ORIGINAL ARTICLE

The study of the elemental composition of humic acids of sapropels of lakes of the upper and Middle Priobye of West Siberia

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Abstract

Background and Objective: For the first time, the elemental composition of humic acids (HA) of sapropel of lakes of the Middle Priobye and the southern Ob-Irtysh basin of West Siberia, formed in different hydrothermal and environmental conditions. Specific features of their elemental composition that are evident in the content of elements, the atomic relations, and the degree of oxidation, indicating the ratio of aromatic and aliphatic parts, and the conditions in which the process of humification carries have been identified. HA of sapropels of the Novosibirsk region is almost two times higher than nitrogen content of HA of sapropels of Khanty-Mansiysk Autonomous Okrug. **Materials and Methods:** It is established that HA of sapropels of the southern part of West Siberia have the relations H/C vary from 0.83 to 1.19, and in the Middle Priobye vary from of 0.87 to 1.24, that argues for the less degree of aromaticity (or "benzoidnost" in Russian) (α), the "maturity" of macromolecules in the taiga region. **Results:** The found values of the degree of oxidation ω indicate that HA of sapropels have restored form and a negative value of ω with the exception of HA of sapropels of some lakes of the Middle Priobye, where there are also the oxidized forms and the positive values of ω. The results can be used for large-scale evaluation of sapropel fields, serve as a source of information for producing humic preparations. Research is needed to develop technology of production of new products for agriculture, medicine, and technology. Principles of analysis of HA can be used by students, young professionals, teachers, and researchers in scientific research institutes, universities. **Conclusion:** Thus, we can assume based on the study of the elemental composition of HA of sapropels of lakes of the Middle Priobye and south of the Ob-Irtysh basin of West Siberia, that their composition and properties are caused to some extent not only by hydrothermal conditions and typology of lakes but also the type of anthropogenic load, the influence of oil production in the northern region.

Key words: Elemental composition, humic acids of sapropels, sapropel, the Middle and South Priobye, West Siberia

INTRODUCTION

Humification of dead plants, animals, organisms, and their metabolites is a global natural process on a planetary scale. The humic substances are included in the composition of organic matter in soils, peat, fossil coal, some shale, and sapropel. They are formed in the result of complex biochemical transformations of organic matter and are a factor in its "conservation", protecting from the total mineralization to some extent.

Lakes of the southern Ob-Irtysh basin differ by peculiar chemical composition of the lake water due to heavy accumulation of salts, especially of sodium, which provide greater rigidity of the water. Cladocera (cladocerans)[1] is dominated by biomass in zooplankton. These processes are less marked in the Middle Priobye, there are significantly less chlorides, sulfates, bicarbonates of calcium, and magnesium and soft water, Copepoda is dominated in zooplankton. Aquatic vegetation includes the same hard and soft plants, but composed of much more wetland vegetation.[2]

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Chemical composition of humic acids (HA) characterizes the specificity of formation of organic matter of regions, reflecting the features of the original plant material, and the conditions in which the process carries.[3,4]

Despite the fact that the practical importance of these studies has not fully used by geochemists and agronomists, the prospect of such works of the majority of experts is not in doubt.

MATERIALS AND METHODS

The samples were collected in the lakes of the Barabinsk and Kuibyshev districts in Novosibirsk oblast and on the territory of Konda district in Khanty-Mansiysk Autonomous Okrug. Sampling was carried out with the most biologically active surface layers of bottom sediments (0-20 cm) with sampler in triplicates diagonally across the lake.

Extraction of HA was carried out according to previously described methods.[5] Determination of carbon, hydrogen, nitrogen, and ash content was determined by elemental analyzer EuroVectormod. EA3000 in NIOCH SB RAS (Novosibirsk). The oxygen content was calculated by difference.

RESULTS

The results of the elemental analysis allow characterizing some features of humic substances of different sapropels and giving some information about the principles of their structure [Table 1].

Low values of ash content are not characteristic of sapropel obtained due to the fact that their processing by hydrohalic acids HCl and HF in a water bath, which contributes to obtaining a low-ash drugs was held at the last stage of isolation of HA.

It is seen that HA of sapropel in Novosibirsk oblast, contain significantly more nitrogen. The estimation of oxygen content in HA of different sapropels is hampered, it was determined in elemental analysis by difference and is essentially determined by sum O+S as in accordance with the applicable practice.

It is more convenient to use not percentage composition of HA specified in the analysis but atomic ratio of elements constituting a simple formula and applying the principles of graphostatics analysis for more informative results.

Atomic ratio H/C, O/C, N/C, as you know, show the number of atoms of hydrogen, oxygen, and nitrogen, which falls in the molecule (particle) of humic substances at one atom of carbon. The smaller this relationship, the greater role is played by the carbon atoms in the construction of molecular structures. Increasing of atomic relations, points to an increase in the proportion of aliphatic fragments and the decrease in the proportion of aromatics in the molecules of humic substances. The relative branching of the side chains, the role of nitrogen-containing compounds in the formation of humic substances was judged by the ratio in each of the pairs.

Not N/C relations but C/N [Table 1][6] calculated for comparison of organic matter of autochthonous and allochthonous origin. It was revealed that autochthonous processes where C/N varies from 13 to 15 dominate in HA of sapropel in Novosibirsk oblast, unlike to HA of the lakes of Khanty-Mansiysk OA, for which the interval of these relations is in very wide range, from 16 to 57, indicating predominance of allochthonous processes, perhaps due to the influence of oil-producing operations. The composition of HA is largely caused by the type of anthropogenic load.[7]

It is useful to use the indicator "degree of aromaticity" (α)[6] for conditional evaluation of aromatic and aliphatic components.

$A = C_{benz.}/(C_{benz.} + C_{aliph.})$, or $\alpha = C_{benz.}/C_{com.} \cdot 100\%$

Where,

$C_{aliph.}$ - Content of aliphatic fragments in the carbon,
$C_{benz.}$ - Content of aromatic fragments in HA in the carbon,
$C_{com.} = C_{aliph.} + C_{benz}$

When it was accepted that the H:C of aromatic part ($H:C_{arom.}$) equals to 0.33, and K – coefficient of the oxygen function is equal to 0.67.[8] The degree of aromaticity of the studied HA (α) varies from 27 to 39%.

$(H:C)_{aliph.} = (H:C)_{ha} + 2(O:C)_{ha} \cdot K\text{-}(H:C)_{arom.}$

$C_{aliph.} = (H:C)_{aliph}/((H:C)_{aliph.} + (H:C)_{arom.})$

It should be noted that a useful criterion for identifying the specificity of humification under different conditions is the degree of oxidation,[9] characterizing the conditions, and the character of sedimentation. According to these data, HA of sapropels have mainly the reduced form and a negative value of ω, except two samples of sapropels in Khanty-Mansi Autonomous Okrug -Yugra, which have the oxidized form and a positive quantity ω [Table 1].

It is possible to calculate a simple formula which, although they are conditional because of the complex fractional composition of the analyzed samples, still useful in studying the trends in the distribution of individual atoms in functional groups [Table 2][9] for the visual evaluation of the composition of HA. The simplest formulas show only the minimum number of atoms included in a molecule of a substance. It is incorrect to put them across the different meaning, or attempt

Table 1: The data of the elemental composition of HA of sapropels

Lakes names	Elemental composition in %				Ash, %	Atomic ratio			$C_{aliph.}$	α, %	Elemental composition in atom %				ω
	C	H	N	O		H/C	O/C	C/N			C	H	N	O	
Khanty-Mansiysk AO															
Medvezhye	59.09	5.47	1.20	34.24	1.10	1.10	0.43	57	0.67	33	39	43	1	17	−0.23
Satyginskiy Tuman	49.45	5.16	2.93	42.46	13.93	1.24	0.64	20	0.73	27	34	42	2	22	+0.06
Srednesatyginskiy T. Туман	55.98	4.51	1.63	37.88	1.18	0.96	0.51	40	0.67	33	40	39	1	20	+0.03
Pyakuto	58.83	4.58	2.40	34.19	3.24	0.93	0.44	29	0.64	36	42	39	1	18	−0.07
Shuchye	58.51	4.29	3.15	34.05	0.00	0.87	0.44	22	0.63	37	42	37	2	19	+0.02
Tursuntckiy Tuman	56.55	5.09	4.21	34.15	2.24	1.07	0.45	16	0.67	33	39	41	2	17	−0.18
Kogalymlor	58.32	5.06	2.08	34.54	2.11	1.03	0.44	33	0.66	34	40	41	1	18	−0.13
Bol. Shuchye	54.82	5.00	3.39	36.79	11.76	1.09	0.50	19	0.68	32	38	41	2	19	−0.08
Novosibirsk oblast															
Russian	55.00	4.96	4.90	35.14	3.29	1.07	0.48	13	0.68	32	38	41	3	18	−0.13
Siberian	58.35	4.35	3.94	33.36	2.35	0.89	0.43	13	0.63	37	42	37	2	18	−0.02
Zarechnoe	54.91	5.13	4.47	35.49	0.91	1.11	0.49	14	0.69	31	37	42	3	18	−0.16
Bol. Kayly	59.51	4.16	5.22	31.11	1.77	0.83	0.39	13	0.61	39	44	36	3	17	−0.05
Peschanoe	55.11	5.52	4.36	35.01	1.78	1.19	0.48	15	0.70	30	37	44	3	17	−0.27

α: Degree of aromaticity (or "benzoidnost" in Russian), ω: Degree of oxidation, HA: Humic acids

Table 2: Atomic fractions and empiric formulas of HA of sapropels

Lakes names	C	H	N	O	Empiric formulas
Khanty-Mansiysk AO					
Medvezhye	4.92	5.42	0.09	2.14	$C_{164}H_{181}N_3O_{71}$
Satyginskiy Tuman	4.12	5.11	0.21	2.65	$C_{59}H_{73}N_3O_{38}$
Srednesatyginskiy T	4.66	4.47	0.12	2.37	$C_{116}H_{112}N_3O_{59}$
Pyakuto	4.90	4.53	0.17	2.14	$C_{86}H_{80}N_3O_{38}$
Shuchye	4.87	4.25	0.22	2.13	$C_{66}H_{58}N_3O_{29}$
Tursuntckiy Tuman	4.71	5.04	0.30	2.13	$C_{47}H_{50}N_3O_{21}$
Kogalymlor	4.86	5.01	0.15	2.16	$C_{97}H_{100}N_3O_{43}$
Bol. Shuchye	4.56	4.95	0.24	2.30	$C_{57}H_{62}N_3O_{29}$
Novosibirsk oblast					
Russian	4.58	4.90	0.35	2.20	$C_{39}H_{42}N_3O_{19}$
Siberian	4.86	4.31	0.28	2.09	$C_{52}H_{46}N_3O_{22}$
Zarechnoe	4.57	5.08	0.32	2.22	$C_{43}H_{48}N_3O_{21}$
Bol. Kayly	4.96	4.12	0.37	1.94	$C_{40}H_{33}N_3O_{16}$
Peschanoe	4.59	5.47	0.31	2.19	$C_{44}H_{53}N_3O_{21}$

HA: Humic acids

to calculate the molecular weight of humic substances on the basis of the formula. This requires to heft molecular weight absolutely.

An important figure according to Van-Krevelen is an atomic relation H/C, which clearly characterizes the class of hydrocarbons. This relation is usually ≈1.0 for HA, which formally indicates the predominance of aromatic structures.[9]

Evaluation of atomic relations allows solving some of the issues of the mechanisms of transformation of plant residues, and certain groups of humic substances. The chart of atomic

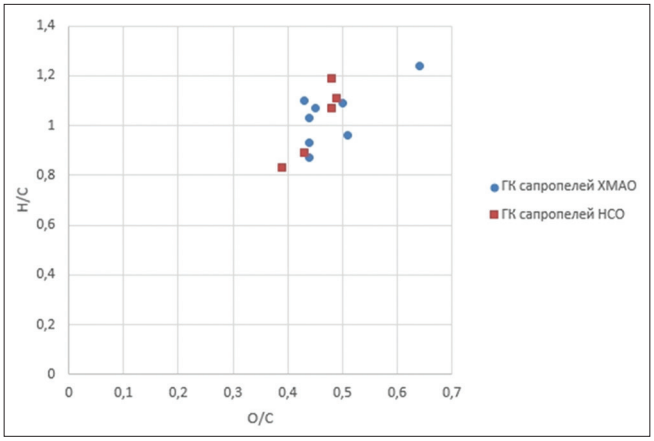

Figure 1: Humic acids of sapropels of Khanty-Mansi Autonomous Okrug-Yugra and November OBL

relations H/C-O/C [Figure 1] is convenient to use for this purpose, it presents the results of the analysis of the elemental composition of HA of the studied sapropels.

HA with atomic relations H/C > 1 are dominated on both schemes. These include three samples of five sapropels of the Novosibirsk oblast and four samples of the seven in Khanty-Mansiysk Autonomous Okrug.

Accurate interpretation of the HA composition through graphostatics analysis is complicated by the fact that there is no complete information about the oxygen function in the molecule and the number of carbon atoms per molecule.

Deductions

Elemental composition of HA of sapropels of the Novosibirsk oblast and Khanty-Mansiysk Autonomous Okrug corresponds to the conditions of sedimentation and depends on the typology of the source lakes formed in different climatic conditions.

Relations H/C vary from 0.83 to 1.24 for the studied HA. The lowest "maturity" has HA of the Middle Priobye (0.87-1.24), and the highest – the Upper Priobye (0.83-1.19) significantly more nitrogen is contained in HA of lakes of Novosibirsk oblast (3.94-5.22%), compared to the northern region (1.20-4.21%), which indicates the predominance of autochthonous processes.

CONCLUSION

Thus, we can assume based on the study of the elemental composition of HA of sapropels of lakes of the Middle Priobye and south of the Ob-Irtysh basin of West Siberia, that their composition and properties are caused to some extent not only by hydrothermal conditions and typology of lakes but the type of anthropogenic load, the influence of oil production in the northern region.

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