

**ORGANIC GEOCHEMICAL CHARACTERIZATION OF HUMIC AND FULVIC ACIDS OF THERMAL WATERS IN DEEP AQUIFERS OF THE PANNONIAN BASIN (SE HUNGARY)**

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The presence and emerging of several organic solutes (e.g. humic acids, hydrocarbon gases, aromatic hydrocarbons, phenols and fatty acids) have been reported in thermal waters (TWs) from Pannonian Basin, their origin only is partly known (Kárpáti et al., 1999, Brukner-Wein, and Sajgó, 1990). In this study we concentrate on one group of the components: humic substances (HS) whose two fractions: fulvic and humic acids (FA and HA) usually are present in natural and ground waters, as parts of the dissolved organic matter (DOM). The aquatic FA and HA of TWs in deep aquifers may have many different origin: e.g. influx with recharge during sedimentation or subsidence; in situ generation in natural or in ground waters; dissolved from lignites where were generated in situ during subsidence. The FA and HA are chemically and physically very active components within their systems: they may physically and/or chemically bound to minerals, they act as detergent (solubilize hydrophobic compounds) and they are sensitive oxidation/mineralization, and their dissolution and precipitation processes occur continuously. The behavior of HS in aqueous solution is therefore of considerable interest, especially in view of the fact that it exists in many varieties, depending on age and origin influenced by other substances present in the environment, and likely on temperature that is in question in this study.

In this work after the isolation of humic substances from three TWs originating from the Makó area (SE Hungary), the FA and HA fractions have been characterized by different methods. Some general data for TWs are summarized in the following Table.

wells	depth [m]	temp. [°C]	pH	m-alk. <sup>1</sup> [mmol/L]	HA <sup>2</sup> [mg/L]	FA+HA <sup>3</sup> [mg/L]	TOC ppm	COD <sup>4</sup> [mg/L]
Makó Spa	993	46	8.90	14.90	6.4	2.89	8.5	8
Makó Hospital/2	1703	74	9.44	25.53	3.2	2.75	17.6	12
Agricult. use (Benkő Ltd.)	2300	92	9.14	44.56	23.2	5.53	257	47

<sup>1</sup>The methylorange alkalinity titrated potentiometrically; <sup>2</sup>measured spectrophotometrically (420nm) using Fluka standard (No: 53680); <sup>3</sup>after isolation measured gravimetrically; <sup>4</sup>Chemical Oxygen Demand

Hot groundwater samples (slightly yellow-greenish yellowish, tar-smelling brownish) were collected from three deep wells with 1332, 2432 and ~4109 mg/L total dissolved solids,

respectively, in February 2006. The temperature was measured on sampling sites, and the pH, alkalinity, UV-VIS absorption, FTIR, fluorescence and other chemical parameters were determined in the laboratory after cooling down. During isolations the methods for preparation of IHSS aquatic HAs and FAs were followed.

In earlier surveys (Varsányi and Bertalané, 1985 and Kárpáti et al., 1999) the HA contents in ~150 TWs were determined on the basis of photometrical analyses using Fluka or Aldrich standards (coming from modern depositional environments), but as it was suspected, this method provided only rough estimations of concentrations in case of TWs (see Table: HA and FA+HA results). It is also corroborated by that the IHSS preparation procedure of HA and FA from waters could not be applied in case of the hottest TW and in the appearance of the precipitates: flocculated (colder ones) lumpy/sticky (hottest) precipitate formed during separation.

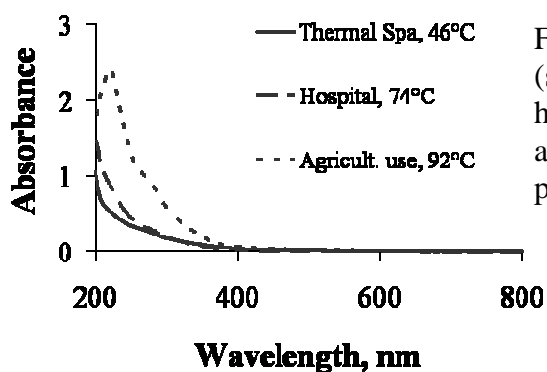


Figure 1. The larger the DOM contents (see COD and TOC values in Table), the higher the UV absorption. Increasing light absorption in the visible range indicates the presence of more and more HA.

The acidity of FA fractions is almost the same and greater than that of the HA samples both on basis of net proton surface and FTIR. On the basis of the previous 2 methods the amount of acidic groups in the HA fractions is significantly different in samples. The FTIR spectra of HA and FA of TWs are complex and the appearance and intensity of absorption bands (aromatic nuclei and carbonyl groups) are different and they also differ from the spectra of FA and HA extracted from coals or from natural waters, reflecting the elevated temperature and the effect of the complex physicochemical environment (facies) in the aquifers.

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