HUMIC ACID AS AN INDICATOR OF SUBSURFACE WATER MOVEMENTS

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ABSTRACT

Concentration of humic acids and their E_4/E_6 ratio in shallow groundwater, deeper subsurface water and thermal water samples were determined. Humic acids were isolated from several samples and their C and H contents were also measured.

The E_4/E_6 and H/C ratios of humic acids differ to each other in shallow ground- and in thermal waters. The E_4/E_6 ratio of humic acids in deeper Pleistocene waters of less Cl⁻ content is similar to that of the shallow groundwaters and those of higher Cl⁻ content is similar to that of the thermal waters. The E_4/E_6 ratio shows an upward migration of deep waters along fault line, where this migration was supposed on the basis of the higher Cl⁻ concentration of waters.

INTRODUCTION

In the Hungarian Great Plain, based on observations regarding the anomalies of well yields, geothermal gradient and Cl⁻ ion concentration, respectively, several authors presumed the presence of structural lines penetrating from the depth to the surface (ERDÉLYI, 1964; URBANCSEK, 1965; SCHERF, 1967). The authors mentioned assume the migration of water along these structural lines from the deeper aquifers.

According to the investigations of CASAGRANDE et al., (1980) each depth interval represents a given horizon of diagenetic transformation. So, it can be assumed that the investigation of the organic material dissolved in the waters offers rather valuable informations than that of the concentration of inorganic salts. Thus, analyzing the organic matter dissolved the question can presumably be answered either the water in the given sedimentary layer can be considered as syngenetic to the sedimentation or it migrated later into the layer from greater or shallower depth.

This paper attempts to conclude to probable movements of subsurface waters by determining the degree of diegenesis of humic acid.

MATERIALS AND METHODS

The amount of dissolved humic acid was determined in 66 samples taken from shallow groundwaters, in 82 samples from Pleistocene layers (depth interval from 75 to 604 m) and in 19 thermal water samples taken from the depth interval from 504 to 1945 meter according to CHALUPA's method (1963).

The absorbance of humic acid in 0.5% NaOH solution was also measured at the wavelength of 465 and 665 nm and their ratio (E_4/E_6) was calculated. The E_4/E_6 ratio

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is suitable — on the basis of KONONOVA's results (CHEN *et al.*, 1977) — to conclude the aromatic or aliphatic character of the humic acids. This ratio is independent of the humic acid concentration in water.

.The humic acid content of two samples of groundwaters, six samples of deeper Pleistocene waters and four samples of thermal waters was isolated in acid medium by n-amylalcohol and after drying by rotation vacuum evaporator the C and H content were determined. Determinations were made by CHN—1 analysator at 800—820 °C, with silverpermanganate catalysator under oxygen atmosphere. The CO_2 and H_2O were carried into a Porapack-Q-filled column by He carrier gas. Their quantities were determined by thermal conductivity measurements after their absorption and desorption.

The comparison of data was carried out by the STUDENT's *t*-test (SVÁB, 1981), if this proved to be necessary.

<div align="center">RESULTS</div>

The average values of the E_4/E_6 quotient are listed in Table 1. Calculating the average values only the water samples containing more than 2.0 mg/l humic acid were involved. When the concentration of humic acid is smaller than 2.0 mg/l the very low absorbance measured at 665 nm makes the calculations uncertain. Having compared the average values of the E_4/E_6 quotient of different waters by the *t*-test it was stated that there is no significant difference between the shallow groundwater and the deeper Pleistocene water, at a confidence level of 5%. The humic acid content in thermal waters were examined separately in waters of lower temperature (35—45 °C) and of higher temperature (more than 70 °C) since their chemical characters are different. The waters of lower temperature derive from Upper Pliocene and Upper Pannonian, those of higher temperature from Pannonian strata. Based on their E_4/E_6 quotients the thermal waters of higher temperature differ both from the shallow groundwaters and from the deeper Pleistocene waters. The E_4/E_6 qoutient of the thermal waters of lower temperature does not differ significantly from the other water types, these waters are transitional ones between the Pleistocene and Pannonian waters.

According to CHEN *et al.* (1977) the ratio E_4/E_6 depends on the molecular weight, thus it is related to the pH-value affecting the molecular weight, to the carbon and oxygen contents depending on the molecular weight and to the carboxyl groups, as well. Smaller E_4/E_6 values refer to greater molecular weight and to higher carbon and lower carboxyl group contents. KONONOVA (CHEN *et al.*, 1977) suggested that the smaller E_4/E_6 ratios refer rather to the aromatic, the greater ones rather to the aliphatic structures. Taking into consideration this suggestion it can be stated that humic acid in the Pannonian thermal waters is rather aromatic, it has a greater molecular weight, and it contains less carboxyl groups ($E_4/E_6 = 2.77$) related to the shallow groundwaters and deeper Pleistocene waters ($E_4/E_6 = 4.44$; 4.30).

In one part of the studied region, i. e. in the Danube — Tisza interfluve, in the territory east of the river Tisza, but close to it, the humic acid concentration is low in the deeper Pleistocene waters, and due to the small absorbance values the E_4/E_6 ratio cannot be determined. In the other areas, however, this value can be fairly well measured. The extremely high Cl^- ion concentration as compared to the environment has been attributed to the waters migrating upward along fault lines. The Cl^- ion concentration is lower than 10 mg/l in water samples almost from the whole area, but it is about 30 mg/l in some samples *(Fig. 1)*. The E_4/E_6 ratios of these two types of water were compared. In the areas where the Cl^- ion concentration is extremely

TABLE 1

The E_4/E_6 quotient in waters of different types

Type of water	Number of samples	E_4/E_6 average	Variance
Shallow groundwater	25	4.44	7.21
Deeper Pleistocene water	37	4.50	1.00
Thermal water of lower temperature	54	4.06	1.30
Thermal water of higher temperature	11	2.77	2.16
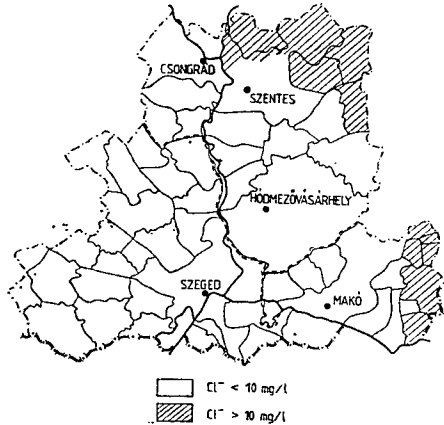
Fig. 1. Regional distribution of Cl^- concentration in drinking waters in the area studied

high as compared to the environment, the average of the E_4/E_6 ratio is 3.9 while in the areas characterized by lower Cl^- ion concentration this value is 4.7. Taking into account the different element number of the groups and the different deviation, based on the t-test the E_4/E_6 ratios show significant differences on a confidence level of 5%.

In Table 2 the waters of more or less Cl^- ion content are compared with the thermal waters based on the E_4/E_6 ratio. The t-test proves that at $P=5\%$ confidence level the average value of the E_4/E_6 ratio of the Pleistocene waters of low Cl^- ion concentration considerably differs both from the waters of greater Cl^- ion concentration and of thermal waters, too. Nevertheless, waters of greater Cl^- ion concentration do not show any considerable differences as compared to the thermal waters.

All these suggest that in the waters of high Cl^- ion concentration the humic acid structure becomes similar to that of the thermal waters and this is a new evidence to the upward migration of abyssal waters along fault lines.

TABLE 2

The E_4/E_6 quotient in the deeper Pleistocene waters of more or less Cl^- ions and in thermal waters

Type of water	Number of samples	Cl^- (mg/l) average	E_4/E_6 average	Variance
Deeper Pleistocene water of less Cl^-	20	6	4.90	1.23
Deeper Pleistocene water of more Cl^-	17	26	3.90	0.22
Thermal water	16	41	3.20	2.03

The H/C atomic ratio was determined from isolated humic acids, the data are listed in Table 3.

The H/C atomic ratios in humic acids isolated from waters of different types

Locality	Type of water	Depth of well (m)	H/C atomic ratio
Apátfalva	shallow groundwater	20	1.90
Nagyér		20	1.85
Nagymágocs	deeper Pleistocene water, <10 mg/l Cl^-	207	1.91
		358	1.79
Apátfalva		386	1.63
Ambrózfalva	deeper Pleistocene water, >10 mg/l Cl^-	189	1.59
Eperjes		386	1.75
Nagyér		498	1.70
Ásotthalom	thermal water, 35—45 °C	415	1.69
Eperjes		580	1.60
Apátfalva	thermal water, >70 °C	1700	1.55
Hódmezővásárhely		1735	1.58

The H/C atomic ratio shows smaller values in the organic matter with more aromatic compounds. TISSOT and WELTE (1978) showed that the H/C ratio is 1.3—1.5 in the organic matter of terrestrial origin and 1.7—1.9 in that of marine origin. According to the present investigations the C/H ratios in the humic acid changes between 1.55 and 1.91. The value is highest in the humic acids isolated from groundwaters (Table 3). This fact corresponds fairly well to that obtained on the basis of E_4/E_6 ratios, i. e. in the thermal waters more aromatic humic acids are found than in shallow groundwaters. The upward migration of the waters supposed by hydrogeological methods can be proved by the E_4/E_6 ratio and the H/C atomic ratio of the humic acid dissolved in deeper Pleistocene water which is similar to that of the thermal waters.

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