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Cause of Elevated As Concentrations in the Baltic Sea and Vistula Lagoon

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Abstract—As is less toxic than Hg, Cd, Pb, Se, Zn, and Cu. The As clarke for clays and shales is 10 ppm. Our samples of bottom sediments from Kurshskii Bay were determined to contain from 15 to 26 ppm As and up to 34 ppm As in the vicinity of the Neman River mouth. Elevated As concentrations (50–114 ppm) were detected in four columns of subsurface bottom sediments (at depths of 10–65 cm) from the Vistula Lagoon. Elevated As concentrations (50–180 ppm) were also found in a few surface samples of sand from the Gdansk Deep near oil platform D-6. These sediments are either partly contaminated with anthropogenic As or contain Fe sulfides and glauconite, which can concentrate As and contain its elevated concentrations. The As concentration in columns of bottom sediments from the Gulf of Finland were at the natural background level (throughout the columns) typical of the area (9–34 ppm). We repeatedly detected very high As concentrations (up to 227 ppm As) in pelitic ooze from Bornholm Deep, in the vicinity of the sunken vessel with chemical weapons. The sources of elevated As concentrations in the Baltic Sea are the following: (1) chemical weapon (CW) material buried in the floor of the Baltic Sea; (2) As-bearing pesticides, agricultural mineral fertilizers, and burned coal and other fuels; (3) kerogen-bearing Ordovician rocks exposed on the bottom; and (4) As-rich Fe sulfides brought to the area together with construction sand and gravel. This mixture was used in paper production and for the construction of hydraulic engineering facilities in the Vistula Lagoon in the early 20th century and later caused the so-called lagoon disease.

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SINTRODUCTION

Arsenic (As) is one of the most poisonous contaminants, whose toxicity is the seventh most hazardous after those of Hg, Cd, Pb, Se, Zn, and Cu. This element is contained in atmospheric dust, the waters of rivers and seas, particulate matter in them, seaweeds and marine animals, modern bottom sediments, and ancient sedimentary and magmatic rocks. The usual As concentrations in "pure" (i.e., anthropogenically uncontaminated) sediments and rocks are 5–10 ppm, although the sediments and rocks of some marine basins are manyfold (and sometimes even one order of magnitude) higher. One of these basins is the Baltic Sea, in which As concentrations are particularly high in areas where significant amounts of warfare poisonous agents were sunken after World War II. These agents were contained in artillery shells, aircraft bombs, various containers, etc. These areas are, first of all, the Borholm Deep (90–105 m deep), the southern part of the Gotland Deep (lying athwart the seaport of Liepaja, Latvia, and having depths of 100–180 m), and some coastal areas of the Baltic and its shallow-water bays [1].

It is interesting to reveal the reasons for high As concentrations in Baltic sediments and to determine whether chemical weapon materials (CW) sunken there 55 years ago are a contamination source [1–3] or high As concentrations at the sinking sites of CW are a mere coincidence [4, 5], and As originates not from the CW but has other sources. It is also important to determine why high As concentrations were detected in the Vistula Lagoon [4] where no CW has been sunken. To solve these problems, we collected and analyzed a few hundred samples of bottom sediments (including a few short and long columns) and used, for comparison, data on columns from the Atlantic Ocean and our earlier materials [6] on As contents in plankton and water and air particulate matter [Table 1].

MATERIALS AND METHODS

Bottom sediments were sampled with Okean-50 bottom grabs, Niemiste tube, and gravity corers 127 mm in diameter. The columns were usually cut first along and then into vertical sections 5 cm long. Sediment columns from the Niemiste tube were cut into sections 1 cm long to a depth of 10 cm and then into sections 2–3 cm long. We used the uppermost 3 cm (layer 0–3 cm) of the grab samples. After their visual description, smaller sample portions were packed into polyethylene pockets for further granulometric analysis, and the remaining portions of the material were further divided into two parts, one of which was then trans-

ferred to the Karpinskii All-Russia Research Institute of Geology (VSEGEI) in St. Petersburg and the other to the Atlantic Branch of the Shirshov Institute of Oceanology, Russian Academy of Sciences, in Kaliningrad. The latter portions were dried and pulverized. Upon their chemical preparation by means of acid dissolution, the samples were analyzed for Ca, Mg, K, Na, Fe, Mn, Cu, Zn, Co, Ni, Cr, and Li by flame atomic absorption on a S-115-M1 spectrophotometer [7, 8] and for Cd, Pb, As, Ag, and Sb on an atomic absorption spectrometer equipped with a KVANT-Z.ETA electrothermal atomizer. The above-mentioned elements were analyzed in compliance with certified techniques for quantitative chemical analysis (QCA): NSAM 450S, NSAN 155-KHS, and others. The analyses were carried out at the chemical analytical laboratory of the Atlantic Branch of the Shirshov Institute of Oceanology, Russian Academy of Sciences, which have been certified by the Committee for State Standards of the Russian Federation (accreditation certificate no. ROSS.RU.513352 of July 1, 2002). The detection limit was 1 ppm for As at MSD of no higher than 30%. In addition to the elements listed above, other elements (Al, Si, P, and various species of C and N) and the granulometric composition of the sediments were determined at the Atlantic Branch of the Shirshov Institute of Oceanology, Russian Academy of Sciences.

In order to obtain information as quickly as possible, the dried samples of bottom sediments transferred to the Karpinskii All-Russia Research Institute of Geology (VSEGEI) were analyzed for As on a SPEKTROSKAN X-ray analyzer (analyst A.G. Grigor'ev). The As contents in bottom sediments from the areas where CW was sunken in the Bornholm Deep, Baltic Sea, obtained by atomic absorption on the KVANT analyzer and by X-ray fluorescence on the SPEKTROSKAN are compared in Fig. 1. Samples for analysis by these methods were collected at the same sites but from different sediment columns, from layers 0–2 cm (because of the scarcity of material for analysis). Because of this, the differences between analyses of individual samples could be caused by both the analytical inaccuracies (including those of QCA) and the natural uneven As distribution in the bottom sediments (particularly where CW was sunken). It is known that XRF analysis on SPEKTROSKAN is analytically less sensitive than atomic absorption with the electrothermal atomization of the samples but is quicker and more suitable for analyzing As-enriched bottom sediments and their quick identification.

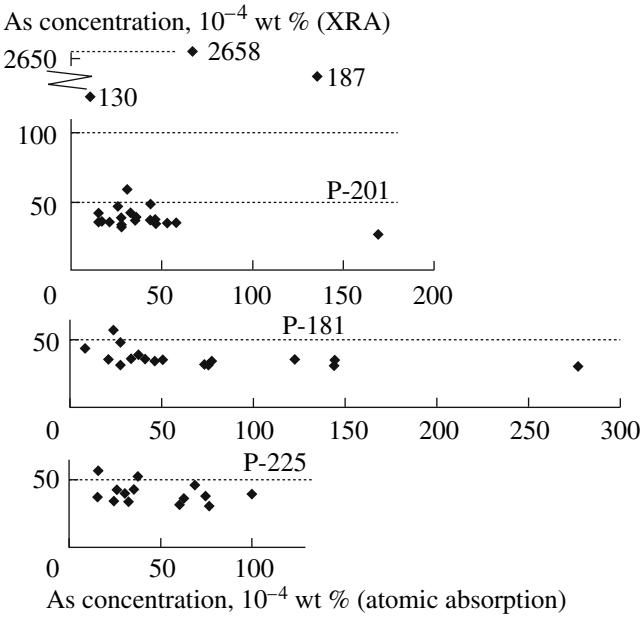

Fig. 1. Comparison of As concentrations in bottom sediment samples from the burial sites of warfare poisonous agents in the Bornholm Deep, Baltic Sea, analyzed on a SPECRTOSKAN X-ray analyzer (XRA) at the Karpinskii All-Russia Research Institute of Geology (VSEGEI) [3] and by atomic absorption on a KVANT.Z-ETA at the Atlantic Branch of the Shirshov Institute of Oceanology, Russian Academy of Sciences [4].

RESULTS AND DISCUSSION

Arsenic Distribution in the Bottom Sediments

At the Bornsholm Deep, samples were collected within three relatively small areas (sites 181, 201, and 205; Fig. 2) at which the bulk of the sunken CW was concentrated. All three areas have water depths of 93–100 m, with the seafloor consisting of terrigenous (clayey) Middle and Late Littorina pelitic greenish gray oozes, which sometimes contain black hydrotroilite films. The oozes are very loose, semiliquid within the uppermost 0–3 cm and very soft beneath and have very high moisture content (70–80% and 60–70% at depths below 20–30 cm). The thicknesses of the loose marine Holocene (with an age of 8000–0 years) oozes exceeds 3–4 m.

The oozes are high in organic carbon (4.95–7.84%), phosphorus (0.05–0.10%), and manganese (0.03–0.90%). In the uppermost 0–3 cm layer of the pelitic oozes of the Bonrholm Deep, strongly elevated As concentrations (100–277 ppm) are typical of samples collected in the immediate vicinity of the sunken vessel, which possibly carried chemical weaponry materials. These oozes have obviously elevated concentrations of Mn (0.10–0.48%) at Fe concentrations corresponding to the average values for sapropelic pelitic oozes (3.25–4.75%) and elevated C_{org} (6.04–6.88%). A trace element other than As contained in the oozes in elevated concentration is Cd (0.10–0.70 ppm), and the oozes show elevated concentrations of P (0.07–0.09%). The column of gray sapropelic oozes in the Bornholm Deep (Site PSH-4027, column length 39 cm) contains 12–41 ppm As at elevated concentrations of Mn (0.15–0.70%), Pb, and Zn (Table 2).

The average As contents in the upper 0–3 cm layer of oozes from the Bornholm Deep is 53 ppm, and these

Fig. 2. As distribution in the uppermost layer (0–5 cm) of bottom sediments in the Baltic Sea. Numerals near sites are As concentrations in the bottom sediments, 10^{-4}% (modified after [4]). The numerals 181, 3201, and 2225 in the Bornholm Deep are the numbers of sites examined in detail. Site D-6 is near oil drilling platform D-6 at the Rybachii Shoal, near the seaport of Klaipeda. Crosses, triangles, and circles show the location of geological observation sites examined by various research vessels; numerals near these symbols are the As concentrations. Psh-4027, GF-3, Kas, and others are the numbers and codes of individual sites; isobaths are in meters. Inset A shows the numbers of sites with the highest As concentrations in various areas in the Baltic Sea (see tables).

Table 1. Average As concentrations (ppm) in plankton, particulate matter in seawater, and Fe–Mn nodules

no.	Material type	As
	Plankton and particulate matter	
1	Oceanic plankton	10
2	Plankton of the Baltic Sea	4.2
3	Particulate matter from the Atlantic Ocean	11
4	Particulate matter from the Pacific Ocean	14
5	Separated particulate matter from the Baltic Sea	14
6	Eolian suspension in air above the Atlantic Ocean	7.4
7	Continental clayey rock	10
	*Fe–Mn crusts and nodules**	
8	Fe–Mn crusts of the Sierra Leone Rise, Atlantic Ocean	45–546
9	Baltic Sea, including:	96–653
	(a) Gulf of Riga	334
	(b) Eland Deep	180–325
	(c) Bornholm Deep (Site PSH-2551)	653
	(d) Gotland Deep	96

* After [8].

oozes contain (also on average) 6.69% C_{org}, 0.09% Mn, and 3.99% Fe. Note that the differences between the As concentrations in samples from sites 181, 201, and 205 (seafloor area ~2 km^2 each) are from 8 to 277 ppm. This suggests that As originates from point sources and is not transported for long distances (of more than 100–200 m) from the sources.

Oozes in the Gdansk Deep at depths of 70–105 m contain relatively little As: from 4 to 39 ppm, i.e., less than its clarke for clays and shales (10 ppm). However, closer to the shore, which is composed of coarse-grained silt, sand, and, sometimes, sand-gravel deposits, the As content in most of our samples notably increases, so that two samples from the vicinity of the Kurshskaya Spit (depths of 10 and 9 m) and near drilling platform D-6 contain 69–180 ppm As (Table 3, Fig. 2). Such high As concentrations were detected in sand and coarse-grained silt in the seashore near the spit (Table 3) and in the sandy–gravel deposits and sand at platform D-6 (in three samples: 69, 102, and 122 ppm). It is worth noting that an elevated As concentration (70 ppm) was detected at a site between the drilling platform and Cape Sambian (seaport Pionerskii) at a depth of 28 m.

Gray terrigenous oozes with hydrotroilite (layer 0–8 cm) from the Northern Baltic Deep (Site PV-1) contain 6–40 ppm As (Table 4); i.e., some layers contain As concentrations equal to its four clarkes for clays and shales. These oozes rest on gray Ancylus clays (layer 9–10 cm) containing 9 ppm As. The Littorina oozes and Ancylus clays are separated by a unit of

Table 2. Concentrations of As and other elements (Fe and Mn in wt %; Cu, Zn, Pb, and As in 10^{-4} wt %) in the silt–pelitic oozes, column PSH-4027, depth 93 m, Bornholm Deep (55° 21.48' N, 15° 43.07' E)

Layer	Fe	Mn	Cu	Zn	Pb	As
3–4	4.35	0.15	33	155	43	13
7–8	4.08	0.30	30	155	38	22
8–9	4.20	0.25	33	155	43	13
9–10	4.08	0.25	25	105	28	13
10–12	4.15	0.30	25	100	23	16
12–14	4.28	0.68	38	120	19	18
14–16	4.20	0.70	33	95	24	28
16–18	4.50	0.48	20	120	22	22
18–20	4.40	0.68	33	145	22	40
22–24	6.00	0.80	25	125	21	34
24–26	4.33	0.75	30	85	19	18
26–28	4.53	0.30	25	120	22	16
28–30	4.20	0.35	25	120	21	12
30–32	4.03	0.83	20	125	19	21
32–34	4.10	0.60	20	130	18	41
34–35	4.08	0.53	33	115	19	17
Average	4.34	0.50	28	123	25	22

Table 3. Chemical composition of sediments from the Gdansk Deep, Baltic Sea, in the vicinity of drilling platform D-6 and of Curian Spit, where the As concentration is 69–180 ppm. Fraction 1–0.1 mm and SiO_{2tot} through Mn are in wt %; Cu through Ba is in 10^{-4} wt % (ppm)

Site	Depth, m	Layer	Type of sediments	Fraction 1–0.1	SiO_{2tot}	Al	Fe	Mn	Na	K	Ca	Mg	Cu	Zn	Ni
4l	29	0–5	GR	32.9	–	–	1.09	0.02	1.24	1.15	1.75	0.48	11	63	27
4807	28	0–3	PS	72.4	80.0	1.75	0.74	0.02	0.64	0.80	0.79	0.20	8	16	22
4812	10	0–5	PS	57.9	80.0	1.37	1.50	0.03	0.63	0.91	1.55	0.50	8	16	29
4793 (6l)	29	0–5	PS	97.2	–	–	0.52	0.02	0.78	0.80	1.23	0.15	9	11	20
10l	29	0–5	PS	68.5	–	–	1.44	0.03	1.09	1.19	2.15	0.90	7	62	27
4810	9	0–3	KA	49.2	–	–	2.01	0.06	0.61	0.84	1.72	0.60	11	22	25

Site	Depth, m	Layer	Type of sediments	Fraction 1–0.1	Cr	Co	Li	Ag	As	Cd	Pb	Sb	Hg	Ba
4l	29	0–5	GR	32.9	30	9	7	0.2	122	<0.1	7	<1	0.01	190
4807	28	0–3	PS	72.4	45	10	<5	0.2	70	0.1	6	<1	0.05	150
4812	10	0–5	PS	57.9	55	<5	<5	<0.1	90	<0.1	6	<1	<0.01	200
4793 (6l)	29	0–5	PS	97.2	23	<5	<5	0.7	69	<0.1	5	<1	0.05	160
10l	29	0–5	PS	68.5	54	7	5	0.1	107	<0.1	7	<1	0.02	320
4810	9	0–3	KA	49.2	50	<5	5	<0.1	180	<0.1	8	<1	0.05	140

mixed sediment: clayey ooze with an elevated Fe concentration (5.88%). This unit was detected to contain 131 ppm As (its 13 clarkes).

The gray pelitic oozes of two columns (GF-2 and GF-3; Fig. 2) from the Gulf of Finland (layer 0–10 cm) were determined to contain 5–27 ppm As at low (0.05–0.06%) Mn concentrations and slightly elevated concentrations of Fe (1.33–5.35%) (Table 5). The As concentrations in these rocks are either close to the clarke values for clays and shales or exceed them (by factors of 2–3) in a few samples.

Column Kas (layer 0–10 cm) differs from the others. Its upper part is made up of weakly oxidized brownish silt–pelitic ooze, which is underlain by gray Ancylus clay. The ooze and clay are separated by a transitional unit of ooze–Ancylus clay. The upper weakly oxidized layer of Littorina ooze (0–2 cm) contains up to 133 ppm As at 7.12% Fe and 1.19% Mn. This unit rests on grayish black ooze with small Fe–Mn nodules and micronodules. The ooze contains 150 ppm As, up to 8.26% Fe, up to 1.81% Mn, and elevated P concentrations (up to 0.56%). The underlying layer (4–7 cm) is transitional ooze–clay, which is, in turn, underlain (at 7–10 cm) by gray Ancylus clay containing up to 7–9 ppm As, 0.08–0.09% Mn, and 4.50–4.93% Fe.

As concentrations from 6 to 45 ppm were determined in the area of the Neman River mouth at the town of Nida in Kurshskii Bay (Fig. 3). These values are also elevated compared to the clarkes for clays. Roughly equal As concentrations (10–45 ppm) were found in the southern part of Kurshskii Bay, with the highest values (45 ppm) detected near the mouth of the Deima River.

The sediments of the Vistula Lagoon were determined to contain 3–57 ppm As in layer 0–3 cm (Fig. 4) and 9–133 ppm As in short (5–66 cm) columns of the oozes. Hence, the sedimentary sequences include units notably enriched in As compared to the upper layer (Fig. 5). Four columns of fine-grained silt, silty–pelitic, and pelitic oozes have average As concentrations of 32, 85, 50, and 30 ppm. It is worth mentioning that the lowest As concentrations (both average for a column and in individual units) were determined in column 104 (depth 3.5 m), which is the closest to the seaport of Kaliningrad. However, the uppermost 10 cm of column 104 include thin lamina with elevated As concentrations (up to 73 ppm). The lamina are also characterized by elevated concentrations of Zn, Pb, Cd, Cr, and P but are poor in Fe (3–4%) and Mn (0.03–0.06%). The highest As concentrations are characteristic of column 102 (depth 4 m), which is located near Vistula Spit. Note that all four columns are characterized by elevated As concentrations in the upper 5–12 cm of the oozes, which obviously accumulated over the past several hundred years. However, the maximum As concentrations of 113 and 97–114 ppm in columns 91 and 102 (respectively) were determined in their lowermost stratigraphic units.

As was mentioned previously [9, 10], practically all seas and oceans show distributions of chemical elements corresponding to the rule of fractions, with most of the usually determined elements distributed according to the rule of the pelitic fraction (<0.01 mm); i.e., the contents of elements increase with increasing contents of the pelitic fraction in the sediments (in the succession sand–coarse-grained silt–fine-grained silt–silty

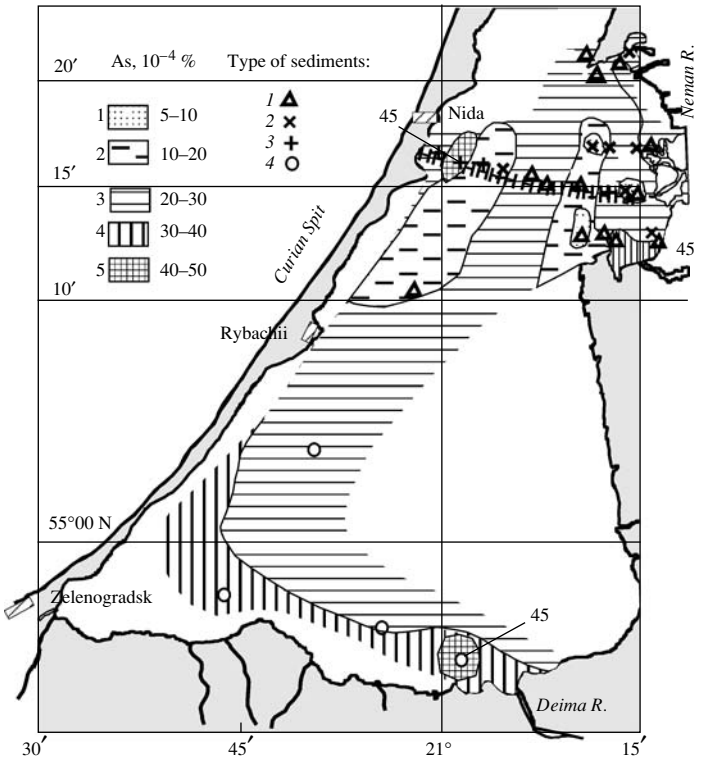

Fig. 3. As concentrations in the upper layer (0–5 cm) of bottom sediments of Kurshskii Bay (ppm = 10^{-4} wt %). Granulometric types of sediments: (*1*) sand; (*2*) coarse-grained silt; (3) fine-grained silt ooze; (*4*) silt–pelitic ooze.

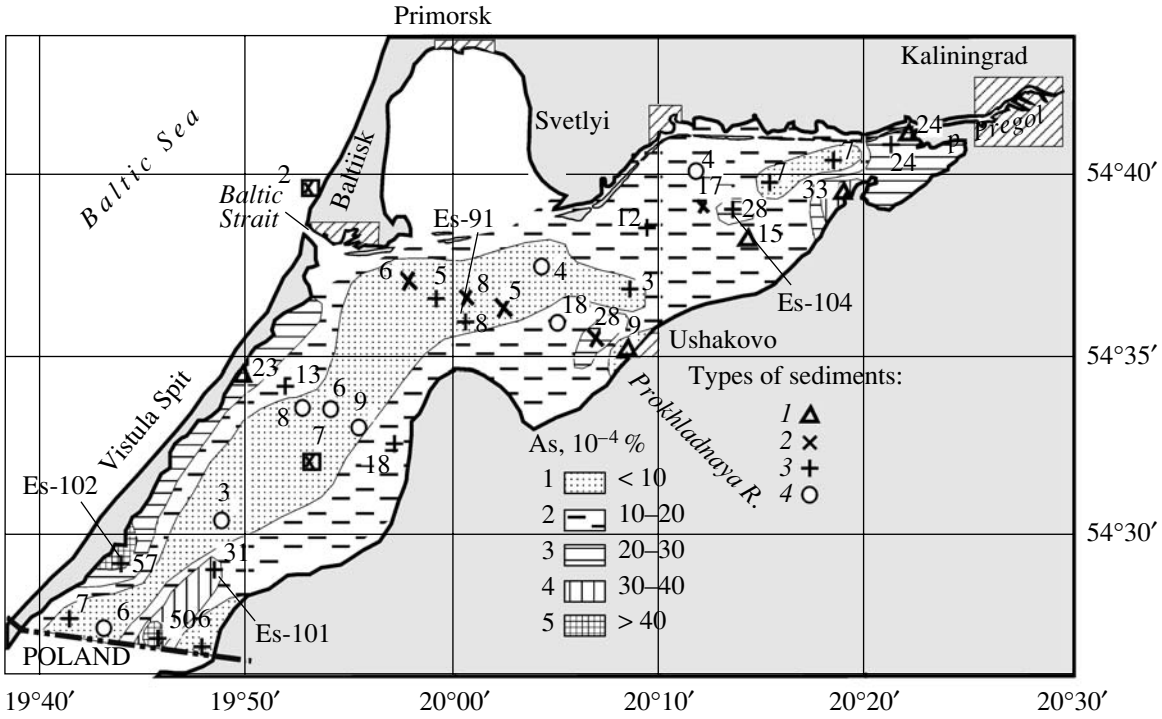

Fig. 4. As distribution in the upper layer (0–5 cm) of bottom sediments in the northern (Russian) part of the Vistula Lagoon. Numerals near sites are the As concentrations (10^{-4} wt %). Es-102 is the number and position of sites at which short (less than 66 cm) columns were collected with a Niemeste tube. Granulometric types of sediments: (*1*) sand; (*2*) coarse-grained silt; (*3*) fine-grained silt ooze; (*4*) silt–pelitic ooze. Symbols of sediment types are positioned in the map at the sampling sites of these sediments.

Table 4. Fe, Mn, P, As, Cd, and Pb concentrations in the silt–pelitic and pelitic oozes in columns from the Northern Baltic Sea and Gulf of Finland

Layer, cm	%			10^{-4}%			Ooze description
	Fe	Mn	P	As	Cd	Pb	
Gulf of Finland: Site Kas – 54 m, 55°57.47′ N, 24°58.88′ E							
0–1	4.89	0.33	0.38	35	0.5	11	Eh barrier +23 mV,
1–2	7.12	1.19	0.49	133	0.6	12	Oxidized brownish ooze
2–3	8.26	1.81	0.56	146	1.1	15	Eh barrier –32 mV,
3–4	7.00	1.56	0.47	150	0.9	13	Grayish black ooze with Fe–Mn nodules
4–5	3.53	0.47	0.22	45	0.5	11	Transitional ooze (clay)
5–6	2.52	0.13	0.07	32	0.4	10	
6–7	4.64	0.09	0.07	34	0.1	8	Gray homogeneous clay (“Ancylus”)
7–8	4.93	0.09	0.07	8	0.1	9	
8–9	4.50	0.09	0.07	7	0.1	9	
9–10	4.66	0.08	0.06	9	0.1	9	
Average for the column	5.20	0.58	0.25	59.9	0.4	10.7	
Northern Baltic Sea: Site PV-1 – 74 m, 59° 35.1′ N, 23° 25.46′ E							
0–1	4.12	0.06	0.09	17	0.3	12	Greenish gray ooze with an uppermost 1-mm oxidized film
1–2	3.66	0.06	0.07	15	0.3	11	Grayish ooze with H_2S smell (with hydrotroillite)
2–3	4.36	0.06	0.08	12	0.6	18	
3–4	4.26	0.05	0.07	6	0.6	21	
4–5	4.30	0.05	0.07	31	0.6	19	
5–6	4.91	0.06	0.07	36	0.5	21	
6–7	4.50	0.05	0.07	40	0.5	20	
7–8	4.75	0.06	0.07	35	0.3	17	
8–9	5.88	0.05	0.05	131	0.2	14	Transitional layer (ooze–clay), Fe sulfides
9–10	4.45	0.06	0.06	9	0.3	17	Gray clay (“Ancylus”)
Average for the column	4.52	0.06	0.07	33.2	0.4	17	

pelite–pelitic ooze). Nothing like this was observed for As: its higher or lower contents can be found in any of the aforementioned granulometric types of sediments (Fig. 6). Hence, As is distributed over the seafloor surface independently of the depth or the distance from the shore. Below we will try to elucidate the reasons for this behavior of As.

Arsenic and Other Contaminating Trace Elements

Sediments with elevated As contents from several sites are also characterized by elevated concentrations of Cd, Pb, Cu, Zn, and some other elements. Elevated (relative to the clarkes) contents of these elements are usually caused by anthropogenic activities. A source of Cd can be both sunken CW and industrial wastes. In the Bornholm Deep, which is characterized by high As concentrations, the Cd contents are also slightly elevated (up to 0.50–0.70 ppm, Table 1). Pelitic oozes in the Gulf of Finland contain 0.20–0.80 ppm Cd (Table 5), and the oozes with Fe–Mn nodules contain up to 1.1 ppm Cd. Both Cd and As are strongly correlated with Fe ($R = 0.55$), Mn ($R = 0.76$), and P ($R = 0.73$). The uppermost unit (0–10 cm) of oozes in the Vistola Lagoon is enriched not only in As but also in C_{org}, P, Pb, and Cd (Fig. 7). The reason for this enrichment is thought to be anthropogenic activity.

Arsenic in Bottom Sediments Elsewhere in the World Ocean

The sediments of the Black Sea and hemipelagic oozes of the Pacific Ocean contain As in amounts within the average values for clays or slightly lower (Table 6). Even pelagic clays of the transitional type from the Pacific Ocean contain 9 ppm As, i.e., roughly the same as in modern oozes in the Baltic Sea at sites away from the sources of this element (i.e., away from river mouths or CW burial sites). The As concentrations of natural pure Ancylus clays in the Baltic Sea accumu-

Table 5. Concentrations of chemical elements in columns of gray terrigenous (T) and pelitic (PL) oozes from the Gulf of Finland

Layer, cm	Type of sediment	SiO_{2tot}	Al	$CaCO_3$	C_{org}	Fe	Mn	Pb	As	Cd
		wt %						10^{-4}%		
Column GF-2, depth 88 m (59° 32.00′ N, 23° 14.40′ E)										
0–1	T PL	51	7.1	1.16	4.33	4.52	0.04	10	16	0.20
1–2	T PL	54	7.8	0.91	3.72	4.66	0.05	17	14	0.30
2–3	T PL	55	7.9	3.50	3.56	4.60	0.05	19	22	0.30
3–4	T PL	54	7.8	1.59	3.76	4.33	0.05	19	18	0.80
4–5	T PL	54	7.7	4.00	4.22	4.22	0.05	19	23	0.30
5–6	T PL	53.8	8	3.41	4.56	5.06	0.05	20	34	0.50
6–7	T PL	53	8.4	2.34	4.34	5.21	0.05	25	15	0.70
7–8	T PL	54	7.9	2.66	4.66	5.32	0.05	26	14	0.80
8–9	T PL	52	7.8	2.84	4.05	5.38	0.05	24	27	0.80
9–10	T PL	52	7.6	3	3.85	5.02	0.06	23	9	0.60
Average		*53.33*	*7.8*	*2.54*	*4.11*	*4.83*	*0.05*	*20*	*19*	*0.53*
Column GF-4, depth 93 m (59° 23.30′ N, 22° 27.77′ E)										
0–2	T PL	52	7.9	1.59	3.47	5.41	0.06	20	7	0.40
2–4	T PL	53.5	7.4	1.25	3.68	4.80	0.05	17	24	0.30
4–6	T PL	51	7.2	2.75	3.70	5.57	0.05	19	13	0.50
6–8	T PL	52	6.7	3.84	5.22	5.55	0.04	16	5	0.80
8–10	T PL	52	7	1.75	4.28	5.33	0.05	23	10	0.80
Average		*52.1*	*7.24*	*2.24*	*4.07*	*5.33*	*0.05*	*19*	*12*	*0.56*

lated over the past 8–9 ka and not contaminated with the products of anthropogenic activity are reported in Table 7.

Arsenic Sources

The Baltic Sea includes various As sources: (1) natural sources (soils, air suspensions, rocks, waters, etc.); (2) chemical weaponry materials; (3) agricultural toxic chemicals; (4) products of the metallurgical industry; (6) combusted coal and other fuels; and (6) Ordovician rocks containing kerogen exposed within insignificant seafloor areas in the Northern Baltic (a generally insignificant As source, As concentrations in the rocks are equal to 150 ppm [11]).

Anthropogenic sources are responsible for 3–12 times As amounts coming from natural sources [12]. The most poisonous contaminants contain As(III) (white arsenic As_2O_3), which is rare in nature (because of its instability) and is synthesized artificially. The As amounts produced by the base-metal industry accounts for 82% (on average) of the overall anthropogenic As contamination [12]. The application of As-bearing pesticides results in the contamination of the soils. According to the standards approved in the Russian Federation (GN 2.11.7.020-94), the approximate permissible concentration (APC) for As in sandy and sandy–clayey soils is 2 ppm, and this value for clayey and loamy soils is 10 ppm. Arsenic is gradually leached from soils, is transported to marine basins, and eventually enriches their bottom sediments. The combustion of various fuel types (particularly coal) and base-metal smelting are associated with As emissions to the atmosphere, its scatter over significant areas, and eventual precipitation with dust, which is washed by rains onto the land or sea. We determined that eolian suspension in air above the Atlantic Ocean contains 7.4 ppm As, whose residence time in the atmosphere does not exceed nine days. The world's industrial production of As(III) amounted to 50000–57000 tons in 2000 [12].

The supply of As by rivers flowing into Kurshskii and Vistula lagoons (this As seems to be related to anthropogenic agricultural activity) can be assayed from the As contents in river deposits and sediments deposited near the mouths of the rivers. Most samples from the Atmata and Skirvite arms in the Neman delta (Fig. 3) contained up to 20–38 ppm As (one sample contained as much as 45 ppm As), i.e., three to five times more than its concentration in pure Ancylus clays of the Baltic Sea.

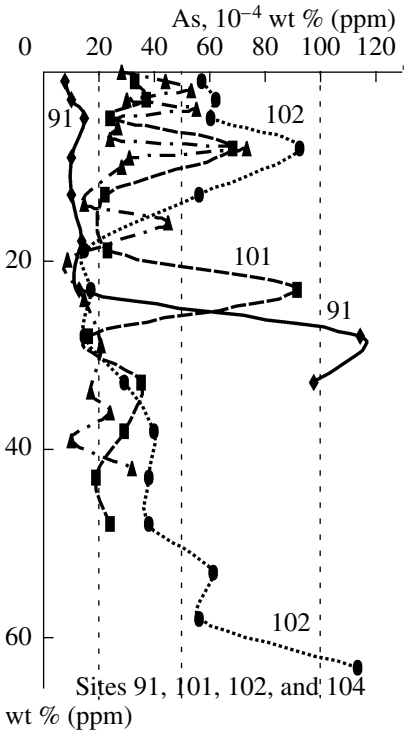

Fig. 5. Distribution of As concentrations (10^{-4} wt % or ppm) in four columns of ooze from the Vistula Lagoon. The location of the columns is shown in Fig. 4 (shown together with the expedition code Es).

The deposits of the Deima (Kurshskii Bay) and Pregol (Vistula Lagoon) rivers (Figs. 3, 4) contain 20–70 ppm As. Near the mouth of the Deima River (Site Es-129, depth 2.8 m, sand), the deposits were determined to contain 45 ppm As.

The deposits of the Pregol River contain 20–70 ppm As, and only one ooze sample from this river (from its deepest part at the center of the town of Kaliningrad, near the viaduct) contained anomalously high concentrations of As (247 ppm) and Cu (368 ppm) (Fig. 8).

Samples from the estuary of the Pregol River, Kaliningrad Bay, also showed somewhat elevated As concentrations: two samples contained 21 ppm As.

These data can be compared with analogous data on the Amazon River. Column PSH-1044 (layer 0–439 cm) was taken near the mouth of this river at a depth of 13 m, and its fine-grained silt fraction contained 7–24 ppm As (14 samples), and some individual lamina contained as much as 56–125 ppm As [13]. Conceivably, these laminae contain authigenic minerals (and/or Fe–Mn micronodules or Fe films) that concentrate As. However, the Mn and Fe contents in these lamina are low.

Hence, the deposits of all of the aforementioned four rivers contain two–five times more As than in the Ancylus clays of the Baltic Sea. The most probable reason for this increase was the washing of the decomposition products of pesticides, herbicides, and fertilizers from fields. The high As concentration (247 ppm) in the ooze sample from the Pregol River (in the central part of the town of Kaliningrad) was most probably caused by anthropogenic industrial activity (metal processing and coal and black oil burning) in Kaliningrad.

In 1946–1949, chemical warfare materials from the territory of Germany were sunken in the sea, mostly in the Skagerrak and Baltic Sea [1, 2, 14]. The sunken warfare poisonous agents (WPA) included the following: (1) vesicants (yperite and yperite-based substances); WPA with As-bearing compounds (Clark 1, lewisite, adamcite, and "arsenic oil"); WPA with P-bearing compounds and harassing WPA (acetonyl chloride, diphosgene, tabun, and sarin); and some other WPA types (cyclone B) [15]. Both lewisite and adamcite contain As. WPA leaks and hydrolysis lead to As release to the environment, i.e., bottom sediments. Because of this, when examining CW dumping sites, we explored first of all seafloor areas where sunken naval vessels were found that supposedly could carry chemical warfare materials, which were, first and foremost, three small areas in the Bornholm Deep (Fig. 2).

In the Bornholm Deep and other Baltic areas, bombs, shells, and containers with poisonous agents were discarded from vessels and scattered over large seafloor territories. Some of the bombs and shells sank within oozed fields in the seafloor and were eventually buried in these deposits, while others occurred on solid (sand and moraine) seafloor surface. The latter were rolled over the seafloor surface and were often uplifted by fishermen in the process of trawling. An insignificant amount of the munitions with poisonous agents was sunken together with the vessels themselves; two of these vessels were detected in the Bornholm Deep. These vessels were examined via submarine TV cameras and side-looking locators. The vessels are halfway submerged into the ooze; their rails are festooned with fragments of nylon fishing nets and trawls [1]. The naval vessels themselves and the steel shells of the bomb, artillery projectiles, and containers have walls 8–10 mm thick and were heavily rusted when occurring under water for 55 years. Their filler chemicals either make contact with seawater (Fig. 9) or fall out and are hosted in the sediment. Portions of these warfare poisoning agents that fell out of their shells and containers and had the consistency of flowing honey were lifted aboard the R/V *Professor Shtockman*. Luckily, nobody was killed or injured.

Most occurrences of anomalously high As concentrations in the upper ooze layer (0–5 cm) are spatially restricted, as was mentioned above, to the sites of two sunken vessels, which possibly contained CW. The As concentrations in deeper ooze layers (5–50 cm) corresponded to the background values characteristic of pelitic oozes in the Bornholm Deep (20–40 ppm) (Table 2). No anomalies in the distributions of other elements (Cu, Pb, Cd, Sb, Ag, Cr, Fe, Mn, Mg, Li, Co, Ni, Na, K, Al, Si, P, N, and C) were detected. The only exception

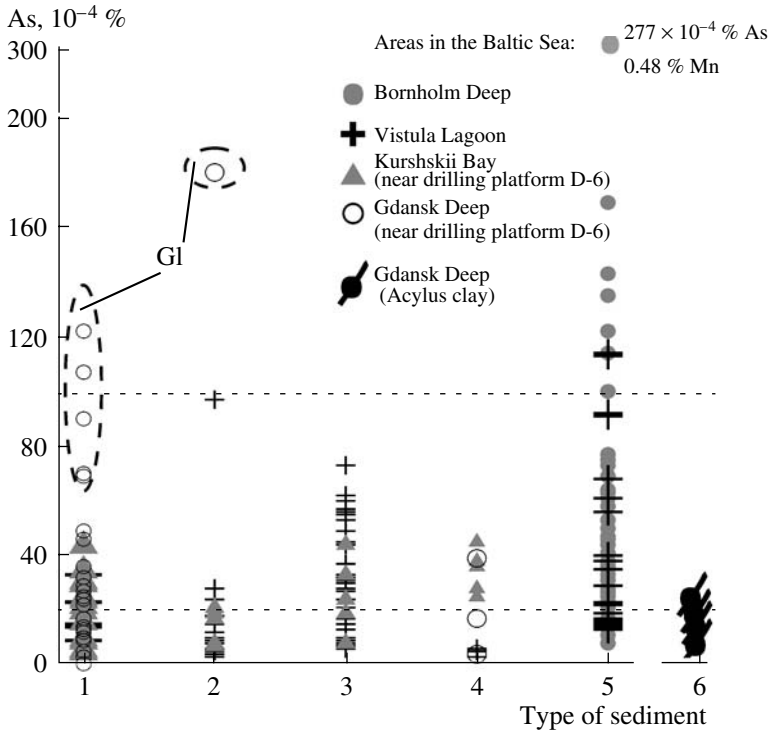

Fig. 6. Dependence of As concentration on the granulometric type of bottom sediments (layer 0–5 cm) in various areas of the Baltic Sea (see Fig. 2). (*1–6*) Types of sediments: (*1*) sand, (*2*) coarse-grained silt, (*3*) fine-grained silt, (*4*) silt–pelitic ooze, (*5*) pelitic ooze, (*6*) lacustrine (*Ancylus*) clay. In contoured samples, Gl—significant admixture of terrigenous glauconite (at opencast mines of the Yantarnyi mining and production complex).

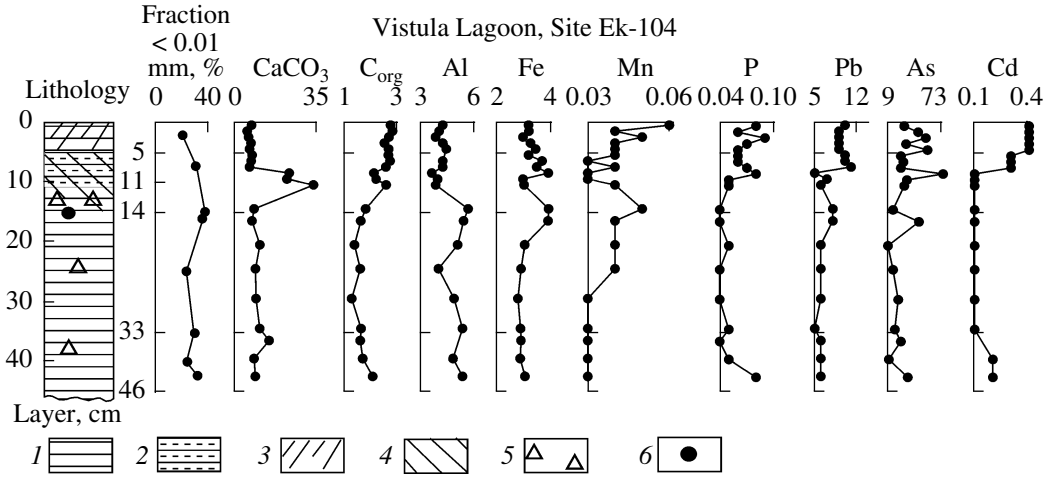

Fig. 7. Concentrations of As and other chemical elements and components in oozes from the Vistula Lagoon (column Es-104) ($CaCO_3$–P in wt %, Pb–Cd in 10^{-4} wt %). Lithological types of sediments: (*1*) pelitic ooze, (*2*) greenish gray silt–pelitic ooze, (*3*) brownish ooze, (*4*) dark gray to black ooze, (*5*) shell fragments, (*6*) wood fragments.

is Mn, whose contents in some samples with As were notably higher than the background concentrations in the gray oozes of the Baltic Sea (up to 0.20% as compared to average values in the gray oozes of the Baltic Sea equal to 0.04–0.05%) and even up to 0.80% in column PSH-4027 (Table 2). The same samples showed somewhat elevated concentrations of Zn and Pb. The warfare poisonous agents (WPA) could contain C, N, and P, but these elements should have been quickly oxidized to nitrates, phosphates, and carbon dioxide and

Table 6. As concentrations in sediments (layer 0–5 cm) from the Baltic Sea in comparison with As concentrations in sediments from the Black Sea and the Atlantic and Pacific oceans

Brief characterization of ooze	As, 10^{-4} %
1. Baltic Sea	
(a) *Northern Baltic Sea*:	
Reduced terrigenous ooze	5–34
(b) *Gulf of Gdansk*:	
Ooze and sand	5–73
Sand and gravel near drilling platform D-6	1–69
(c) *Vistula Lagoon*:	
Reduced ooze:	
layer 0–5 cm	8–62
layer 20–60 cm	13–114
(d) *Bornholm Deep*:	
Ooze (layer 0–5 cm)	8–277
*2. Black Sea**	
Modern sapropelic ooze (2.0–22.6% C_{org})	6
Ancient Black Sea sapropelic ooze (4.5–16% C_{org})	6–8
New Euixinian clay (0.5–1.0% C_{org})	5–6
*3. Atlantic Ocean***	
(a) Modern terrigenous and Late Quaternary fine-grained silty and silt–pelitic oozes near the mouth of the Amazon River (Site PSH-1044, layer 0–430 cm, depth 13 m)	11–25
(b) Same oozes but containing Fe-bearing crusts and nodules (layers 0–10 and 180–210 cm)	56–125
*4. Pacific Ocean**	
Littoral volcanic–terrigenous (reduced) ooze	3
Hemipelagic siliceous clayey ooze	2–3
Bathyal pelagic transitional clay	9

Notes: * According to [19];
** According to [13].

removed from the burial sites in a dissolved form. The same pertains to other hydrolysis products of WPA in seawater, for example, to secondary acids: HCl, HF, HCN, and others [4]. As a consequence of this reaction, the pH of the bottom waters was determined in August 1997 to be decreased to 6.36–6.78 [2]. The newly formed acids mix with seawater and pore waters and are removed outside the WPA burial site. Conversely, As is gradually disseminated in the water mass and is not removed outside the burial zones but is instead redeposited in the nearby bottom sediments. Upon leakage of chemical warfare, their hydrolyzed poisonous agents undergo the following transformations: lewisite (2-chlorvinyldichlorarsin)—chlorvinylarsenic acid—inorganic As species.

Speciation of Excess Arsenic Amounts in Bottom Sediments

Excess As in oozes is commonly thought to originate from chemical warfare, first of all, lewisite [3, 4]. However, the analysis of correlations between elements and the chemical analysis of some authigenic–diagenetic minerals and aggregates, such as Fe–Mn nodules and crusts and Fe sulfides, indicates that they contain 10–100 times more As than pure (uncontaminated) Ancylus clays. This can be particularly clearly seen in analyses of "pure" nodules and sulfides (Table 8). If the sediments contain Mn micronodules or tiny sulfide grains, these sediments have notably elevated As concentrations (Table 4). The presence of Mn micronodules can be identified by high or elevated concentrations of Mn or both Mn and Fe. The rocks show a clearly pronounced correlation between As and Mn in the former situation and of As with Mn and Fe in the latter ($R = 0.86$ and 0.85, respectively; Table 9). If the sediments contain Fe sulfides, these rocks show elevated concentrations of both Fe and As (Table 4, column PV-1, layer 8–9).

A strong correlation between As and Mn was also detected in the oozes of the Bornholm Deep ($R = 0.81$), Vistula Lagoon ($R = 0.46$), and Gdansk Deep ($R = 0.53$) (Figs. 10, 11). This suggests that As released during CW hydrolysis in the Bornholm Deep was immediately incorporated into solid particles, together with Mn. These were either amorphous Mn carbonates and rhodochrosite [13] or fresh gel-like particles of Mn hydroxides, which adsorbed As. Moreover, the oozes of this deep are quite rich in amorphous Fe sulfide (hydrotroilite) and contain pyrite crystals and aggregates. As could also be partly incorporated into the Fe sulfides, although the oozes of this deep display no strong correlation between As and Fe ($R = 0.34$).

Mn hydroxides are responsible for some above-clarke As contents in the Vistula Lagoon (the correlation coefficient between As and Mn $R = 0.46$), Kurshskii Bay ($R = 0.32$), Gdansk Deep ($R = 0.53$), and correspondingly, column Kas in the Gulf of Finland ($R = 0.84$). Ooze samples mixed with Ancylus clay (these oozes contain notable admixtures of sand and silt particles) from column PV-1 (layer 8–9 cm) contain As incorporated into Fe sulfides, as follows from the high concentrations of both Fe and As.

Elevated As concentrations (50–180 ppm) were also found in a number of surface sand samples and sand–gravel sediments (0–5 cm) from the Gulf Deep, near the Rybachii Shoal, in the vicinity of drilling platform D-6, and north of Cape Sambian (Table 10, Fig. 2). This fact suggests that the rocks were possibly either contaminated with anthropogenic As or contain Fe sulfides and Fe–Mn micronodules. However, the microscopical analysis of the 0.5–0.05 mm size fractions (Table 10)

Table 7. Differences in the concentrations of As (10^{-4} wt %) and other elements (wt %) and the fractions of <0.01 mm (%) in terrigenous Early Littorina oozes and Ancylus clays of the Gdansk Deep (site PSH-4803, depth 95 m, 55° 08.00′ N, 19° 37.00′ E)

Layer, cm	Fraction <0.01 mm	As	Fe	$CaCO_3$	C_{org}	Sediment type*
Early Littorina ooze						
201–202	49.3	4	4.09	3.00	4.12	fgso
202–203	49. 3	6	4.05	2.41	3.90	fgso
203–204	53.1	8	4.67	1.50	3.32	spo
204–205	49.7	5	6.23	2.59	2.42	fgso
Transitional ooze						
205–206	49.7	4	5.91	1.50	2.13	fgso
206–207	49.7	16	5.66	1.84	2.75	fgso
Ancylus ooze						
207–208	55.7	2	5.88	2.66	1.78	spo
208–209	57.5	4	5.66	2.75	1.58	spo
326–328	–	13	6.56	4.59	1.87	spo. sulfides ?
332–333	66.8	5	5.88	3.00	1.61	spo
333–334	66.0	4	5.15	2.66	1.52	spo
334–335	73.0	9	5.05	3.66	1.64	po
335–336	76.3	13	5.42	3.90	1.73	po sulfides ?

Note: * Sediment types: fgpo—fine-grained pelitic ooze; spo—silt–pelitic ooze.

indicates that the sediments contain no appreciable amounts of these authigenic minerals. They are rich in glauconite, which was transported to this area (platform D-6—Kurshskaya Spit) from the pulp of the Amber plant at the settlement of Yantarnyi. Although no As was detected in the glauconite, it can be hypothesized that this mineral can carry excess As amounts.

Arsenic in Seawater and Hydrobionts

The average As concentrations in oceanic water is 1–2 mg/l [12], and this element changes its valence from As^{5+} to As^{3+}. As is contained in seawater in the following four major groups of species: arsenates $HAsO_4^{2-}$, arsenites $HAsO_2$, methyl arsenates $CH_3AsO(OH)O^-$, and dimethyl arsenates $(CH_3)_2AsO_2^-$. Arsenates are the most thermodynamically stable As species, which predominates in the ocean; 95–100% As occurs in nature in the form of inorganic compounds (mostly arsenates), and 2–5% are organic compounds (mostly methyl arsenates). Methyl arsenates are concentrated generally in the euphotoc zone (the primary production zone), in which the maximum concentration of methyl arsenates amounts to 0.015–0.23 ppm, whereas their average concentration at a depth of 400 m decreases to 0.0083 ± 0.0006 μg/l. Dimethyl arsenates are also concentrated mostly in the euphotic zone of the ocean. Planktonic algae are able to synthesize methyl arsenate compounds, which, in turn, can reduce arsenates to arsenites. Low mobile As(III) that predominates in reduced environments in the form of arsenites ($HAsO_2$) is transformed into more mobile arsenate species ($HAsO_4^{2-}$) under reduced conditions [12].

Hydrobionts consume exclusively inorganic As, taking up 75% of it and releasing 25% unchanged. Inorganic As [particularly arsenites As(III)] are the most dangerous for marine species (the threshold concentrations for inverterbrata and fishes are 700–1000 μg/l). As(V) (arsenites) are much less toxic (approximately by a factor of

Table 8. As concentrations (10^{-4} wt %) in Fe–Mn nodules and crusts and in Fe sulfides

1. Fe–Mn *nodules and crusts**	
Crusts from the Sierra Nevada Rise, Atlantic Ocean	45–546
Baltic Sea,	96–653
including:	
(a) Gulf of Riga	334
(b) Eland Deep	180–325
(c) Bornholm Deep (Site PSH-2551)	653
(d) Gotland Deep	96
2. *Iron sulfides*	
Sulfides in Baltic oozes	270–440

* According to [18].

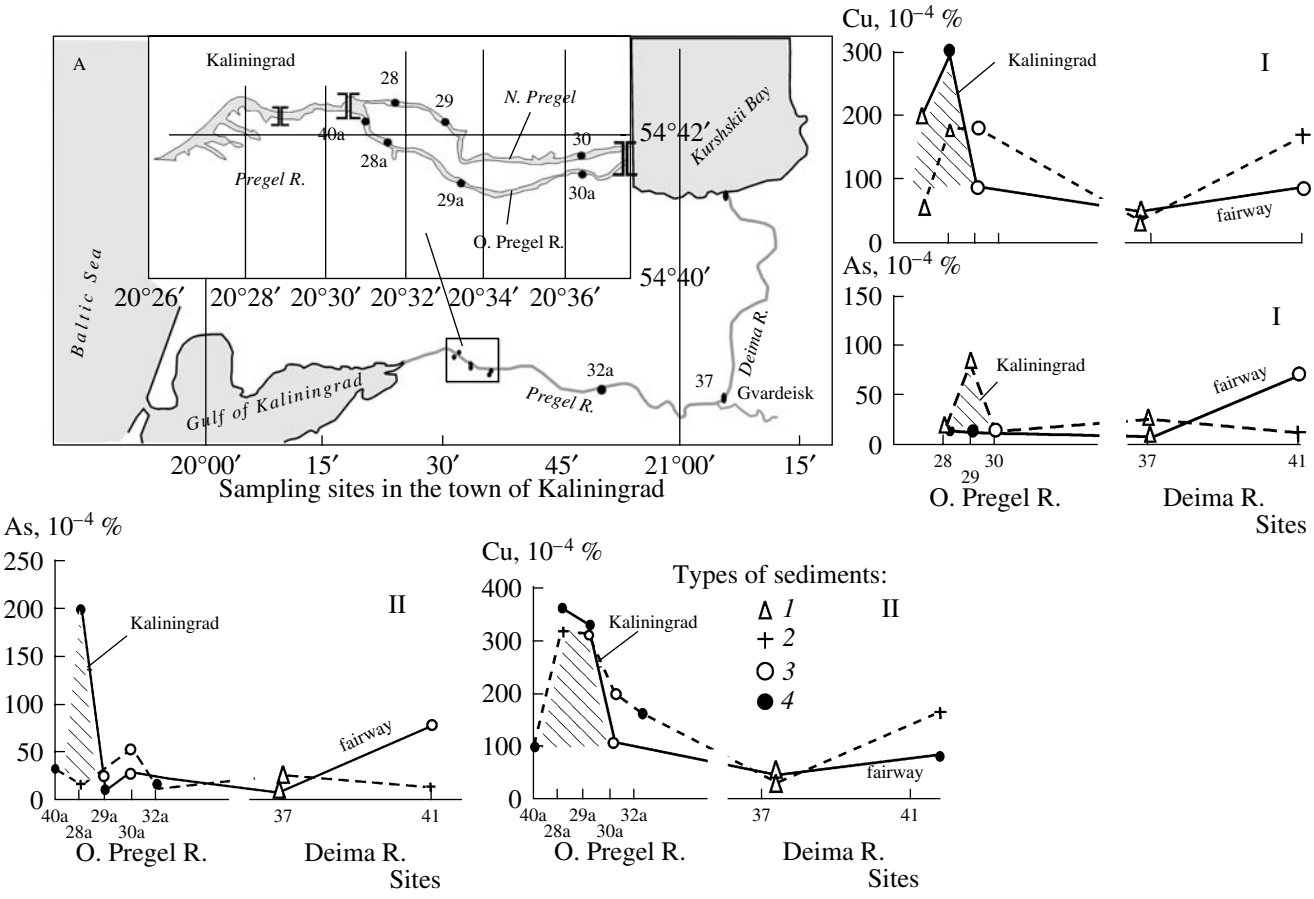

Fig. 8. As and Cu distributions in the bottom sediments of the Pregel and Deima rivers (concentrations are in 10^{-4} wt %, as of 2001). (A) Schematic map of the rivers and sampling sites (with sample numbers); (I) first sampling series; (II) second sampling series. Granulometric types of sediments: (*1*) sand, (*2*) fine-grained silty ooze, (*3*) silt–pelitic ooze, (4) pelitic ooze. Pregel River: O—Old Pregel; N—New Pregel. The shaded portions of the distribution correspond to the maximum Cu and As concentrations.

three) than arsenites. Marine organisms in oceans and seas contain from 1 (mollusks) to 80 (crustaceans) μg/l As. Marine fish tissues can contain from 0.08 to 2.27 ppm As [12], with sanitary standards for As in fish varying from 1 to 5 ppm (according to various data sources). Phytoplankton and separated particulate matter from the Baltic Sea contain 4.2 and 14 (on average) ppm As, respectively (Table 11).

Table 9. Correlation matrix (20 samples) for the concentrations of Fe, Mn, P, As, Cd, and Pb in silt–pelitic and pelitic oozes from the Gulf of Finland (sites Kas and PV-1)

Element	Fe	Mn	P	Pb	As	Cd
Fe	1	0.82	0.77	0.06	0.83	0.55
Mn	20	1	0.94	–0.10	0.83	0.76
P	20	20	1	–0.13	0.76	0.73
Pb	20	20	20	1	–0.01	0.45
As	20	20	20	20	1	0.59
Cd	20	20	20	20	20	1

Hazardous Factors of Elevated Arsenic Concentrations

The question arises whether high As concentrations in the bottom sediments are hazardous for humans living on Baltic shores. No alarming information was received over the past decades on human diseases related to As that had been contained in the sunken warfare materials. Marine organisms, first of all, fish can, as was mentioned above, accumulate As. However, the As concentrations accumulated in these organisms are harmless for human beings. At the same time, fish living at the sites of sunken warfare, particularly, where these materials are contained in corroded containers or shells aboard the vessels has not been analyzed for As (at least we are not aware of such published data). Fishermen catch this fish when trawling waters above the sunken vessels [1], and, hence, part of the sold fish orig-

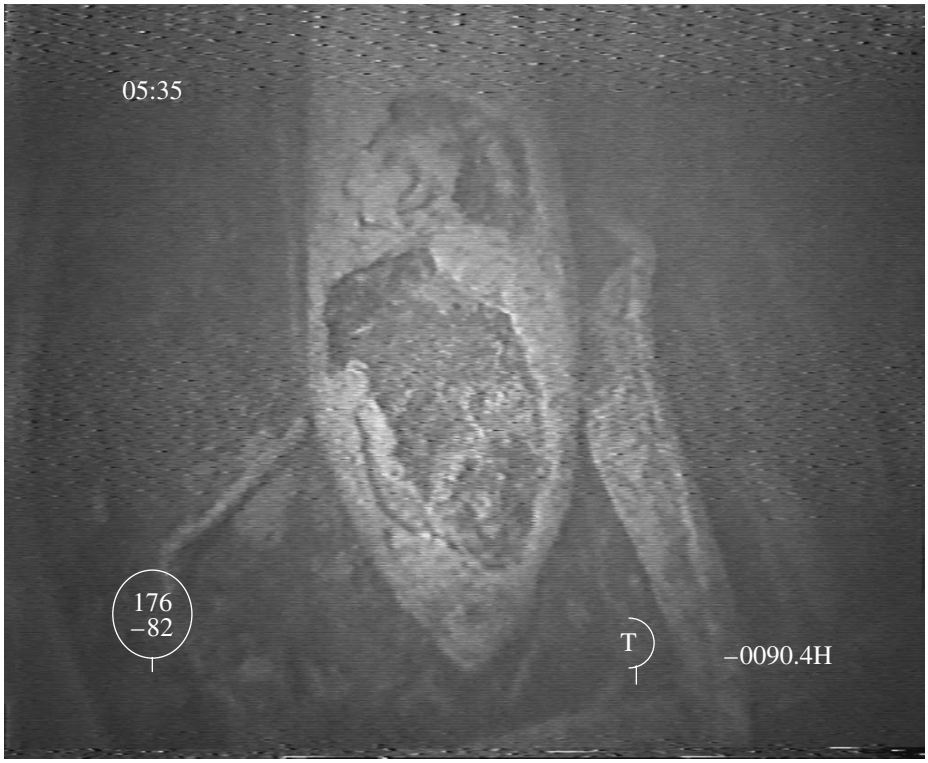

Fig. 9. Corroded steel shell of an aircraft bomb that rested for 55 years on the floor of the Bornholm Deep, Baltic Sea, billed with warfare poisonous agents [1].

inates from these areas. Obviously, not all fish imported to our country is subject to sanitary examination and food control.

The bitter experience of the Vistula Lagoon indicates that As can cause not only animal, livestock, fish, and human diseases but also their deaths. According to numerous papers by German researchers published in 1924–1925 (see [17] for a review of these data), human beings (700 events) and animals inhabiting the shores of the lagoon began suffering an unusual and previously unknown disease, which often resulted in the deaths of animals and humans (7 events). Another episode of this disease took place in 1932 (257 events, including 4 lethal ones).

A number of years of the strenuous work of a German team of medical, oceanological, and other special-

Table 10. Mineral composition of the whole-rock fraction 0.5–0.05 mm of sediment samples from the Gdansk Deep, Kravtsovskoe field (D-6), in which high As concentrations were detected

Site	Depth, m	Layer, cm	Content of fraction, %	Contents of minerals, %				
				quartz and feldspars	glauconite	ore and opaque minerals	other minerals: garnet, carbonate, limonite, apatite, amphiboles, micas, zircon, rutile, and others	As, ppm
PSH-4807	28	0–3	25.9	78.0	8.0	5.0	9.0	70
PSH-4810	9	0–3	48.8	82.0	15.0	5.0	8.0	180
PSH-4812	10	0–5	40.8	78.0	12.0	4.0	6.0	90
4L	29	0–5	0.5	76.0	8.0	3.0	13.0	122
10L	29	0–5	1.0	65.0	2.0	15.0	18.0	107
6L	29	0–5	–	–	–	–	–	69

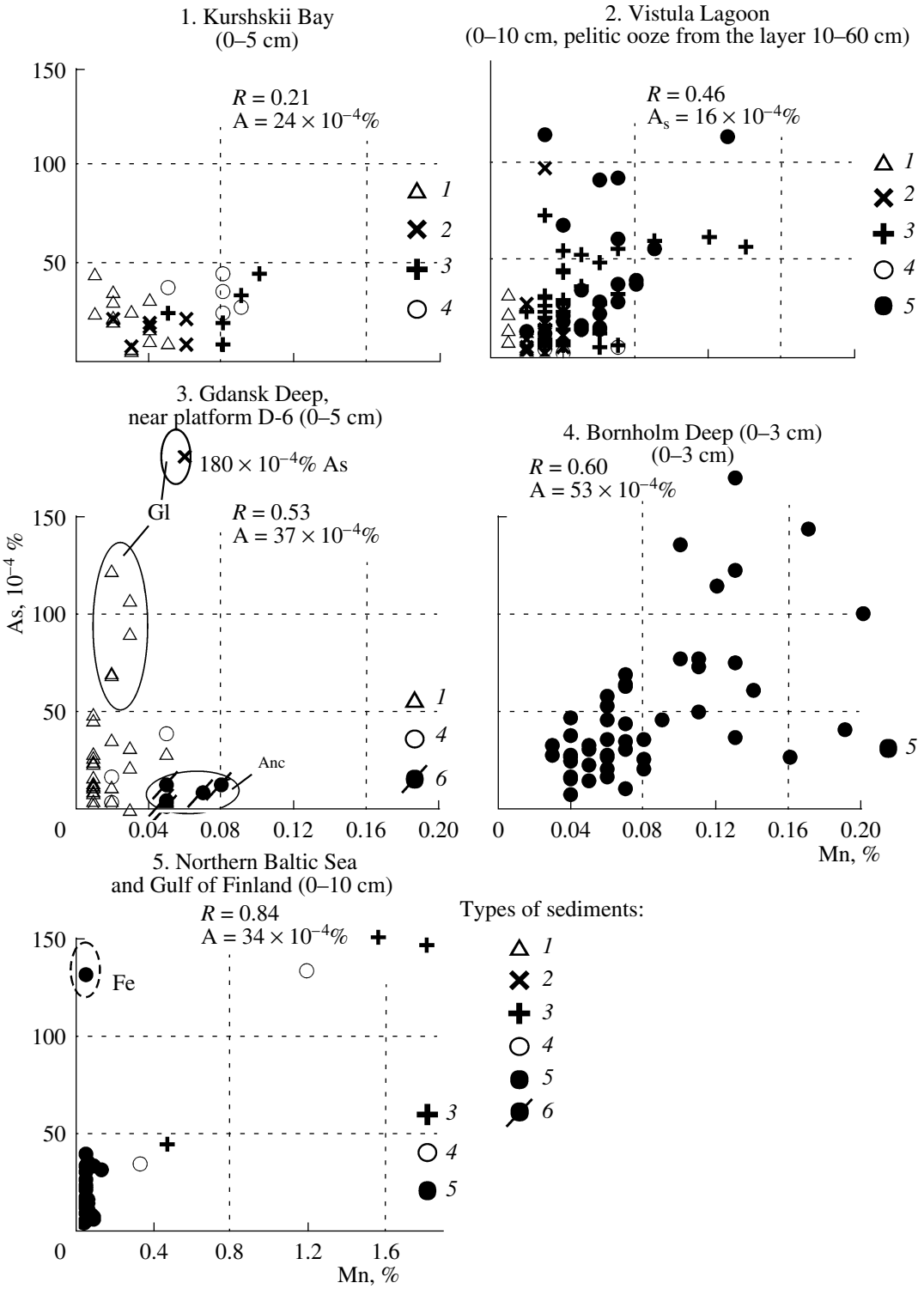

Fig. 10. Correlations between the As and Mn concentrations in bottom sediments at various sites in the Baltic Sea. *R* is the correlation coefficient for As and Mn; A is the average As concentration in the upper layer of bottom sediments in the aforementioned areas in the Baltic Sea. For the Vistula Lagoon, R and A (A_s) are given only for the uppermost layer (0–5 cm) of sediment, i.e., without data on pelitic oozes from the columns. Granulometric types of sediments: (*1*) sand; (*2*) coarse-grained silt; (*3*) fine-grained silty ooze, (*4*) silt–pelitic ooze; (*5*) pelitic ooze; (*6*) samples of *Ancylus* (Anc) clay (Site PSH-4803, layer 207–336 cm); *gl*—samples with glauconite; *Fe*—sample supposedly enriched in Fe sulfides.

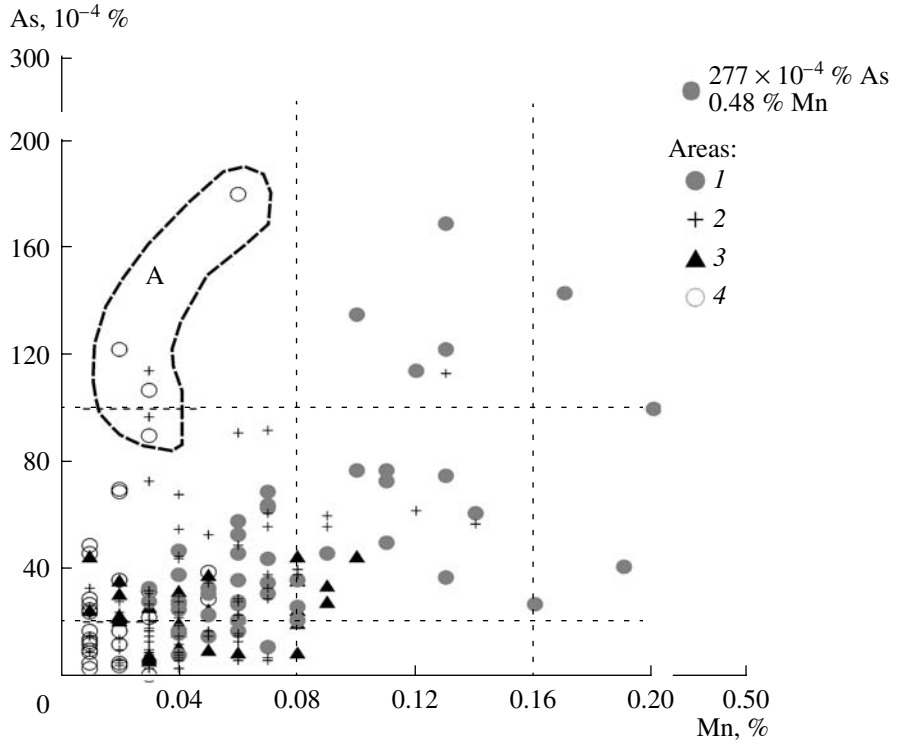

Fig. 11. Correlation between the As concentrations in the upper ooze layer of all types of sediments (layer 0–5 cm) from the whole territory of the Baltic Sea (see Fig. 2) and the Mn concentrations in the same oozes. Sampled areas: (*1*) Bornholm Deep, (*2*) Vistula Lagoon, (*3*) Kurshskii Bay; (*4*) Gdansk Deep (near platform D-6). A—contoured samples from the Vistula Lagoon (crosses) and the vicinity of platform D-6 (samples with glauconite).

ists resulted in the identification of the causes of this strange disease, which was termed the disease of the lagoon [16]. The diseases and deaths were induced by As contained in sulfides in the bottom sediments of the lagoon. These sulfides were brought, together with sand–gravel mixtures, from Spain. The mixture was utilized in the paper-producing industry. When the sand–gravel mixture with sulfides was processed in ovens, the sulfides decomposed and released As. The waste mixture was transported via the Königsberg navigation channel and dumped into the Vistula Lagoon [16]. The foreign gravel–sand mixture was also spread over the lagoon bottom to improve fish spawning grounds. Occurring in an oxidizing environment, the sulfides oxidized and released As in the waters of the lagoon and eventually into food chains (plankton—fish—humans).

In order to check whether elevated As concentrations occur in the bottom sediments of the Vistula Lagoon, we examined this element in four short (<50 cm) columns. Indeed, As was proved to be contained in elevated concentrations (most commonly no higher than 20–114 ppm) in some ooze layers in these columns. Inasmuch as the lagoon is shallow (2–6 m in depth), its bottom oozes are roiled during storms and then redeposited. These oozes can also be stirred (to depths of 30–40 cm) in the process of bioturbation by seafloor species. Because of this, we did not detect any sedimentary layer formed during the disease of the lagoon (1910–1930), and our four columns show uneven As distributions in the vertical sections.

Table 11. Average As concentrations (10^{-4} wt %) in plankton and particulate matter in seawater

no.	Material	As
	Plankton and particulate matter	
1	Oceanic plankton	10
2	Plankton from the Baltic Sea	4.2
3	Particulate matter from the Atlantic Ocean	11
4	Particulate matter from the Pacific Ocean	14
5	Separated particulate matter from the Baltic Sea	14
6	Eolian suspension in air above the Atlantic Ocean	7.4
7	Clayey sedimentary rock of continents	10

Fish are still taken from the lagoon for eating. According to data of the Atlantic Research Institute of Marine Fisheries and Oceanography (AtlantNIRO) in Kaliningrad, fish from the Vistula lagoon contains from 0.04 to 0.29 ppm As [17]; i.e., As concentrations in it are much lower than the aforementioned sanitary standards for all fish types. No episodes of As-related diseases have been reported over the past decades for the populations of the Vistula Lagoon shores.

CONCLUSIONS

Our research demonstrates that the bottom sediments from various areas of the Baltic Sea may contain As concentrations higher than its clarkes for clays and shales.

The highest As concentrations (up to 227 ppm) in the pelitic oozes of the Bornholm Deep are spatially restricted to the burial sites of poisonous warfare materials. Additional As amounts can come there to the bottom sediments from leaking containers, shells, and bombs containing As compounds and the hydrolysis of the poisonous agents (first of all, lewisite) when in contact with seawater. This contamination is now of local character and is still not hazardous for the environment.

Elevated (to 180 ppm) As concentrations in the Gdansk Deep were likely caused by the presence of Fe sulfides or Fe–Mn micronodules in the sands, as well as glauconite, which are enriched in As, or by additional anthropogenic contamination (both factors could act simultaneously).

Elevated As concentrations (50–114 ppm) in the sediments of the Vistula Lagoon could also be caused by the occurrence of Fe sulfides enriched in As or by the additional anthropogenic contamination of these sediments. The possible sources of this contamination were as follows: (a) the rewashed gravel and sand–gravel mixtures that contained much Fe sulfides rich in As, which were transported there in the 1920s for the needs of the paper-producing industry and as a construction material for waterworks in the lagoon (As in the sediments could be partly redeposited); (b) soils treated with As-bearing pesticides; and (c) the atmosphere, into which As was emitted during the burning of As-bearing fuels.

We believe that the ecosystem of the Vistula Lagoon is potentially endangered by the contamination of its bottom waters with arsenic as a consequence of the roiling and redeposition of arsenic-rich bottom sediments during storms and the loosening of these sediments by bottom fauna and subsequent arsenic transfer through food chains. The elucidation of the roles of these processes require further complex monitoring of the lagoon.

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