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THE INPUT OF ORGANIC MATTER TO THE BALTIC FROM THE VISTULA RIVER

1. INTRODUCTION

Despite considerable efforts we still did not succeed in determining the importance of organic substances present in sea water for processes occuring in it. So far, experiments conducted have enabled us to determine only the amounth of organic substances in sea water [32]. This situation is also true for the Baltic Sea. The papers published on the subject dealt with the determination of concentration of organic carbon in sea water [5, 6, 30] and its dynamics [6, 15, 23]. Only a few papers dealt with the quality of organic compounds present in sea water [5, 14, 27]. The results obtained so far indicate that a considerable fraction of organic matter present in sea water consists of humus-type substances [32]. Humic substances present in ocean water are mainly of authigenic origin. Humic substances of land origin present in land-locked seas with large inflows of rever water can constitute a considerable part of organic matter in these reservoirs [20].

The presence of humic substances of land origin in sea water is limited to a large extent by flocculation processes occurring in the water-mixing zone, followed by sedimentation of the suspension formed [10, 11, 28]. This process brings about the change of concentration of yellow substances in the water of the Baltic Sea, of various salinity [5] and decrease of content of high molecular weight compounds (probably of humus-type) with increase of salinity in this water [4].

Investigations of humic substances isolated from sea water and bottom sediments indicate that they are effective complexing agents of di- and trivalent metals. Moreover, these substances have a considerable effect on optical properties of sea water and play an important role in the processes of sediment diagenesis.

The content of organic compounds of land origin in sea water can be determined by an investigation of their isotopic composition. An alternative procedure is to use a method of balancing the inflow and outflow of these compounds.

The purpose of the present paper was to determine the concentration of organic compounds, including humic substances, in water from the Vistula, and to determine selected physico-chemical properties of humic substances isolated from the water. These data can be used for the determination of inflow of organic compounds into the Baltic Sea and for comparison of physico-chemical properties of these substances with the properties of humic substances found in the Baltic Sea.

2. EXPERIMENTAL

The flows of the Vistula given in this paper refer to the Tczew profile. The reception area rise below Tczew is small and it can be assumed that the data presented here determine the amount of water flowing into Gdańsk Bay. Samples of the Vistula water (ca 10 dm^3) were collected weekly during the period January 10, 1977 — January 15, 1978 in Kiezmark, about 15 km from the estuary of the Vistula into Gdańsk Bay. Samples of water (100 dm^3) were also collected from the same spot in April, July and November 1977 and in January 1978.

The content of suspended matter in collected water samples was determined by filtration through a glass-frit filter GF/F — Whatman. Organic carbon content (C_{org}) in suspended matter was determined by means of a wet oxidation method [1]. Organic carbon content in filtered water samples was determined by wet oxidation employing potassium persulfate [17, 21]. Suspended matter collected on glass-frit filters was repeatedly extracted with 0.5 $\underline{M}$ NaOH. The alkaline extract containing humic substances (HS) was subsequently separated into portions containing fulvic acids (FA) and humic acids (HA) after acidifying it to pH 2 [2]. FA and HA content was determined spectrophotometrically, measuring absorption at 270 nm. Humic substances in filtered Vistula water (ca 6 dm^3 of water acidified to pH 2) were absorbed on a column packed with Amberlite XAD 2, followed by elution with a small volume (ca 25 cm^3) of 1 $\underline{M}$ ammonium hydroxide. The content of humic substances was determined spectrophotometrically at 270 nm. The effectiveness of adsorption with respect to FA constituting the main component of humic substances is about 95$^{0}/_{0}$, whereas the effectiveness of desorption is approximately 80$^{0}/_{0}$ [26, 31]. Application of the methods described above permitted the isolation from large water samples of humic substances (suspended and dissolved) in quantities sufficient for their elemental analysis (C, H, N) as well as for obtaining their ir (KBr pellet was used for reference), uv and visible absorption spectra.

3. RESULTS

Average weekly flows in the Vistula in 1977 are shown in fig. 1 and table 1. Average yearly flow in 1977 and in the period 1971—76 is also pictured in fig. 1. The content of suspended matter in collected water samples is illustrated in fig. 2. Fig. 2. also shows the content of organic carbon in suspended matter and percentage of organic carbon in suspended matter.

Table 1
Tabela 1

Average weekly flows of the Vistula and the mass of suspended and dissolved humic substances carried off weekly to the Bay of Gdańsk

Średnie tygodniowe przepływy rzeki Wisły oraz masa węgla organicznego i substancji humusowych wnoszona do Zatoki Gdańskiej w ciągu tygodnia

No	Date Data	Average weekly flaws Średnie tygodniowe przepływy	Suspended matter Zawiesina			Water Woda	
			SM	C_{org}	HS	C_{org}	HS
			x 10^6 kg	x 10^6 kg	x 10^6 kg	x 10^6 kg	x 10^6 kg
		$m^3 s^{-1}$					
1	2	3	4	5	6	7	8
1	10.01	520	5977.4	1255.3	514.66		
2	17.01	720	9583.2	2108.3	1011.98		
3	24.01	830	10545.2	2109.0	927.98		
4	31.01	770	10714.5	1682.2	723.34		
5	7.02	1050	14610.8	2673.8	1176.46		
6	14.02	1270	20745.5	5082.6	2388.84		
7	21.02	1760	26620.0	3593.7	1509.36		
8	28.02	2010	52290.2	6850.0	3151.00		
9	7.03	3160	74560.2	15284.8	4738.28	11470.8	6882.5
10	14.03	3300	35937.0	2695.3	1385.38	8984.3	11499.8
11	21.03	2740	54704.1	6564.5	3544.82	11935.4	15277.4
12	28.03	1845	27905.6	4185.8	1758.06	6250.9	8676.2
13	4.04	1525	20297.8	4262.5	1380.06	4613.1	6273.9
14	11.04	1555	22578.6	4854.4	1893.22	4421.6	5040.7

c.d. tab. 1

1	2	3	4	5	6	7	8
15	18.04	1985	31224.0	5464.2	2732.10	7205.6	11096.5
16	24.04	1770	33196.4	5311.4	2496.36	10173.1	7324.6
17	2.05	1520	26668.4	4800.2	2400.12	5517.6	5848.7
18	9.05	1425	25001.6	4500.4	2037.16	7500.5	5250.3
19	16.05	1180	30697.7	3376.6	2296.18	5854.0	4683.2
20	23.05	1145	29094.5	5528.0	4321.74	6165.3	5178.8
21	30.05	1325	24048.8	4428.8	1891.24	8016.3	6653.5
22	6.06	1165	16211.0	2918.0	2042.58	5779.6	4623.7
23	13.06	1060	7054.3	1340.3	670.16	6348.9	4698.2
24	20.06	870	8421.6	1684.4	1044.32	5053.0	2930.7
25	27.06	835	18691.5	3551.3	1704.62	5152.8	3503.9
26	4.07	790	15772.4	3627.7	1958.94	3506.6	3296.2
27	11.07	745	13521.8	2974.8	1427.92	5994.6	6354.3
28	18.07	840	15754.2	2205.6	1190.60	5831.2	6218.5
29	25.07	840	15754.2	2520.6	1058.66	4726.3	4726.3
30	1.08	820	10914.2	2510.2	1807.36	4655.5	4748.6
31	8.08	810	11271.2	2254.2	1127.10	6272.9	6586.5
32	15.08	1165	11277.2	2368.2	1012.00	6542.2	6935.1
33	22.08	1215	24257.5	5094.0	2139.46	6321.6	6068.8
34	13.08	1865	37234.7	5585.3	2680.92	8913.8	9002.9
35	5.09	1945	40008.7	5801.2	2900.58	10472.9	11834.3
36	12.09	1190	16558.9	2732.2	1147.54	7343.5	6882.6
37	19.09	1005	12160.5	1702.4	561.80	6749.1	5534.2
38	26.09	985	14302.2	3003.5	1321.52	4111.9	4029.7
39	3.10	1230	20092.1	8036.8	3053.98	7739.2	3560.0
40	10.10	1155	6987.8	419.3	251.56	7337.2	6970.3
41	17.10	1005		1580.9	727.20	5715.4	5486.8
42	24.10	940	9099.2	3184.6	1464.94	4094.6	3849.0
43	31.10	850	3599.8	774.0	232.20	3882.6	4697.7
44	7.11	855	7759.1	1784.6	356.92	4448.6	4715.5
45	14.11	850	9556.5	2389.1	1053.22	4114.0	5142.5
46	21.11	1005	10944.5	1860.5	781.40	4013.0	4253.7
47	28.11	985	8938.9	2056.0	822.38	5303.7	4189.9
48	5.12	935	5656.8	1188.0	653.38	4344.7	3397.4
49	12.12	875	5293.8	1164.7	582.34	2541 0	3404.9
50	19.12	640	5033.6	1661.2	764.16	2090.9	2822.7
51	26.12	825	11979.0	3354.1	1341.64	3344.1	4213.6

The humic substances content in suspended matter, the fulvic acids content in this matter and percentage of fulvic acids in total amount of humic substances are shown in fig. 3. The humic acids content in suspended matter is equal to the difference between the total content of humic substances and that of fulvic acids. The same holds for the percentage of humic acids. Both these quantities can easily be found from plots shown in fig. 3.

The organic carbon content in the samples of water studied is shown

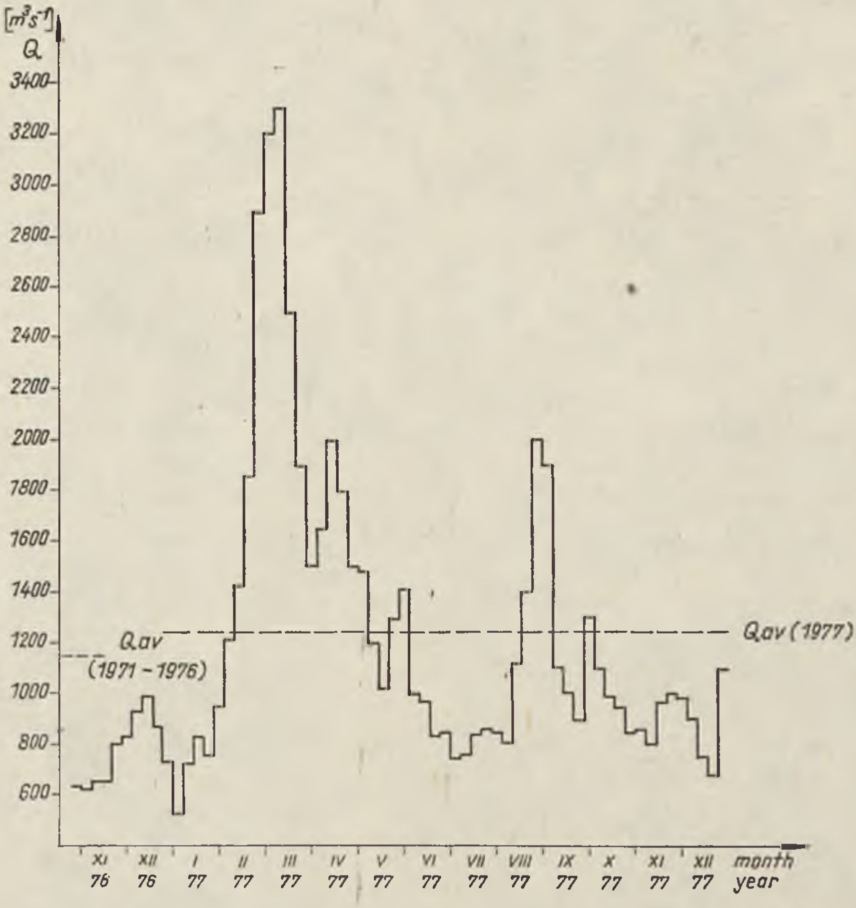


Fig. 1. Average weekly flows of the Vistula in 1977. Dotted line indicates the average flow for 1977 (Q_{av} 1977) and for 1971—76 (Q_{av} 71—76)

Ryc. 1. Średnie przepływy Wisły w 1977 roku

in fig. 4. The fulvic acids content, as well as humic acids content are also shown in fig. 4.

The percentage of humic acids in the total amount of organics contained in suspended matter and percentage of humic substances in the total amount of organics dissolved in water are illustrated in fig. 5. The data presented were calculated assuming that C_{org} constitutes 50% of the mass of organic matter.

Typical IR absorption sectra of humic substances isolated from water and those of humic acids and fulvic acids from suspended matter are shown in fig. 6. Typical UV and VIS absorption spectra of studied compounds in 0.05 M $NaHCO_3$ solution are given in Figs. 7 and 8, respectively. Table 1 contains the data characterizing the masses of suspended matter, C_{org} and HS in suspended matter, dissolved C_{org} and HS in the Vistula water outflown to Gdańsk Bay. The dates given in column 2 denote the days of collection of water samples. The average flows for the week preceeding the sampling are given in column 3. Table 2 contains the data concerning the average yearly concentrations of individually studied components and defining of their total masses outflown to Gdańsk Bay. The data determining the elements of balance of organic substances in the Baltic Sea are given in table 3. The data defining the elemental composition of humic substances isolated from large water samples are presented in fig. 4.

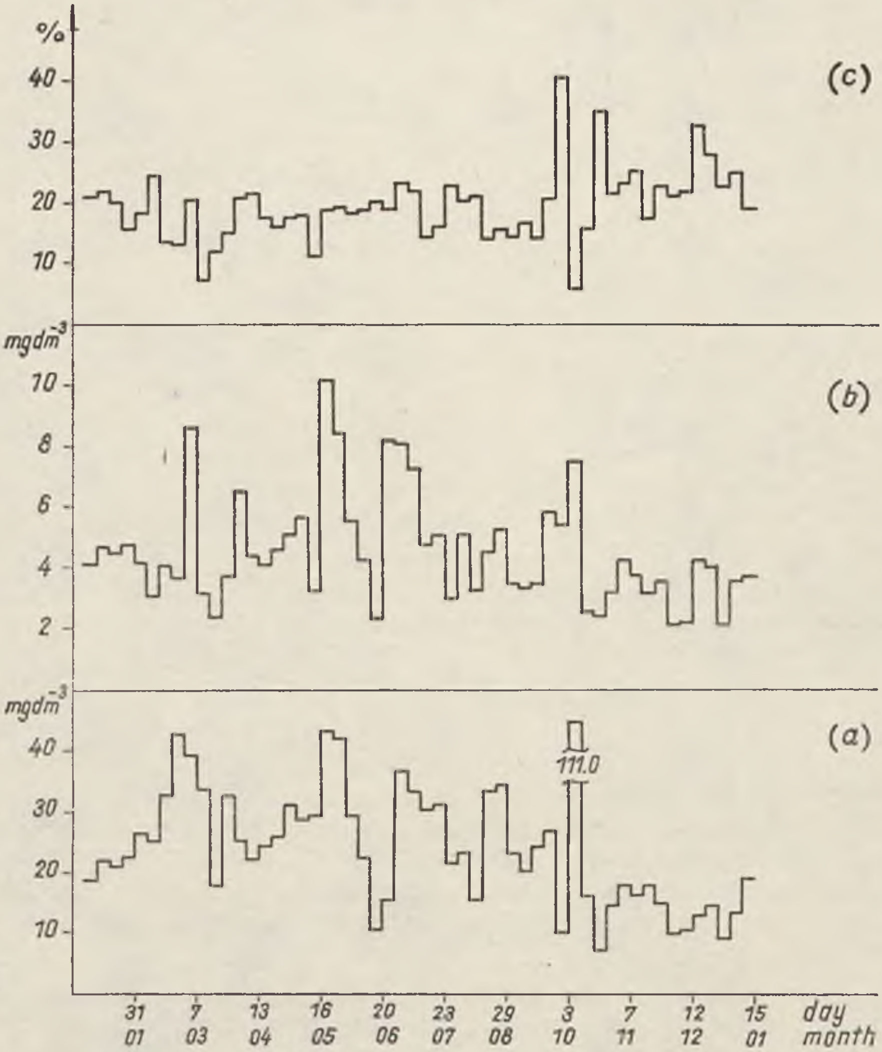


Fig. 2. Concentration of suspended matter in the Vistula water (a), organic carbon content in suspended matter (b), and percentage of organic carbon in suspended matter (c)

Ryc. 2. Stężenie zawiesin w wodzie Wisły (a), zawartość węgla organicznego w zawiesinie (b), procentowy udział węgla organicznego w zawiesinie (c)

4. DISCUSSIONS

Average weekly flows in 1977 reached the level of 800—1000 $m^3 s^{-1}$. At the end of February and in March a temporary increase of flow was observed due to the spring rise of water. A similar situation recurred at the turn of August and September.

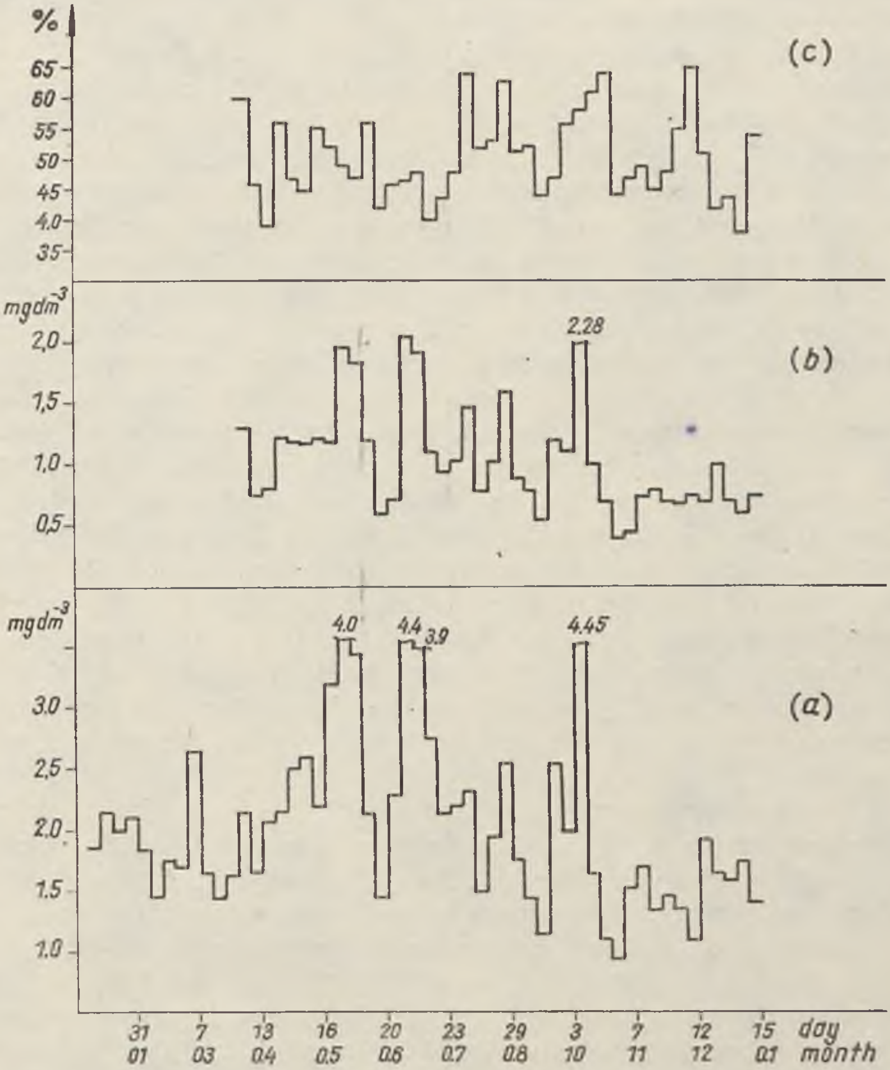


Fig. 3. Humic substances content in suspended matter (a), fulvic acids content in suspended matter (b), and percentage of fulvic acids in humic substances of suspended matter (c)

Ryc. 3. Zawartość substancji humusowych w zawiesinie (a), zawartość kwasów fulwinowych w zawiesinie (b), procentowy udział kwasów fulwinowych w substancjach humusowych (c)

The average concentrations of suspended matter (SM), particulate organic carbon (POC), and dissolved organic carbon (DOC) exhibited substantial variations. The concentration of suspended matter fluctuated from 7.4 mg dm^{-3} (October 24, 1977) to 43.2 mg dm^{-3} (May 23, 1977). The lowest monthly average of SM concentration was 16.0 mg dm^{-3} (June), and the highest one — 34.6 mg dm^{-3} (May) — fig. 2a.

No evidence was found of any correlation between the SM concentration and the average weekly flows.

The organic carbon content in the SM of the Vistula in 1977 demonstrated variation similar to the variation of SM concentration. The highest POC concentration, equal to 10.2 mg dm^{-3}, was observed on May 23, 1977, and the lowest, equal to 2.3 mg dm^{-3}, in December. The highest monthly average of POC concentration (6.6 mg dm^{-3}) was observed in May, and the lowest (3.2 mg dm^{-3}) — in December (fig. 2b).

The consequence of conformity between the concentration changes of SM and POC is the calculated stable percentage fraction of POC in SM, which is shown in fig. 2c. The average value of the percentage fraction of POC in SM is 20.4%. It should be remembered that the content of organics in suspended matter is about twice as high as the organic carbon content in the SM. In the literature available little data have been found concerning the organic carbon content in the SM of the rivers discharging into the Baltic Sea. Emelyanov [7] gives the value of 25—50% for the C_{org} in SM. Burton [11] gave the values of 10—100 mg dm^{-3} as the most typical concentrations of SM in river water, and 30% as the organic carbon content in this SM. Suspended matter inflown into the Baltic Sea with the river water undergoes relatively rapid sedimentation or, alternatively, is rapidly diluted in sea water. Emelyanov [7] observed considerable differences between the average composition of SM isolated from water of the Baltic Sea and river water.

The average percentage of humic substances in the organics of suspended matter is 24.1% which corresponds to 2.1 mg dm^{-3} of HS in the collected water samples. The HS content in supended matter varies considerably: the highest values were observed in May, July and October (4.0, 4.4, and 4.45 mg dm^{-3}, respectively), and the lowest — in January, August and November (1.45, 1.15, and 0.95 mg dm^{-3}, respectively), see fig. 3a. Characteristic of the Vistula suspended matter is strong correlation between the POC content and the HS content. This results in small variations in the percentage of humic in the substances in particulate organic matter (POM). The average percentage is equal to 24.1%, whereas the highest values, observed in May, June and July, were 34.0, 35.2 and 36.1, respectively. The lowest values, observed in February, March, and November, were 15.7, 16.3, and 15.0, respectively. The average content of HS in POM in summer is equal

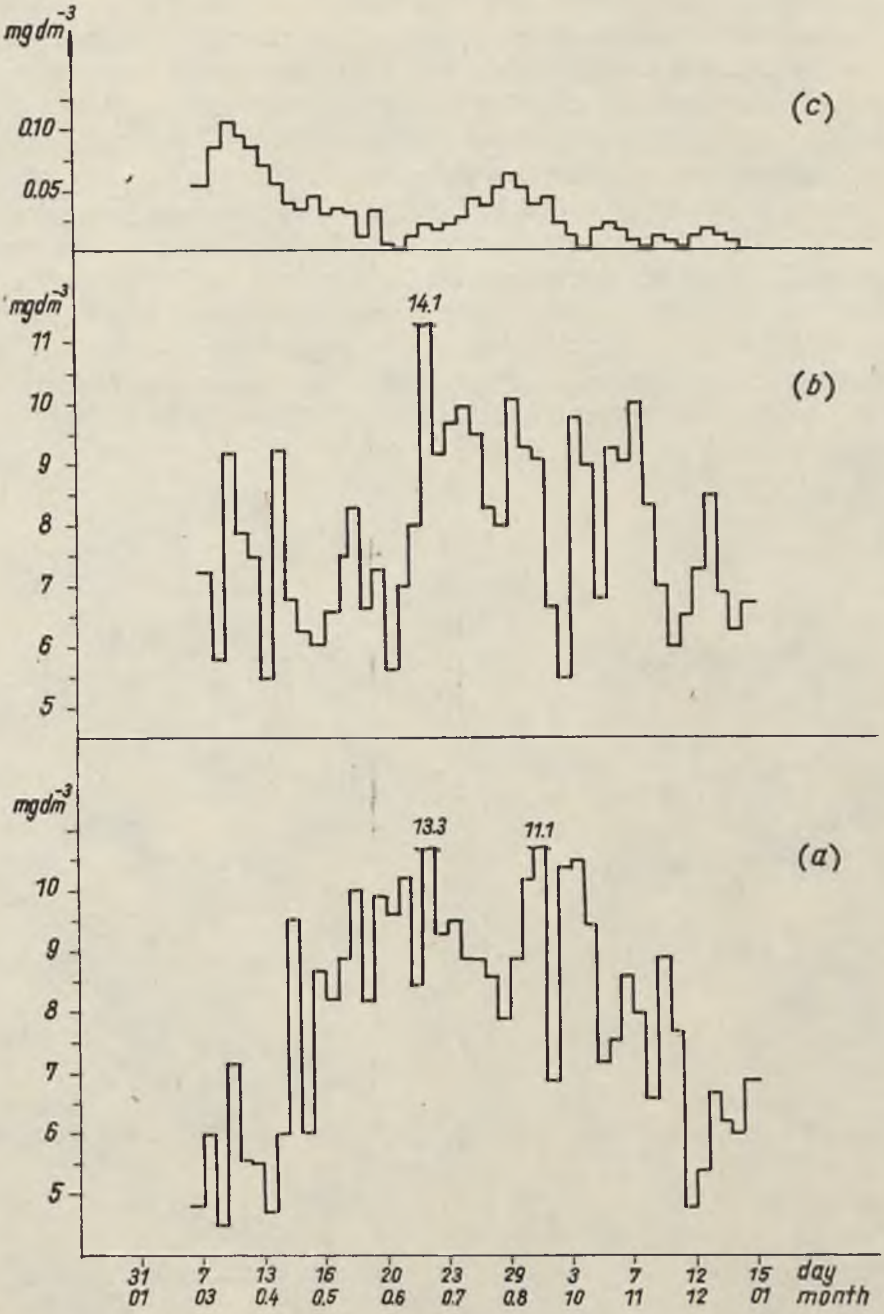


Fig. 4. Organic carbon concentration in the Vistula water (a), and the concentration of fulvic (b) and humic (c) acids.

Ryc. 4. Stężenie węgla organicznego w wodzie Wisły (a), stężenie kwasów fulwinowych (b) oraz kwasów humusowych (c) w tej wodzie to 26.8%, and in winter — 22.2% (fig. 5a). The humic substances in the suspended matter consist of two fractions: fulvic acids (FA) and humic acids (HA). Considerable differences in physiochemical properties of these acids (e.g. solubility, molar absorptivity, oxygen functional groups content, stability constants of complexes with di — and trivalent metals) indicate the need for the determination of the amount of each of the two fractions in the HS [25, 13, 19]. The average percentage of FA in the HS of suspended matter (particulate humic substances — PHS) is 52.3%, which corresponds to 1.1 mg dm^{-3} of FA in the Vistula water (fig. 3c). The highest values were observed in May, June and October (1.95, 2.05, and 2.28 mg dm^{-3}, respectively) — fig. 3b. The lowest content of particulate fulvic acids (PFA) was found at the end of 1977 and at the beginning of January 1978 (the average values for November was 0.75 mg dm^{-3}). The determinations of PFA in suspended

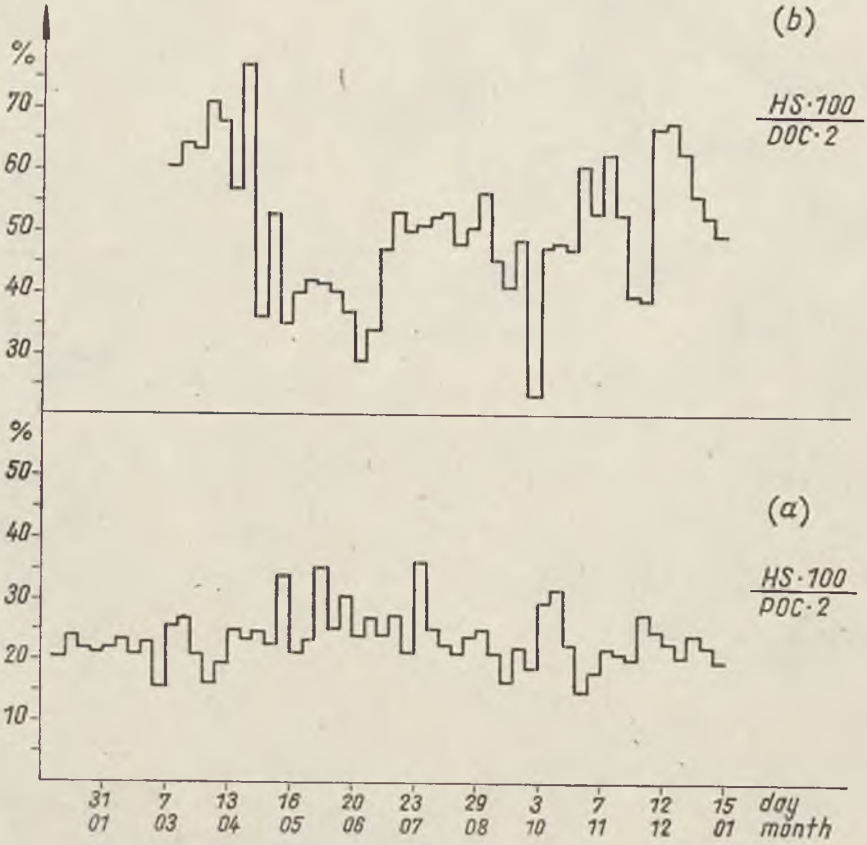


Fig. 5. Percentage of humic substances in organics of suspended matter (a), and percentage of humic substances in organic matter of water (b)

Ryc. 5. Procentowy udział substancji humusowych w materii organicznej zawiesin (a) oraz procentowy udział substancji humusowych w rozpuszczonej materii organicznej (b) matter were not carried out in the period January—March 1977. The highest concentraction were found in May and June 1977 (1.35 mg dm^{-3} on average).

The average concentration of DOC in the Vistula water is equal to 7.1 mg dm^{-3}. The lowest and highest concentrations were found to be 4.5 mg dm^{3-} (February) and 13.3 mg dm^{-3} (June), respectively. The highest average monthly concentrations of DOC were found in June and July (9.6 and 10.0 mg dm^{-3}, respectively), whereas the lowest were observed in February, March and December (4.8, 5.7, and 6.3 mg dm^{-3}, respectively) — fig. 4a. The DOC concentrations determined for the Vistula are higher than those observed for rivers in the western part of the Soviet Union discharging into the Baltic Sea. For the latter, Emelyanov [7] published values ranging from 3.5 to 5.5 mg dm^{-3}. The humic fraction of dissolved organic matter (DOM) consists primarily of fulvic acids (DFA), the average concentration of which is 7.8 mg dm^{-3}. The concentration of dissolved humic acids (DHA) is equal to 0.03 mg dm^{-3}. The highest average concentrations of DFA were observed in July, August and October (9.6, 9.1 and 8.7 mg dm^{-3}, respectively). The lowest average concentration was found in May (6.8 mg dm^{-3}) — fig. 4b. The average concentrations of DHA reached the highest values in March and April (0.08 and 0.06 mg dm^{-3}, respectively), as well as in September (0.05 mg dm^{-3}) — fig. 4c. The average percentage of DHS in DOM is equal to 56.0%. The highest average monthly percentage fractions were found in April (62.2%) and December (61.3%), whereas the lowest were observed in May (40.0%), June (37.8%), and September (42.8%) — fig. 5b.

The data characteristic of average monthly concentrations of individual indices are summarized in table 2. The data compiled there were subsequently used for calculating the total mass of POC, PHS, DOC and DHS introduced into the Baltic Sea with water from the Vistula. Assuming that the Vistula water constitutes 8.0% of the total amount of water inflown into the Baltic Sea and that the concentrations of individual species are uniform for all rivers, the masses of these species input into the Baltic were calculated. The elements of balance of organic carbon and humic substances for the Baltic are given in table 3. The total amount of DOC introduced into the Baltic with river water constitutes about 3.54% of the DOC present in the Baltic (assuming that the volume of water in the Baltic is equal to 22,000 km^3, and the concentration of C_{org} — 4.3 mg dm^{-3}). Evaluating these data it should be remembered, however, that most (80—90%) of the organic compounds present in river water undergoes flocculation and is converted into the suspended form. The total amount of DOC and POC introduced into the Baltic with river water is 5.545 million tons. The amount of organic carbon deposited yearly in the bottom sediments is equal to

Table 2
Tabela 2

Average monthly and yearly concentrations of humic substances suspended and dissolved in the Vistula water

Średnie miesięczne i roczne (w 1977 roku) stężenie węgla organicznego i substancji humusowych obecnych w wodzie rzeki Wisły w postaci zawieszonej i rozpuszczonej

N°	Month Miesiąc	Suspended matter Zawiesina			Water Woda	
		SM	C_{org}	HS	C_{org}	HS
		$mg\ dm^{-3}$	$mg\ dm^{-3}$	$mg\ dm^{-3}$	$mg\ dm^{-3}$	$mg\ dm^{-3}$
1	January	21.3	4.5	2.0		
2	February	31.8	3.7	1.3	4.8	
3	March	31.0	4.8	1.7	5.7	7.4
4	April	26.0	5.1	2.2	6.3	7.6
5	May	34.6	6.6	2.8	7.9	6.8
6	June	16.0	5.2	2.3	9.6	7.0
7	July	31.2	5.7	3.2	10.0	9.6
8	August	27.3	4.6	2.0	8.7	9.1
9	September	23.5	4.7	1.8	9.1	8.2
10	October	13.2	4.0	2.1	8.8	8.7
11	November	16.5	3.6	1.5	8.0	7.9
12	December	11.9	3.2	1.5	6.3	7.1
13	1977 av.	23.70	4.65	2.03	7.1	7.94

Table 3
Tabela 3

Elements of the balance of organic carbon and humic substances for the Baltic Sea

Wybrane elementy bilansu węgla organicznego i substancji humusowych do Morza Bałtyckiego

Amount entering the Baltic Sea Masa wnoszona do Morza Bałtyckiego	Vistula water Wody Wisły	Rivers water Wody wszystkich rzek
	$\times 10^9$ kg	$\times 10^9$ kg
Organic carbon (C_{org})		
— dissolved (DOC)	269.0	3351.2
— particulate (POC)	176.2	2194.8
Humic substances (HS)		
— dissolved (DHS)	300.9	3748.5
— particulate (PHS)	76.9	959.7

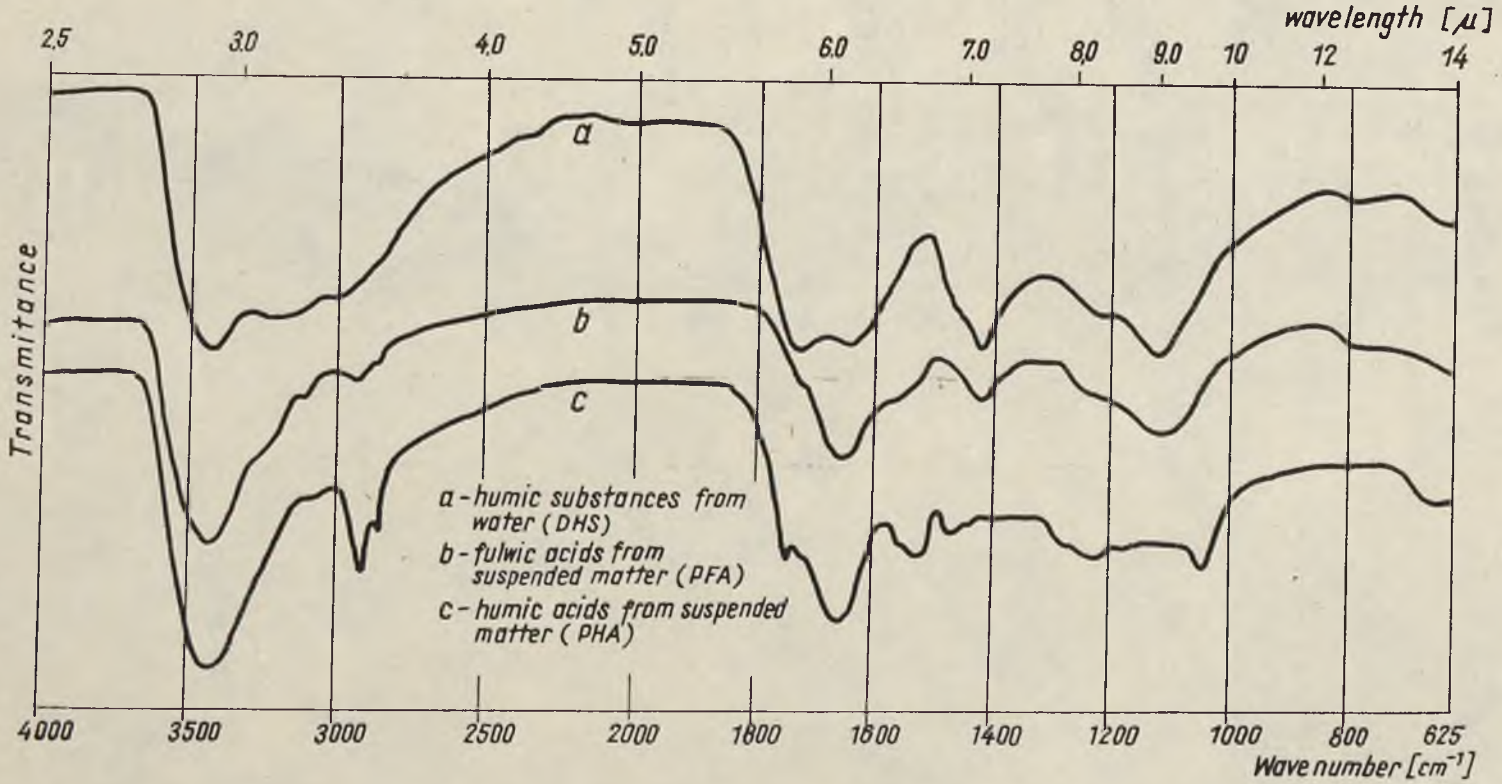


Fig. 6. Typical IR absorption spectra of humic substances isolated from suspended matter and water of the Vistula

Ryc. 6. Typowe widma absorpcyjne w podczerwieni (IR) substancji humusowych wyodrębnionych z zawiesin i wody Wisły

3.88 milion tons [21]. Taking into account the exchange of water characteristic for the Baltic [9], it can be estimated that C_{org} of land origin have to be mineralized to a considerable extent in Baltic Sea water. Considering the fact that the percentage of HS in suspended matter and in river water is similar to that of bottom sediments (ca 50%) [8, 19] it can be assumed that the humic substances of land origin represent a large part (approximately 58%), of the total mass of HS in the bottom sediments of the Baltic. The distribution of HS of land origin will depend to a large extent on the region. The investigations of physico-chemical properties of HS collected in various regions of the Baltic Sea indicate that the properties typical for land humus are observed only in coastal sediments and in the vicinity of river estuaries [19, 20].

Humic substances in amounts sufficient for the determination of their fundamental physico-chemical properties (elemental composition IR, UV, VIS absorption spectra) were isolated from the water samples (ca 100 dm^3) collected in April, July and November 1977 and in January 1978. Typical absorption spectra in the visible range of isolated samples indicate that fulvic acids isolated from suspended matter exhibit a steady decrease of absorption with the wavelength. A similar relationship is observed for the FA isolated from the Vistula water. In the

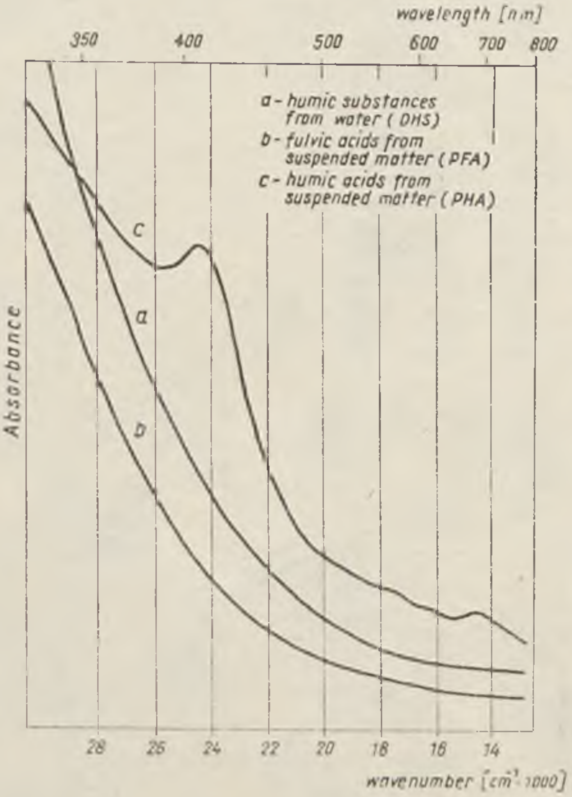
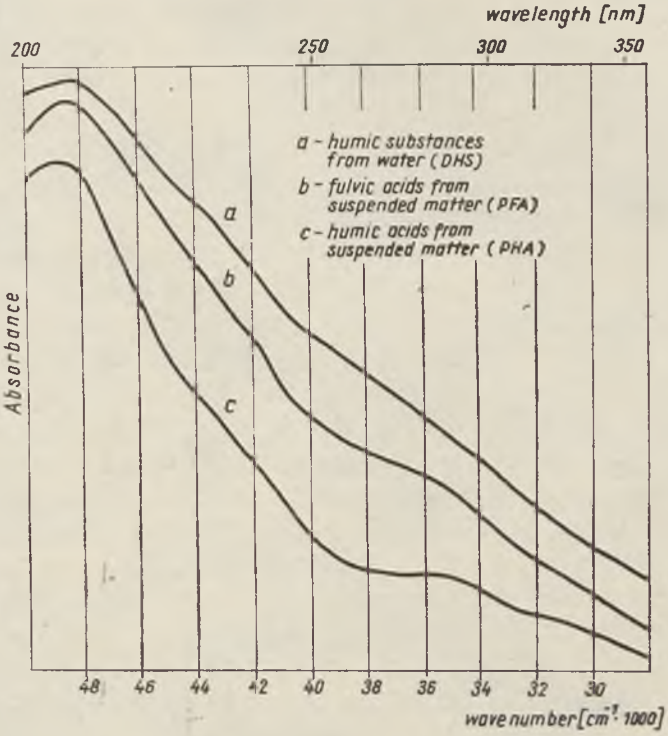


Fig. 7. Typical absorption spectra in the visible range of humic substances isolated from suspended matter and the Vistula water

Ryc. 7. Typowe widma absorpcyjne w zakresie widzialnym (VIS) substancji humusowych wyodrębnionych z zawiesin i wody Wisły

Fig. 8. Typical uv absorption spectra of humic substances isolated from suspended matter and water from the Vistula

Ryc. 8. Typowe widma absorpcyjne w nadfiolecie (UV) substancji humusowych wyodrębnionych z zawiesin i wody Wisły



case of humic acids, the spectra exhibit two inflexion points, at 665 and 430 nm (fig. 7). A similar dependence was found for HA from bottom sediments of the Baltic Sea [19]. The inflexion points in the absorption spectrum of HA result from the presence of vegetable dyes or, more precisely, of their fragments, e.g. dihydroxyperilenequinone derivatived in the molecules of humic acids [12, 14, 16]. Since biochemical degradation of vegetable dyes occurs rapidly [24] it seems probable that the inflexion points discussed here are caused by compounds formed from fresh-water phytoplankton. This conclusion is confirmed by lack of distinct maxima in the spectra of PHA isolated from the sample collected, in January 1978. The ratio of absorbance at 465 and 665 nm ($A_{4/6}$) is frequently used as an empirical indicater of the degree of condensation and aromatization of HS molecules. A higher $A_{4/6}$ values indicates a lower degree of aromatization of analyzed compounds. $A_{4/6}$ values for FA from the Vistula water range from 9.3 to 9.6 (only for the sample collected in January $A_{4/6} = 7.4$), for FA from suspended matter $A_{4/6} = 4.2$—4.8, and for HA from suspended matter $A_{4/6} = 2.9$—3.7. These results indicate that the HS fraction containing the majority of condensed and aromatic compounds is PHA, whereas the fraction containing the least amount of condensed and aromatic compounds is DFA. This interpretation of VIS absorption is also confirmed by the nature of UV absorption spectra. A broad maximum in UV absorption spectrum in the range 275—249 nm, resulting from the presence of aromatic molecules [28] is least pronounced for DFA solutions and most pronounced for PHA solutions (fig. 8).

Characteristic of IR absorption spectra of investigated compounds are very strong and broad absorption bands, which makes their interpretation more difficult. Similar difficulties are encountered in the interpretation of IR spectra of HS isolated from soil and bottom sediments [28]. However, one can find in these spectra, certain absorption maxima that are attributed to the presence of hydroxyl and amino groups (wave number 3500—3300 cm^{-1}), methyl and methylene groups (2950—2800 cm^{-1}) carbonyl groups (ca 1700 cm^{-1}), aromatic rings (1650—1600 cm^{-1}), and hydroxyl groups of polysacharides (ca 1050 cm^{-1}). Particularly pronounced, are absorption maxima corresponding to methylene groups in the IR spectrum of PHA. This spectrum also has distinct maxima at 1700 and 1650 cm^{-1}. Absorption spectra of FA are much less clear, which is due to the fact that ammonium salts of these acids were analyzed. Nevertheless, one can distinguish a distinct maximum at 1050 cm^{-1} and a less pronounced maximum at 1650 cm^{-1}. In an IR spectrum of DFA one observes a broad maximum in the range 3000—2600 cm^{-1}, which is not observed in an IR spectrum of PFA (fig. 6).

Table 4
Tabela 4

Elemental composition of the humic substances isolated from water and suspended matter of the Vistula

Skład elementarny substancji humusowych wyodrębnionych z wody i zawiesiny rzeki Wisły

Type of substance Rodzaj substancji	Elemental composition (%) Skład elementarny (%)				C/H av.	C/N av.
	C	H	N	O		
Humic substances of water (DHS)	43.36—50.55	5.82—6.78	6.90—8.76	39.22—35.92	8.23	6.91
Humic substances of suspended matter						
— humic acids (PHA)	52.80—54.83	6.30—7.05	5.93—8.60	37.15—31.17	7.77	8.77
— fulvic acids (PFA)	46.69—48.65	6.45—6.67	8.95—9.92	39.13—34.18	6.98	4.51

Elemental composition of DHS and PHS is shown in table 4. The high nitrogen content in analyzed samples of FA in comparison with HA should be noted. This can be partially attributed to the fact that the isolation and concentration procedure for FA involved the application of ammonium hydroxide, which is difficult to separate [18]. The C (H ratio/C = carbon content, H = hydrogen content) is higher than 10. According to Bordovsky [3], land humus has a C/H value lower than 10, whereas for sea humic the C/H ratio is lower than 10. The elemental composition of analyzed compounds is similar to that of HS isolated from the bottom sediments of the Baltic Sea [19, 20].

5. CONCLUSIONS

Investigations carried out in 1977 proved that the average concentration of POC in the Vistula water was 4.1 mg dm^{-3} and the average concentration of DOC was 7.1 mg dm^{-3}. The HS content in POM was equal to 2.1 mg dm^{-3} (24%), of which 52% the PFA content (1.1 mg dm^{-3}), and PHA content — 48% (1.0 mg dm^{-3}). The calculated concentrations permitted the validation of some elements of organic balance in the Baltic Sea. On this basis it was concluded that the fraction of organic matter of land origin constitutes about 20% of the total amount of organic matter in the Baltic Sea. The determination of some physico-chemical properties of humic substances permitted the elucidation of some elements of their chemical structure, which are similar to that of HS isolated from the bottom sediments of the Baltic Sea.

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OKREŚLENIE ILOŚCI I JAKOŚCI SUBSTANCJI HUMUSOWYCH WPROWADZANYCH DO MORZA BAŁTYCKIEGO Z WODAMI WISŁY

Streszczenie

W pracy przedstawiono wyniki cotygodniowych, prowadzonych w 1977 roku, badań nad zawartością zawiesin (SM), węgla organicznego w zawiesinach (POC), substancji humusowych w zawiesinach (PHS) w tym — kwasów fulwinowych (PFA) i kwasów humusowych (PHA), oraz rozpuszczonego węgla organicznego (DOC) i rozpuszczonych substancji humusowych (DHS) w tym kwasów fulwinowych (DFA) i kwasów humusowych (DHA). Na podstawie średnich tygodniowych przepływów Wisły (ryc. 1) obliczono średnią tygodniową masę węgla organicznego i substancji humusowych wprowadzanych do Morza Bałtyckiego z wodami Wisły (tab. 1). Stężenia SM, POC oraz udział procentowy POC w SM przedstawiono na ryc. 2. Na ryc. 3 przedstawiono stężenie PHS, stężenie PFA oraz udział procentowy PFA w PHS. Procentowy udział PHS w materii organicznej zawiesin oraz DHS w rozpuszczonej materii organicznej przedstawiono na ryc. 5. Na ryc. 4 przedstawiono natomiast wyniki oznaczania stężenia DOC oraz stężenia DFA i DHA. Średnie miesięczne i roczne stężenia węgla organicznego i substancji humusowych przedstawiono w tab. 2. Przedstawione dane posłużyły do obliczenia elementów bilansu węgla organicznego i substancji humusowych dla Morza Bałtyckiego (tab. 3). Charakterystykę własności fizykochemicznych substancji humusowych przeprowadzono na podstawie ich składu elementarnego (tab. 4), widm absorpcyjnych w podczerwieni (ryc. 6), widm absorpcyjnych w świetle widzialnym (ryc. 7) i widm absorpcyjnych w nadfiolecie (ryc. 8).

REFERENCES

LITERATURA

1. Bojanowski R., Pempkowiak J., *Oznaczenie węgla organicznego metodą utleniania na mokro*, Studia i Materiały Oceanologiczne Komitetu Badań Morza, 8, 1974, 109.

2. Bojanowski R., Pempkowiak J., Kupryszewski G., *Humic substances in the Baltic sediments,* Oceanologia, 7, 1977, 105.
3. Bordovsky O., *Accumulation of organic matter in bottom sediments,* Marine Geology, 3, 1965, 33.
4. Brown M., *High molecular — weight material in Baltic Seawater,* Marine Chemistry, 3, 1975, 253.
5. Carlberg S., *A study of the distribution of organic carbon and oxidability in Baltic waters,* Medd. Havsfiskelab. Lysekil, 141, 1972, 21 pp.
6. Ehrhard M., *The particulate organic carbon and nitrogen and the dissolved organic carbon in the Gotland Deep in May 1968,* Kiel, Meeresfors., 25, 1969, 71.
7. Emelianov E., *Wzwieszennoje wieszczestwo w wodach Bałtijskogo moria,* [w:] *Geołogia Bałtijskogo moria,* red. W. Gudelis, E. Emelianov, Maksłos, Wilnus 1976, 159—187.
8. Gorszkowa T., *Organiczeskoje wieszczestwo w Bałtijskom morie i jego biołogiczeskoje znaczenije,* Trudy WNIRO, 75, 1966, 191.
9. Grasshof K., *The hydrochemistry of landlocked basins and fjords,* [w:] *Chemical oceanography,* eds. I. Riley, G. Skirrov, Acad. Press, London 1975, vol. 2, 456—598.
10. Hairs M., Basset Ch., *Dissolved and particulate humic acids in an East Coast Estuary,* Est. Coast. Mar. Sci., 1, 1973, 107.
11. Head P., *Organic processes in estuaries,* [w:] *Estuarine Chemistry,* eds. J. Burton, P. Liss, Acad. Press., London 1976, 54—92.
12. Ischiwatari R., *Chemical characterization of fractionated humic acids from lake and marine sediments,* Chem. Geol., 12, 1975, 113.
13. Jackson T., *Humic matter in natural waters and sediments,* Soil Sci., 119, 1974, 56.
14. Josefsson B., *Determination of dissolved organic compounds in natural waters,* Ph. D. Thesis. Göteborg Univ., Göteborg 1973.
15. Jurkowskis A., Formych T., Grotanje B., *Cikł izmienienij organiczesko cwjazannogo uglieroda, azota i fosfora w Bałtijskom morie w 1974,* Okieanołogija, 16, 1976, 79.
16. Kudama K., Hurst H., *Green humic acids and its possible origin as a fungal metabolite,* Nature, 214, 1967, 631.
17. Menzel D., Vaccaro R., *The determination of organic carbon in sea water,* Limnol. Oceanogr., 9, 1964, 138.
18. Montoura R., Riley I., *The analytical concentration of humic substances from natural waters,* Anal. Chim. Acta, 76, 1975, 97.
19. Pempkowiak J., *Własności substancji humusowych z osadów dennych Morza Bałtyckiego,* praca doktorska, Zakład Oceanologii PAN, Sopot 1977.
20. Pempkowiak J., *Substancje organiczne w wodach Morza Bałtyckiego,* Studia i Materiały Oceanologiczne Komitetu Badań Morza PAN, 17, 1977, 205.
21. Pempkowiak J., *Oznaczanie zawartości węgla organicznego w wodach naturalnych,* Chem. Anal. (w druku).
22. Pempkowiak J., Bojanowski R., Kupryszewski G., *Humic substances in the Baltic sediments,* [w:] *10th Conference of Baltic Oceanographers,* Paper No. 18, Göteborg 1978.
23. Pęcherzewski K., Ławacz W., *Węgiel organiczny w wodach Bałtyku Południowego,* Studia i Materiały Oceanologiczne Komitetu Badań Morza PAN, 17, 1977, 241.
24. Povoledo D., Murray D., Pitze M., *Pigments and lipids in the humic*

acids of some canadian lake sediments, [w:] *Humic substances,* eds. D. Povoledo, H. Golterman, Centr. A.P.D., Wageningen 1975, 233—258.

25. Rashid H., King L., *Molecular weight distribution measurements on humic and fulvic acid fraction from marine clays on the Scotian Shelf,* Geochim. Cosmochin. Acta, 33, 1968, 147.
26. Riley I., Taylor D., *The analytical concentration of tracers of dissolved organic materials from seawater with Amberlite XAD-1,* Anal. Chim. Acta, 46, 1969, 307.
27. Schlungbaum G., Nausch G., *A few remarks on the occurence of substances with a phenolic character in the Southern Baltic,* [w:] *3rd Soviet -Swedisch Symposium,* Stockholm 1975.
28. Schnitzer M., Khan S., *Humic substances in the environment,* Marcel Dekker, New York 1971.
29. Skopincew B., *Organiczeskoje wieszczestwo w wodach moriej (wodnyj gumus),* Trudy GOIN, 19, 1950, 3.
30. Skopincew B., Timofiejewa S., *Sodierżenije organiczeskogo ugleroda w wodach Bałtijskogo i Siewiernogo moriej,* Trudy MGI, 25, 1962, 161.
31. Strouermer D., *The characterization of humic substances in sea water,* Ph. D. Thesis. Mass. Inst. Technol., Woods Hole 1976.
32. Williams I., *Biological and chemical aspects of dissolved organic material in sea water,* [w:] *Chemical oceanography,* eds. I. Riley, G. Skirrov, Acad. Press., London 1975, vol. 2, 301—364.