total organic carbon as well as that of fulvic acid content relative to humic acid content I deduced that humic content decomposes into smaller organic compounds and molecules of fulvic acid fraction decay in higher degree than those of humic acid fraction with increasing depth (T1). Second, I could conclude the decrease of average molecular weight of humic substances in thermal waters with increasing depth on the basis of the appearance of ¹H-NMR spectra and ESI-FT-ICR mass spectra; namely sharpening NMR signals especially in case of fulvic acids, and the decrease of relative intensity of peaks related to double charged compounds, respectively; as well as the blue shift of fluorescence excitation and emission wavelength values in a function of the depth may also indicate some reduction in the size of molecules.

T6. *Difference between atomic ratios of humic substances measured by elemental analysis and calculated from molecular formulas determined by ESI-FT-ICR mass spectrometry*

Atomic ratios of humic substances measured by elemental analysis and calculated from molecular formulas determined by mass spectrometry after electrospray ionization are different. On the other hand the depth-dependent change of atomic ratios, namely decreasing O/C and increasing H/C atomic ratios, obtained by ESI-MS is similar to those from elemental analysis, thus the direction of compositional changes can be studied by ESI-MS, too.

T7. *Dissimilarity determined by ESI-FT-ICR mass spectrometry between humic and fulvic acids isolated from thermal waters using XAD-8 resin and organic matter content of thermal waters concentrated on C18-SPE column*

The patterns of atomic ratios occupied on van Krevelen diagram for operationally defined humic and fulvic acids isolated according to the procedure recommended by IHSS using XAD-8 resin as well as for those of organic matter content of thermal waters retained by C18-SPE column which were calculated from molecular formulas determined by ESI-FT-ICR mass spectrometry differ. Although both stationary phases retain hydrophobic compounds from aqueous solutions, the isolation procedure affects the composition and characteristics of identified molecules of organic matter.

Scientific publications

Papers related to the present thesis

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