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Organic Polysulphides in Bottom Sediments of the Gulf of Finland

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Abstract

In the samples of bottom sediments of the Gulf of Finland in its eastern part, 43 organic compounds containing sulphur were identified and estimated quantitatively by means of gas chromatography – mass spectrometry. It is shown that polysulphides are widespread in the bottom sediments of the investigated part of the Gulf of Finland. An increase in the concentrations of sulphur-containing compounds with an increase in the salt content of water and with an increase in the depth of the gulf from the east to the west was detected. The high concentration of sulphur-containing organic compounds in bottom sediments in the region from the west edge of the island of Kotlin to 28 degrees of eastern longitude provides evidence that there exist the conditions for the formation of hydrogen sulphide zones stable in this region.

INTRODUCTION

The formation of hydrogen sulphide and organic sulphides occurs in sea sediments under the lack of oxygen and excess of organic matter as a result of the processes of the bacterial reduction of sulphate ions. The qualitative and quantitative composition of the formed sulphur-containing organic compounds is unknown [1–3]. In spite of the clearly expressed biological activity and toxicity of almost all the known mercaptans and sulphides [4, 5], as a rule, these compounds are not considered as dangerous pollutants of the sea bottom sediments. In addition, their presence in bottom sediments can be a kind of indicator of the stability of anaerobic processes in the bottom layer of water bodies and leading to ecological catastrophes, for example in the form of the mass mortality of hydrobionts.

The conditions for the formation of stable hydrogen sulphide zones and for the synthesis of organic sulphides are existing in the eastern part of the Gulf of Finland (from the island of Gogland to the island of Kotlin) at a depth of 20–40 m. A low degree of vertical mixing of water layer, as well as high salt content and high concentrations of the organic matter are observed here, which creates permanent lack of oxygen in the bottom layer (from 10–20 % saturation to full anoxia) [6]. According to the data reported in [7–9] on the occurrence and the species composition of micro and macro zoobenthos, the deep-water part of the Gulf of Finland is most depleted of the amount and species variety. Vast regions near the mouth of the Vyborg Bay and near the island of Moshchny are at present almost lifeless. In the Neva bay, permanent increase in the number of zoobenthos organisms with morphological deformations is observed. The observed trends provide evidence of the critical state of the ecosystem and point to the high degree of toxicity of bottom sediments.

The present investigation deals with the estimation of the quantitative content of organic sulphur compounds identified in the bottom sediments of the eastern part of the Gulf of Finland. Establishment of the structures of individual compounds with the help of mass spectrometry of low and high resolution was described in our previous publications [10–13].

MATERIALS AND METHODS OF INVESTIGATION

Samples were collected in 19 points of the Gulf of Finland form the upper surface of bottom sediments. Samples were taken with the help of Petersen bottom sampler with the capture area of 0.025 m^2 (Table 1).

The samples were examined by means of gas chromatography – mass spectrometry. Chromatograms and low resolution mass spectra were recorded with QP-5000 chromato-mass spectrometer of Shimadzu Company. The high resolution mass spectra were recorded with AutoSpec instrument of VG Company; recording in the mode of tandem mass spectrometry was carried out with the Polaris Q instrument (ion transverter) of Finnigan Company. Extraction procedures, sample preparation for analysis and chromatographic conditions were described in detail in our previous works [10–13]. The deduction of the most probable structures for unknown compounds was performed according to the following algorithm [10–13]:

– Among the total number of mass spectra of non-identified compounds, the mass spectra containing the ions characteristic of sulphur organic compounds were chosen.

– For the chosen non-identified compounds with the established peak appearing times (for which sulphur was assumed to be present), the exact total formulas were determined by means of chromatography and high resolution (not less than 5000) mass spectrometry. The presence of one or several sulphur atoms in the molecule was confirmed.

– On the basis of the obtained total formulas of the molecular and fragmented ions, the deduction of the most probable structure for the compound under investigation was carried out using the rules of fragmentation of sulphur-containing organic compounds under the action of the electron impact.

TABLE 1

Coordinates of stations and sampling dates

Station No.	Station code	Latitude	Longitude	Sampling date
1	#20	60°09'	29°42'	09.10.1997
2	#21	60°04'	28°53'	09.10.1997
3	#25	60°01'	29°24'	09.10.1997
4	#40	60°05'	29°25'	20.08.2001
5	#42	60°04'	28°54'	22.08.2001
6	#43	59°55'	29°56'	23.08.2001
7	#44	60°01'	28°04'	21.08.2001
8	#45	60°08'	29°25'	21.08.2001
9	#46	60°05'	29°42'	20.08.2001
10	#47	60°04'	29°18'	21.08.2001
11	#48	60°20'	28°41'	23.08.2001
12	#49	59°56'	30°08'	23.08.2001
13	#50	60°02'	29°23'	20.08.2001
14	#51	59°59'	29°52'	23.08.2001
15	#52	60°01'	28°34'	21.08.2001
16	#53	59°53'	28°37'	21.08.2001
17	#54	60°08'	29°42'	21.08.2001
18	#55	60°07'	29°14'	21.08.2001
19	#60	60°04'	29°08'	21.08.2001

TABLE 2

Characteristics of sulphur-containing organic compounds formed in the bottom sediments of the Gulf of Finland

No.	Compound	M_r	CAS number	Time of peak appearance, min
1	Thiolmethyl(methyl)sulphoxide	110	196713-87-8	8.6
2	1-Amylmercaptan	104	110-66-7	8.8
3	Diallylsulphide[a]	114	592-88-1	9.7
4	Methyl(allyl)disulphide[a]	120	2179-58-0	11.0
5	Dichloromethyl-thiylsulphenylchloride	182	256337-09-4	11.3
6	Dimethyltrisulphide	126	3658-80-8	12.4
7	1,3-Dithiane	120	505-23-7	13.8
8	Chloromethyl(dichloromethyl)disulphide	196	256337-09-4	14.7
9	Diallyldisulphide[a]	146	2179-57-9	15.4
10	1,2,4-Trithiolane	124	289-16-7	16.0
11	3,4-Dithiacyclohexene[a]	118	210237-55-11	6.1
12	1-Octylmercaptane	146	111-88-6	16.6
13	Bis(dichloromethyl)disulphide	230	97925-52-5	16.6
14	1,2,4-Dithiacycloheptane	152	844476-52-4	17.1
15	2-Pentylthiophen	154	4861-58-9	17.7
16	1,2,3-Trithiacyclohexane	138	3325-33-5	17.8
17	Tetrathiacyclopentane	142	19901-14-5	19.0
18	3,4,5-Trithiacyclohexene	136	290-30-2	19.1
19	1,2,4-Trithiacyclohexane	138	38617-72-0	19.3
20	Dimethyltetrasulphide	158	5756-24-1	19.6
21	Cyclopropylhydrotrisulphide[a]	138	848194-73-0	19.9
22	4,5-Dimethylthiazole	113	3581-91-7	20.0
23	2-Hexylthiophene	168	18794-77-9	20.7
24	1,2-Dithian-3-thiol	152		20.7
25	1,3-Dithain-2-thiol	152	92507-40-9	20.8
26	Dimethyltetrasulphide-2-oxide	174		21.0
27	Bis[1-methylpropyl)sulphide	146	626-26-6	21.8
28	Diallyltrisulphide[a]	178	2050-87-5	22.0
29	1,3,5-Trithiacyclohexane	138	291-21-4	22.3
30	Bis(dichloromethyl)trisulphide	262	256337-07-2	23.0
31	1,2,4,5-Tetrathiacyclohexane	156	291-22-5	23.5
32	1,2,3,4-Tetrathiacycloheptane	170	121270-33-5	24.1
33	1,2,3,4-Tetrathiacyclohexane	156	153393-16-9	24.2
34	1,2,3,5-Tetrathiacyclohexane	156	19901-14-5	24.4
35	4,5-Dithia-3-thioncyclopentene[a]	134	499774-03-7	24.8
36	Pentathiane	174	18091-79-7	26.4
37	1,2,4,6-Tetrathiacycloheptane	170	292-45-5	28.4
38	1,2,4,6-Tetrathiacyclooctane	184	844476-53-5	28.6
39	2,5-Dibutylthiophen	196	6911-45-1	28.8
40	1,2,4,5,7,8-Hexathiacyclononane[a]	234	81531-38-6	30.6
41	1,2,3,5,6-Pentathiacycloheptane	188	292-46-6	31.5
42	1,2,3,4,5-Pentathiacyclooctane	202	114792-74-4	31.8
43	1,2,3,4,5,6-Hexathiacycloheptane	206	17233-71-5	33.8
44	$C_6H_{10}S_4$ (or $C_6H_{10}O_2S_3$)	210	16007-20-8	35.1

Notes. 1. The mass spectra of compounds **5**, **8**, **11**, **13**, **14**, **16–19**, **21**, **24**, **26**, **30**, **33**, **34**, **36**, **38** have been recorded for the first time. 2. Compounds **5**, **8**, **11**, **13**, **14**, **21**, **24**, **26**, **30**, **38** have been previously unknown.

[a]Other isomers are possible.

– In order to determine the structures and routes of mass fragmentation more accurately, we used the tandem mass spectrometry.

Estimation of the quantitative content of the detected compounds was carried out using the internal reference (2-fluoronaphthalene) introduced into the sample immediately before extraction. The sensitivity coefficient of the mass spectrometric detector (MD) in the pair 2-fluoronaphthalene/diethyldisulphide was taken into account. When calculating the concentrations, the response of MD for all the sulphur-containing organic compounds was accepted to be equal to the response of MD for diethyldisulphide.

RESULTS AND DISCUSSION

The characteristics of sulphur-containing organic compounds discovered during the investigation are presented in Table 2 in the order of elution from the chromatographic column. It should be noted that the elemental sulphur in S_6 and S_8 forms was present in all the examined samples.

Analysis and treatment of the data thus obtained allowed us to identify 43 compounds containing sulphur; among them, 15 aliphatic, 24 cyclic (21 saturated and 3 unsaturated) and 4 heteroaromatic compounds were detected. The exact total formula and structure of one of the detected compounds which is a cyclic polysulphide (**44**, see Table 2) were not established due to the low concentration of the compound in the sample. The mass spectra of 17 compounds (**5**, **8**, **11**, **13**, **14**, **16–19**, **21**, **24**, **26**, **30**, **33**, **34**, **36**, and **38**) were recorded for the first time; 10 of them (**5**, **8**, **11**, **13**, **14**, **21**, **24**, **26**, **30**, and **38**) were previously unknown but by present the CAS numbers have been already assigned to them (except the compounds **24** and **26**), see Table 2. It should be noted that the compounds **5**, **8**, **13**, **30** are potentially dangerous chlorinated polysulphides.

The data on the content of the detected polysulphides are presented in Table 3 as a sequence of decreasing total content of sulphur-containing organic compounds in the investigated samples. The same Table shows the data on the salt content of the near-bottom water and the depth at the sampling sites. The spatial distribution of the total content of sulphur-containing organic compounds in bottom sediments in the eastern part of the Gulf of Finland is shown in Fig. 1.

It is known [1, 2] that a condition for the occurrence of the chemical processes of sulphate reduction and the formation of organic sulphides is the set of three constituents: the low concentration of dissolved oxygen (<0.11 ml/l), high concentration of the organic

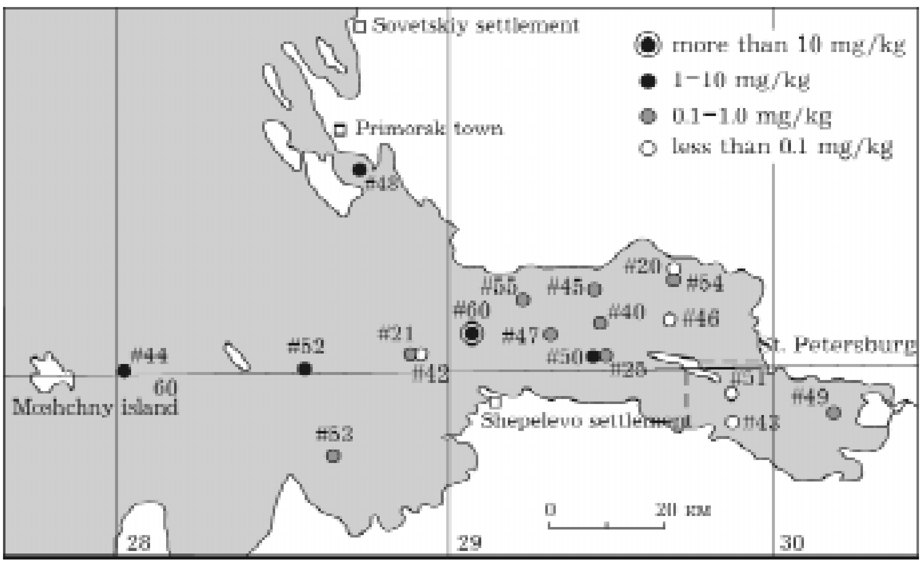

Fig. 1. Spatial distribution of the total amount of sulphur-containing organic compounds in the bottom sediments of the Gulf of Finland (eastern part).

TABLE 3

Concentrations of the detected sulphur-containing organic compounds in the investigated samples, mg/kg of bottom sediments of natural humidity

No.	Compound	#60	#44	#48	#52	#50	#53	#54	#49	#21	#47	#45	#25	#55	#40	#51	#43	#20	#46	#42
1	Thiolmethyl(methyl)sulphoxide	0.10	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
2	1-Amylmercaptan	–	–	–	–	–	0.14	–	–	–	–	–	–	–	–	–	–	–	–	–
3	Diallylsulphide[a]	0.36	–	0.07	0.11	0.02	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4	Methyl(allyl)disulphide[a]	0.42	–	0.06	0.03	0.01	–	0.02	0.07	–	0.02	–	–	–	–	0.02	–	–	–	–
5	Dichloromethyl-thiylsulphenylchloride	–	–	–	–	–	–	–	–	0.01	–	–	–	–	–	–	–	–	–	–
6	Dimethyltrisulphide	0.13	–	0.05	–	0.08	0.17	–	–	–	–	–	–	–	–	–	–	–	–	–
7	1,3-Dithiane	2.7	0.24	1.3	0.20	0.26	–	0.25	0.18	–	0.07	–	–	–	0.06	–	–	–	–	–
8	Chloromethyl(dichloromethyl)disulphide	–	–	–	–	–	–	–	–	–	–	–	0.01	–	–	–	–	–	–	–
9	Diallyldisulphide[a]	2.0	–	0.16	0.10	0.06	–	0.30	0.11	–	0.03	–	–	–	–	–	–	–	–	–
10	1,2,4-Trithiolane	7.3	1.0	–	0.65	0.40	0.03	–	0.15	–	0.18	0.30	–	0.17	0.02	–	0.01	–	–	–
11	3,4-Dithiacyclohexene[a]	–	0.03	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
12	1-Octylmercaptane	–	–	–	–	–	0.25	–	–	–	–	–	–	–	–	–	–	–	–	–
13	Bis(dichloromethyl)disulphide	–	–	–	–	–	–	–	–	0.47	–	–	0.28	–	–	–	–	–	–	–
14	1,2,4-Dithiacycloheptane	–	–	0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
15	2-Pentylthiophen	–	–	–	–	–	0.02	–	–	–	–	–	–	–	–	–	–	–	–	–
16	1,2,3-Trithiacyclohexane	1.5	0.57	0.22	–	–	–	–	–	–	0.05	–	–	–	–	–	–	–	–	–
17	Tetrathiacyclopentane	–	0.03	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
18	3,4,5-Trithiacyclohexene	0.50	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
19	1,2,4-Trithiacyclohexane	0.07	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
20	Dimethyltetrasulphide	0.07	–	0.03	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
21	Cyclopropylhydrotrisulphide[a]	0.08	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
22	4,5-Dimethylthiazole	–	–	0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
23	2-Hexylthiophene	–	–	–	–	–	0.04	–	–	–	–	–	–	–	–	–	–	–	–	–
24	1,2-Dithian-3-thiol	–	0.04	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
25	1,3-Dithain-2-thiol	–	0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
26	Dimethyltetrasulphide-2-oxide	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.01	–	–
27	Bis[1-methylpropyl)sulphide	0.10	–	0.01	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

TABLE 3 (Ending)

No.	Compound	#60	#44	#48	#52	#50	#53	#54	#49	#21	#47	#45	#25	#55	#40	#51	#43	#20	#46	#42
28	Diallyltrisulphide[a]	0.42	–	0.02	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
29	1,3,5-Trithiacyclohexane	0.60	0.42	0.11	0.09	0.05	0.05	0.06	0.13	–	–	–	–	0.03	0.02	–	–	–	–	–
30	Bis(dichloromethyl)trisulphide	–	–	–	–	–	–	–	–	0.01	–	–	0.01	–	–	–	–	–	–	–
31	1,2,4,5-Tetrathiacyclohexane	–	0.30	0.04	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
32	1,2,3,4-Tetrathiacycloheptane	2.1	1.1	0.19	0.15	0.09	0.03	0.11	0.05	–	0.10	–	–	–	–	–	–	–	–	–
33	1,2,3,4-Tetrathiacyclohexane	–	–	0.20	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
34	1,2,3,5-Tetrathiacyclohexane	0.5	0.30	–	0.07	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
35	4,5-Dithia-3-thioncyclopentene[a]	0.08	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
36	Pentathiane	–	0.09	0.02	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
37	1,2,4,6-Tetrathiacycloheptane	0.30	0.76	0.03	0.09	0.03	–	–	–	–	–	–	–	–	–	–	–	–	–	–
38	1,2,4,6-Tetrathiacyclooctane	–	0.82	0.02	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
39	2,5-Dibutylthiophen	–	–	–	–	–	0.12	–	–	–	–	–	–	–	–	–	–	–	–	–
40	1,2,4,5,7,8-Hexathiacyclononane[a]	–	0.16	–	0.04	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
41	1,2,3,5,6-Pentathiacycloheptane	0.25	1.3	0.11	0.06	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
42	1,2,3,4,5-Pentathiacyclooctane	0.35	0.32	0.05	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
43	1,2,3,4,5,6-Hexathiacycloheptane	1.5	1.6	0.15	–	0.22	–	–	–	–	–	–	–	–	–	–	–	–	–	–
44	$C_6H_{10}S_4$ (or $C_6H_{10}O_2S_3$)	–	0.13	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Total	21.5	9.2	2.3	1.6	1.2	0.85	0.75	0.7	0.5	0.45	0.3	0.3	0.2	0.1	0.02	0.01	0.01	<0.01	<0.01
	Depth, m	23	20	10	31	21	25	12	2.5	36	28	22	24	28	24	4	3	12	14	35
	Salt content[b], %	1.81	3.85	2.14	2.90	1.77	3.30	0.32	<0.1	d/a	1.82	0.68	d/a	1.43	0.71	<0.1	<0.1	d/a	0.42	2.81

Notes. 1. Dash means that a compound was not detected at the level of sensitivity of the method (0.001 mg/kg). 2. d/a means the data are absent.

[a]Other isomers are possible.

[b]Salt content of near-bottom water is presented (the data of the Institute of Zoology, RAS).

matter, and the high concentration of sulphate ions in water where the enzymatic decomposition of organic compounds occurs. These conditions occur in the investigated part of the Gulf of Finland mainly to the west from the island of Kotlin [6]. The data obtained (see Table 3 and Fig. 1) confirm this fact and provide a good illustration of the increase in the concentration of sulphur-containing organic compounds in the direction from east to west as the salt content and the depth increase. However, we cannot but mention several features. For instance, in the Neva Bay (station 49), in spite of the small depth (2.5 m), rather high concentration (0.7 mg/kg) of sulphur-containing organic compounds is observed. This can be explained by the fact that the station is situated in the first barrier zone where a sharp decrease in the water flow velocity occurs (where the Neva flows into the bay); as a result, the substantial part of the organic matter is deposited and accumulated in bottom sediments of the inner estuary. Sulphur-containing organic compounds can arrive with the water flow of the Neva and precipitate with the suspended matter due to the hydrophobic nature. In addition, permanently high concentration of organics in bottom sediments and rugged topography cause oxygen deficiency near the bottom (in some zones) and the formation of sulphides in spite of the small depth and low salt content in this part of the gulf. In the region from 30 degrees of eastern longitude to the western edge of the island of Kotlin (see Fig. 1), the lowest concentrations of sulphur-containing organic compounds in bottom sediments were detected (<0.1 mg/kg). The mobility of water mass, in combination with small depth (up to 15 m) and low salt content (up to 0.4 %) prevent the occurrence of stable hydrogen sulphide zones and the formation of organic sulphides. However, due to the presence of barriers (shoals, dams), the formation of temporary dead spaces and the occurrence of sulphate reduction processes become possible at separate regions. To the west from the island of Kotlin to 28 degrees of eastern longitude (station 44, see Table 3) the concentration of sulphides in bottom sediments increases from 0.1 to 10 mg/kg. This is connected with a decrease in water flow rate and an increase in salt content to the west from the island of Kotlin, which causes the formation of the second barrier zone where the hydrodynamic and salt barriers are combined [6]. As a result of the active organic coagulation processes and the deposition of suspended particles, the accumulation of silt sediments and organic matter occurs in the sedimentation basin of the Shepelevo stretch occurs; thus we observe the highest concentration of sulphur-containing organic compounds in the sample taken at station 60: 21 mg/kg. In spite of the small depth (10 m), the high sulphide content (2.3 mg/kg) was detected in the sample of bottom sediments taken at station 48. The most probable additional source of sulphur-containing compounds in this part of the Gulf of Finland may be the industrial discharge from the pulp and paper plant (Sovetskiy settlement) and wastewater from the town of Primorsk.

SUMMARY

1. For the first time, a potentially dangerous class of compounds, namely chlorinated polysulphides, was discovered in natural objects, in particular in bottom sediments.

2. It is demonstrated that polysulphides are widespread in relatively high concentrations in the bottom sediments of the Gulf of Finland.

3. The fact that the detected sulphur-containing organic compounds are not used in industry, the major part of them is commercially unavailable and some of them have been recorded for the first time provides evidence that natural processes participate in their formation.

4. For the bottom sediments of the eastern part of the Gulf of Finland (to the east from the meridian of the Moshchny island), a characteristic feature is the presence of elemental sulphur and sulphur-containing organics mainly in the form of cyclic and linear polysulphides.

5. Since the formation of organic sulphur is a reversible long-standing process taking from several months to several years under anaerobic conditions, the high concentration of sulphur-containing organic compounds in the bottom sediments in the region from the west edge of the island of Kotlin to 28 degrees of east-

ern longitude provide evidence that here exist the conditions for the formation of stable hydrogen sulphide zones in this region.

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