

HUMIC ACIDS IN SUBSURFACE WATERS FROM THE SOUTHERN GREAT PLAIN, HUNGARY

I. VARSÁNYI*

ABSTRACT

Subsurface water samples from different depths were analysed in the Southern part of the Great Hungarian Plain. Permanganate oxidizability and concentration of humic acid were measured. These data showed that there are humic and non-humic organic material in subsurface waters of different ages. The proportion of this organic materials is characteristic on the age of the waters. On the basis of this proportion can be concluded the reaction of organic materials taking place in waters after burial.

INTRODUCTION

The aim of our investigation is to draw conclusions on the diagenetic changes affecting the organic material in shallow subsurface and deeper Pleistocene and thermal waters. For this purpose the KMnO_4 consumption i.e. the permanganate oxidizability of waters and the quantity of total humic acid were determined in waters of different types.

MATERIALS AND METHODS

66 shallow (5—30 m), 82 deeper (75—604 m) subsurface waters and 19 thermal water samples (504—1945 m) were analysed. These waters come from the wells of the Southern part of the Great Hungarian Plain.

Estimating permanganate oxidizability analysis were made in the presence of sulfuric acid. The determination of total humic acid was carried out by CHALUPA'S (1963) method; after adding into the water sample sulfuric acid and n-amylalcohol, the mixture was shaken and separated, and than the amylalcohol phase reextracted by dilute NaOH solution. The alkaline extract was measured colorimetrically at 420 nm wavelength. Calibration curve was used to calculate the results.

The data were evaluated by mathematical methods of statistics. Regression analysis was made. The regression constant and coefficient and the correlation coefficient were calculated between O_2 consumption and humic acid content in different types of waters.

RESULTS

The waters are characterised by the permanganate oxidizability (O_2 consumption) and the concentration of total humic acid (THA) of waters and by the O_2

consumption of 1 mg of the THA $\left(\frac{\text{O}_2 \text{ cons}}{\text{THA}} \right)$.

* H-6726 Szeged, Csíz u, 7/6, Hungary

The average of these results for different types of waters are summarized in Table 1. Because of the great number of the data only the average values are listed in the Table 1 but each result is used for making Fig. 1. The thermal water was divided into two groups: the first group is the thermal water with lower (35—45 °C) temperature and the second one is with higher (>70 °C) temperature. These two types seem to differ from each other on the basis of their chemical character. The thermal water with lower temperature comes from Upper Pliocene and Upper Pannonian strata, the water samples of the other group come from Pannonian strata.

Relation between O₂ consumption and the concentration of humic substances can be seen on Fig. 1. The regression constants and coefficients and the correlation coefficients were computed for all the curves (Table 2). On the basis of Fig. 1. and Table 2 it can be concluded that the closest connection between O₂ consumption and the concentration of THA is in deeper Pleistocene and in 35—45 °C thermal waters (r: 0.93, 0.95). In shallow subsurface waters and in >70 °C thermal waters

TABLE I

O₂ consumption, humic acid concentration and O₂ consumption of 1 mg of the humic acid in different types of waters

Type	Number of the samples	O ₂ cons. mg/l	THA mg/l	Number of the samples*	O ₂ cons* mg/l
Groundwater	66	10.2	5.2	25	2.54
Deeper Pleistocene water	79	4.2	4.6	33	0.77
35—45 °C thermal water	6	8.3	9.7	5	0.95
>70 °C thermal water	13	17.2	6.5	11	3.30

* Number of the samples contains the samples with >2 mg/l humic acid concentration

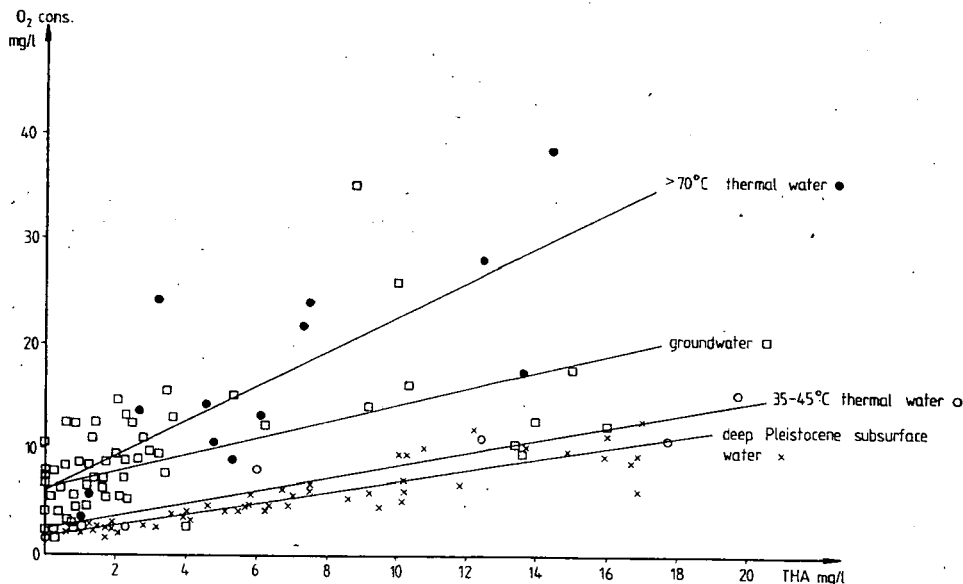


Fig. 1. Relation between O₂ consumption and concentration of humic acid

TABLE 2

The regression constants (*b*) and coefficients (*m*) and the correlation coefficients (*r*) between O₂ consumption and THA in different types of waters

Type	Number of the samples	<i>b</i>	<i>m</i>	<i>r</i>
Groundwater	66	6.57	0.77	0.87
Deeper Pleistocene water	79	1.78	0.52	0.93
35—45 °C thermal water	6	2.23	0.62	0.95
>70 °C thermal water	13	6.67	1.60	0.75

the correlation is not so close but it is strong enough to suppose the connection (*r*: 0.87, 0.75).

The O₂ consumptions extrapolated to 0 mg/l THA content (*b*) are higher values for shallow subsurface and >70 °C thermal waters (6.57, 6.67 mg/l) than for the deeper Pleistocene and 35—45 °C thermal waters (1.78, 2.23 mg/l).

The three curves are parallel and two of them — the curves of the deeper Pleistocene and 35—45 °C thermal waters — run very close to each other. The slope of >70 °C thermal waters is greater than that of the other ones. These results are reflected by the regression coefficients too.

DISCUSSION

According to our results we supposed that a larger quantity of oxidizable organic material other than humic acid may be present in shallow subsurface — and thermal waters. This assumption is on the basis of *b*: 6.57, 6.67 values which means the O₂ consumption when the concentration of humic acid is 0 mg/l.

Because of their different slope (*m*; 0.77, 1.60) we concluded that the quantity of non-humic organic materials is proportional to the quantity of humic substances in the >70 °C thermal waters having a higher (*m*; 1.60) regression coefficient, but in shallow subsurface waters it is independent of the quantity of humic acid and approximately constant.

The O₂ consumption/THA ratios were regarded as a function of the concentration of humic acid on the Fig. 2, Fig. 3 and Fig. 4. The O₂ consumption/THA curve of shallow and deeper groundwater (Fig. 2, Fig. 3) is exponential, i.e. the ratio is decreasing with increasing THA concentration. The curve of thermal waters (Fig. 4) is not exponential. The O₂ consumption — neglecting the O₂ consumption of inorganic ions — consists of two parts: one belongs to the humic acid (O₂ cons₁), the other to the non-humic acid (O₂ cons₂). So:

$$\frac{O_2 \text{ cons}}{THA} = \frac{O_2 \text{ cons}_1}{THA} + \frac{O_2 \text{ cons}_2}{THA}$$

It can be supposed that in the waters of the same age, the precursors of organic material, the circumstances of sedimentation and the diagenetic alteration before and after burial are similar, so the oxidizability of humic acid is similar in the waters derived from the strata of the same age. In this case the O₂ cons₁/THA ratio is independent of the concentration of humic acid. It is constant (*k*₁) and corresponds to the O₂ consumption of 1 mg of humic acid.

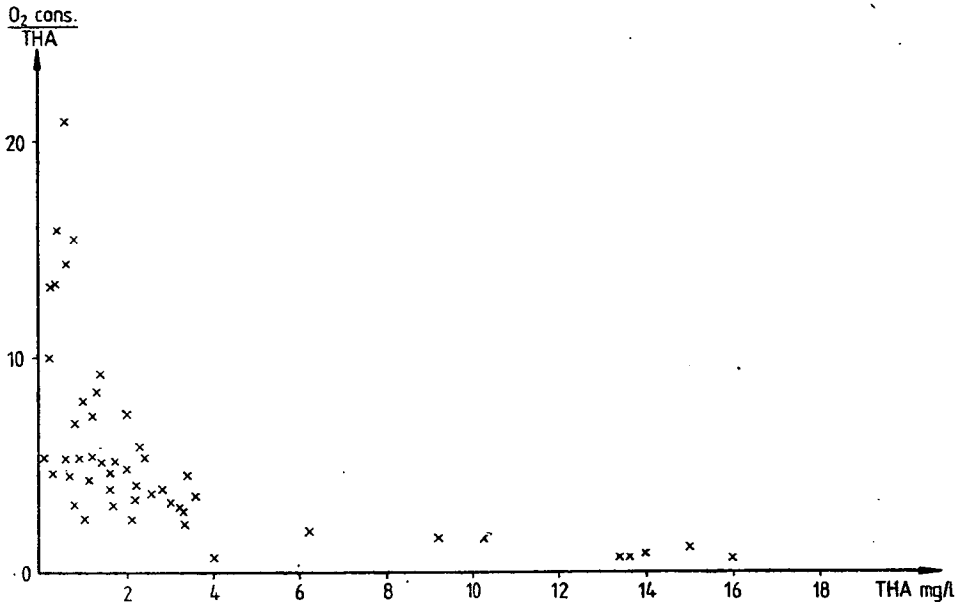


Fig. 2. Relation between O_2 cons./THA ratios and the concentration of humic acid in shallow subsurface waters

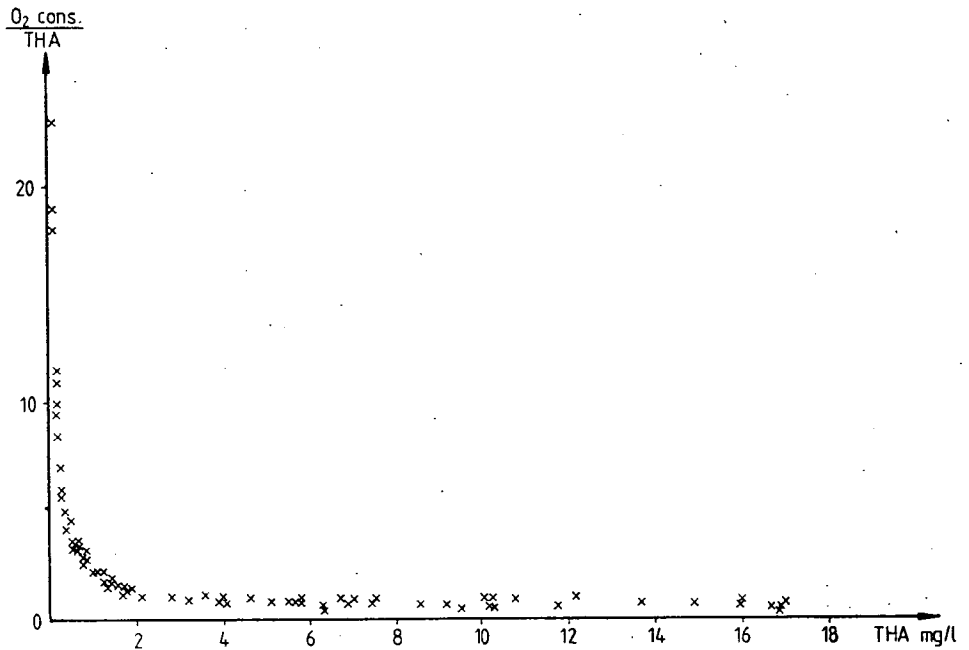


Fig. 3. Relation between O_2 cons./THA ratios and the concentrations of humic acid in deeper Pleistocene subsurface waters

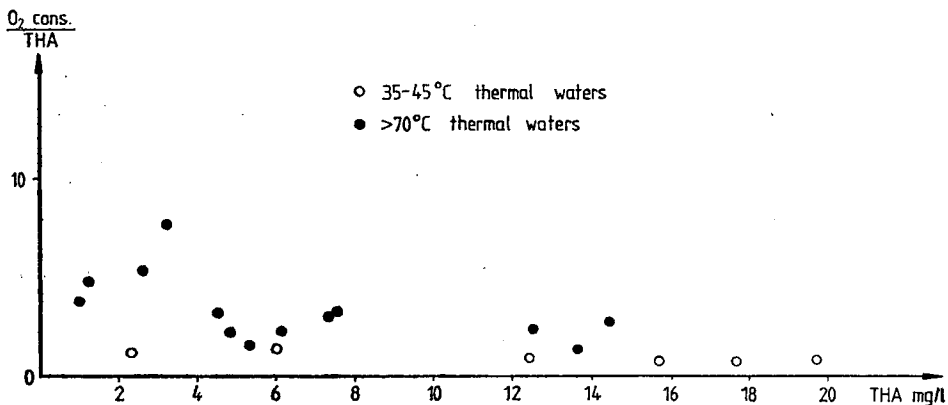


Fig. 4. Relation between O₂ cons./THA ratios and the concentration of humic acid in thermal waters

$$\frac{O_2 \text{ cons}}{THA} = k_1 + \frac{O_2 \text{ cons}_2}{THA}$$

Interpreting this equation two cases have to be taken into consideration. One is when the quantity of non-humic oxidizable organic materials are constant, the other is when the quantity of them depends on the concentration of humic acid. In this latter case the precursor of the non-humic oxidizable organic materials may be humic acid or its condensation derivatives.

When the quantity of non humic oxidizable organic materials is constant, the O₂ cons₂ is constant too independently of the humic acid concentration, so the O₂ cons₂/THA ratio decreases with increasing THA concentration. The O₂ cons/THA ratio converges to k₁ constant when THA concentration is high enough to neglect O₂ cons₂/THA ratio. The connection is exponential between the O₂ cons/THA and humic acid concentration. This is in shallow and deep subsurface Pleistocene waters (Fig. 2, Fig. 3) in which the quantity of non-humic oxidizable organic materials is constant independently of the humic acid concentration. In these cases the regression constant (b) between O₂ consumption and humic acid concentration gives the O₂ consumption of the non-humic organic materials. These are 6.57 mg/l and 1.78 mg/l for shallow groundwaters and deep Pleistocene subsurface waters, respectively. On the basis of these data there is a larger quantity of the non-humic oxidizable organic materials related to the total oxidizable organic materials in shallow groundwater than in the deeper Pleistocene waters.

When the quantity of the non-humic organic materials depends on the humic acid concentration:

$$O_2 \text{ cons}_2 = k_2 \cdot \text{humic acid concentration}$$

with the k₂ proportion factor. Its values depend on the proportion of the humic and non-humic organic materials. In this case

$$\frac{O_2 \text{ cons}}{THA} = k_1 + k_2$$

According to this equation the O_2 cons/THA ratio independent of the humic acid concentration and it is a constant value. The regression coefficient of the connection between O_2 cons and humic acid concentration gives the k_1 and the regression constant gives the k_2 values. On the Fig. 4 it can be seen that there is not exponential connection between O_2 cons/THA ratio and humic acid concentration, though the scattering of the O_2 cons/THA ratio is higher at lower humic acid concentrations.

On the basis of the data it has been assumed that because of the elevated pressure and first of all elevated temperature the degradation of humic acid and of its condensation derivatives starts in the Pannonian thermal waters. During this degradation water-soluble oxidizable non-humic organic materials are formed. Their quantity is proportional to the concentration of humic acid from which they formed.

CONCLUSIONS

Evaluating the $KMnO_4$ *i.e.* O_2 consumption of waters and their humic acid content it can be concluded as follows:

- In waters of different age and depth there are humic and non-humic organic materials.
- The proportion of humic and non-humic organic materials differs in the waters of different types.
- On the basis of the connection between O_2 consumption and humic acid concentration the shallow and deep Pleistocene subsurface waters and the thermal waters can be distinguished. In the ground waters large quantity of non-humic oxidizable organic material is related to the total organic material. In the deep Pleistocene subsurface waters humic acid predominates, and in the thermal waters the proportion of non-humic organic materials is increased again. The thermal waters with lower temperature (35—45 °C) are between Pleistocene and Pannonian thermal waters.
- In the thermal waters the degradation of humic acid takes place and non-humic organic materials are formed.

REFERENCE

CHALUPA, J. (1963): Humic acids in water I. Methods of preparation and determination. Scientific Papers from Institute of Chemical Technology, Prague 1963. 18—47.

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