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Heavy metals contamination of the sediments of the south-eastern Baltic Sea: the impact of economic development

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Abstract. The scope of the study was to assess the impact of potential sources of Cu, Zn, Co, Ni, and Cr on bottom sediments of the Russian sector of the south-eastern Baltic Sea. A total of 68 samples were taken and analyzed for grain-size (laser diffraction and sieve method) and heavy metal concentration (atomic absorption spectroscopy method). To avoid the influence of the sorption capacity of the fine-grained sediments to accumulate the pollutants, the normalization of the heavy metal concentration to Fe was applied. The environmental indices (contamination factor and modified degree of contamination) were calculated. The research has shown the contribution of oil platform, pipelines, ports and wastewater treatment facilities on the geochemical composition of bottom sediments. The authors have identified the level of heavy metals contamination of the middle parts of the Curonian and Vistula spits as a result of alongshore transport of pollutants.

Keywords*: heavy metals; bottom sediments; normalization; environmental indices; Russian sector of the Baltic Sea*

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INTRODUCTION

Copper (Cu), zinc (Zn), cobalt (Co), nickel (Ni), and chrome (Cr) are among the most hazard heavy metals potentially toxic to living organisms in concentrations exceeding the threshold level (Gerlach 1981; Rainbow 1995; Leivuori 2000; HELCOM 2010; Zalewska *et al.* 2015). It is known that even a slight increase in their concentration can lead to potentially deleterious effects in living organisms and in the trophic chain in general (Nemerow 1991; Kersten *et al.* 1994; Swedish EPA 2000; Uścinowicz *et al.* 2011; Zalewska *et al.* 2015). Potentially harmful elements (PHEs) accumulate in bottom sediments of aquatic systems together with organic matter and fine grained (silty clay) sediments (McCave 1984; Szefer *et al.* 1995; Kennish 1997; Pempkowiak *et al.* 1998, 1999; Beldowski, Pempkowiak 2003; Ducrotoy, Elliott 2008; Nemirovskaya *et al.* 2014; Zaborska *et al.* 2014; Krek *et al.* 2018; Remeikaitė-Nikienė *et al.* 2018). Sediments are the only natural indicator reflecting the continuous processes (Clifton, Hamilton 1979; Brugmann 1981; Bryan *et al.* 1985). High anthropogenic pressure on the catchment area of the Baltic Sea and its marine environment results in a high concentration of PHEs (Leivuori *et al.* 2000; Cox, Preda 2005; Gonzalez-Mendoza *et al.* 2007; Yurkovskis, Poikane 2008; Díaz-Asencio *et al.* 2009; HELCOM 2010; Garnaga 2012; Yan *et al.* 2015). In this study we will use term PHEs for five heavy metals (Cu, Zn, Co, Ni, and Cr).

All previous assessments of the bottom sediment contamination of the Russian sector of the south-eastern Baltic Sea have been reduced to a quantitative description of separate PHEs concentration in different types of sediment and lacked a detailed analysis of the negative impact of individual sources of contamination. The comparison of PHEs concentrations in silty clay and coarse sediments has not been done (Emelyanov 1998; Emelyanov *et al.* 2002 , 2012). In this paper an objective value of the normalization using Fe as a normalizing element was calculated. It allowed to compare the concentration of heavy metals in different types of bottom sediments and to identify the contribution of separate anthropogenic sources to this contamination.

The Russian sector of the Baltic Sea is located in the eastern part of the Gdansk Basin between the exclusive economic zone of Poland, Lithuania and Sweden, with maximum depths of approx. 110–112 m.

Bottom sediments and sources of sedimentary material supply

The distribution of different sediment types on the sea bottom is very important for environmental assessment. As a rule, PHEs are narrowed down to the silty clay fraction having the highest sorption capacity (McCave 1984; Szefer *et al.* 1995; Pempkowiak *et al.* 1998, 1999; Beldowski, Pempkowiak 2003; Zaborska *et al.* 2014; Nemirovskaya *et al.* 2014). In the Gdansk Basin, the main source of coarse grained sediment is the abrasion of the coastal zone (Emelyanov *et al.* 2002). On the coast and underwater coastal slope, the glacial and fluvioglacial Quaternary deposits are exposed to wave erosion (Petrov 2010; Blazhchishin 1998). Till deposits are represented by sandy and clay loam with gravel and pebbles whereas fluvioglacial deposits are formed by different grained sand, often mixed with gravel or pebble (Petrov 2010).

The exposed Pre-Quaternary glauconite and quartz ferruginous sandstones are mainly located in the coastal zone of the Sambia Peninsula. These sandstones can be an additional source of Fe in bottom sediments (Dodonov *et al.* 1976; Blazhchishin *et al.* 1978). Quartz and glauconite dominate in the mineral composition of the sandstones whereas troilite (FeS), chromite ($FeCr_2O_4$), ilmenite ($FeO{\cdot}TiO_2$ or $FeTiO_3$), diopside $CaMg(Si_2O_6)$ and zircon ($ZrSiO_4$) are considered mineral admixtures (Information bulletin 2013; Krek *et al.* 2018). Shallow coastal slope mainly contains modern marine sands of different grain size, ranging from coarse to fine-grained. Coarse sand predominates in areas prone to abrasion and, as a rule, are rewash till (Petrov 2010).

Silty clay material formed by the coastal abrasion is carried to the Gdansk Deep via the so-called transition zone at the depths of 40–80 m (Emelyanov *et al.* 2012). On the slopes and bottom of the Gdansk Deep, under the pycnocline (coinciding with the oxycline and the halocline, the depths of more than 80 m), fine grained sediments usually accumulate (Blazhchishin 1998; Emelyanov *et al.* 2002; Petrov 2010; Uścinowicz *et al.* 1998, 2011). The rate of modern sedimentation in the Gdansk Deep is from 1.5 to more than 2 mm per year (Mojski 1995), and, for example, in the “PraNemunas Trough”, the values of the sedimentation rate are 1.0–1.3 mm/year (Mažeika *et al.* 2004). In the mud of the Gdansk Deep, there are gas-bearing sediments, usually associated with tectonic faults (Ulyanova *et al.* 2012). Subaqatic tills formed during the last deglaciation and clays formed during early stages of the development of the Baltic Sea can be found on the sea bottom in the area of the Gdansk-Gotland threshold (Uścinowicz 1999; Petrov 2010; Dorokhov *et al.* 2018). Silty clay sediments consist mainly of quartz and a group of clay minerals (illite, montmorillonite, kaolinite and chlorite) (Emelyanov *et al.* 2002; Uścinowicz *et al*, 2003).

The river inflow is the main source of terrigenous sediments in the Baltic Sea. Both with sediment load the contaminants are transported to the sea by the rivers. The main rivers inflowing the south-eastern part of the Baltic Sea are Vistula and Neman (or Nemunas) rivers, which are the second and fourth largest rivers in the Baltic catchment, the Pregolya River (both with Deima River) may be considered a middle- or small-scale Baltic River. Their average runoffs are of 32 (Kubiak-Wójcicka, Bąk 2018), 25 (Stonevičius *et al.* 2017) and 1.53 km^3 per year (Cieśliński, Chlost 2017), respectively. The drainage area of these rivers includes the territory of Poland, Ukraine, Belarus, Lithuania, and Kaliningrad Oblast (Russia). Therefore, the potential sources of heavy metals may be located in different countries.

Economic activity

Rivers, industrial and municipal wastewater treatment facilities and atmospheric deposition are considered to be the most common sources of PHEs (Kennish 1997; HELCOM 2007). The study area is not an exception. In addition, there are other local sources related to anthropogenic activities typical of this region.

Although marine transport is much less developed in the south-eastern part of the Baltic Sea compared to its western part or the North Sea, it is one of the major sources of pollution (Bulycheva *et al.* 2014). In addition, the main potential sources of pollution are amber mining in the coastal zone, extraction and transportation of oil, dumping and the use of coastal areas for recreation and tourism (Ulyanova, Danchenkov 2016).

There are local sources of pollution; for instance, dumping site offshore the Port Pionersky and an organized discharge of sewage water from purification facilities in the coastal zone of the northern Sambia Peninsula (combined sewage and water treatment facilities in resort towns). A similar dumping site is located to the north of Baltiysk, accumulating the dredged material from the Kaliningrad Sea Canal. In the area of Yantarny settlement, an amber combine discharges its sewage and overburden rock in the coastal zone of the sea (Krek *et al.* 2018). Oil platform D6 and an oil pipeline connecting the platform with an oil storage terminal on the coast were put into operation in 2003. In 2017, the construction of a new terminal for storage and regasification of liquefied natural gas began offshore Kulikovo settlement. Sea vessels that sank in the Baltic Sea at different times are another (often neglected) source of entry of PHEs into bottom sediments (Ulyanova, Danchenkov 2016).

Coastal settlements are additional sources of environmental pressure on the coastal zone, since there are several waste water discharge points in the area. This negative impact increases by an order of magnitude during the holiday season.

The purpose of the study was to assess the impact of potential sources of Cu, Zn, Co, Ni, and Cr on bottom sediments of the Russian sector of the south-eastern Baltic Sea.

MATERIALS AND METHODS

Field study

Samples of bottom sediments (0–5 cm) were taken by a BoxCorer with a capture area of 0.062 m^2 in July (14–28) and October (24–26) 2017 from the r/v

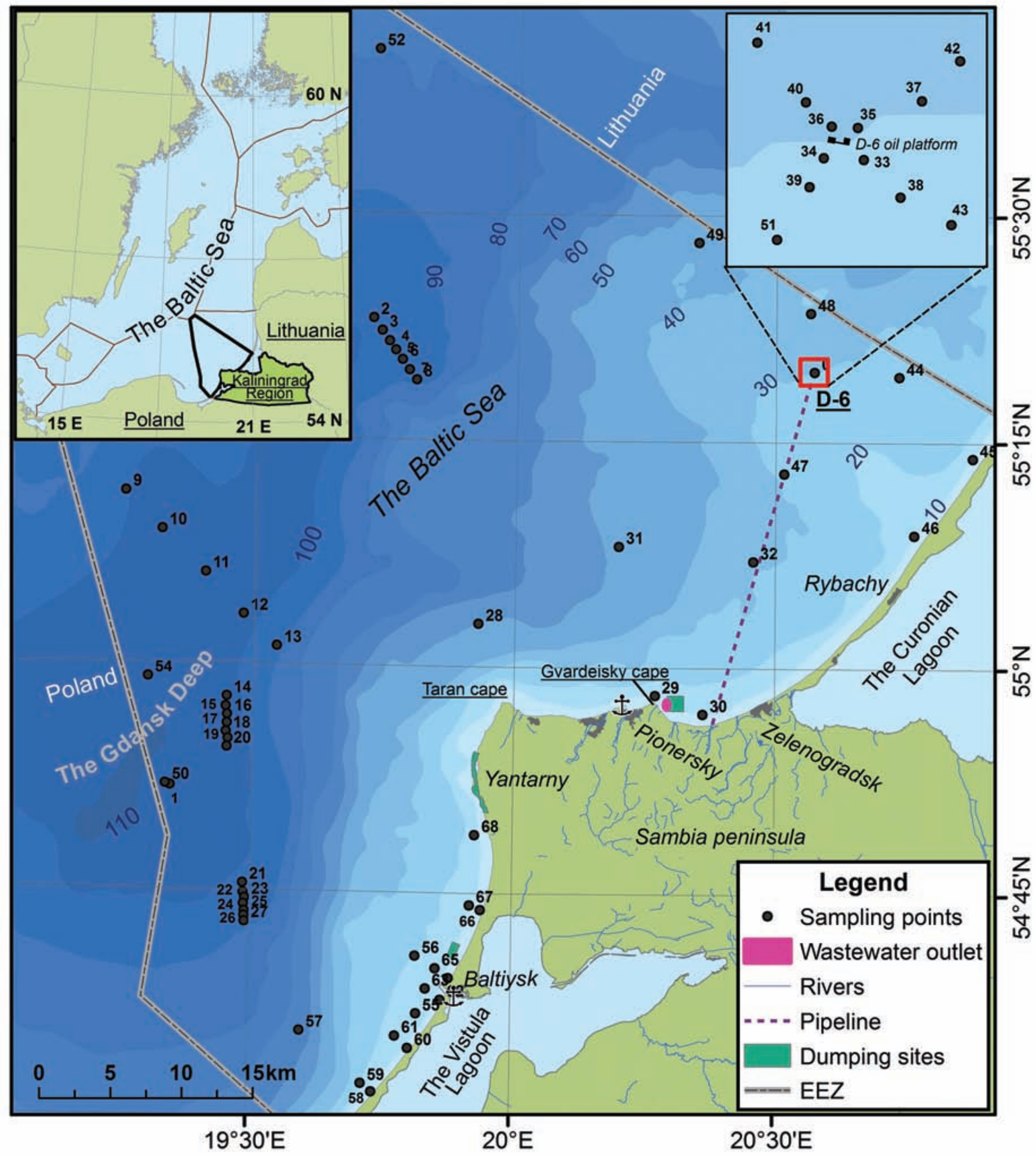

Fig. 1 Location of sampling points in the Russian sector of the south-eastern Baltic Sea

Akademik Nikolai Strakhov (Fig. 1). Samples were packed in plastic bags and stored at a temperature of 4°C until their delivery to an onshore laboratory. A total of 68 samples were taken and analyzed.

Laboratory tests

Grain size analysis

The grain size analysis of the coarse grained material was done by sieving. The Krumbein phi scale was used (Krumbein 1934) for the identification and classification of sediment. The following grain diameters were employed in the equation: 4.0; 2.8; 2.0; 1.4; 1.0; 0.71; 0.5; 0.355; 0.25; 0.18; 0.125; 0.09; and 0.063 mm.

Laser diffraction was used for the grain size analysis of mud. Samples were prepared as follows. Organic matter was removed by treatment with H_2O_2. To disaggregate component grains, sodium tripolyphosphate was added and then each sample was sonicated with an ultrasonic bath immediately before analysis. To measure the particle size, a Fritsch Laser Particle Sizer Analysette 22 Compact with a measuring range of 0.3–300 μm was used. The results of particle sizes measuring were reduced to a scale of the following sizes: 0.2; 1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 15; 20; 25; 30; 35; 40; 45; 50; 63; 80; 100; 125; 150; 160; 200; 250; and 300 μm. The classification of the results of the analysis was done according to Folk (1954) nomenclature using GRADISTAT v.8 (Blott, Pye 2001).

Chemical analysis

Determination of Fe, Cu, Zn, Co, Ni, and Cr content was performed by the atomic absorption spectroscopy (AAS) method using a Varian AA240FS spectrometer with a range of 185–900 nm. The samples were prepared according to Khandros, Shaidurov (1980). Samples were initially dried naturally in the air in a controlled clean environment for a week. Then, the samples were transferred to an oven and dried at 40°C. The samples were then ground to powder with a mortar and pestle and kept in a pre-cleaned container for future use. The samples (about 0.25 g) were weighed on the VT–500 torsion balance, placed in a refractory container and dried at a temperature of 600°C in the PM–10M oven to the state of red glow. Then 5 ml of HF and 1 ml of $HClO_4$ were added to the samples. The samples were placed in a Kombiplax-Sand bath at a temperature of 400 °C until the acids evaporated completely. Then 5 ml of HCl were added to completely dissolve the sediment and after that, double distilled water was added to the analyzed material until its weight reached 50 ml.

For every twentieth test there was a double. The results of the measurements were compared with certified reference standard (BIL-1) measurements to eliminate possible errors. Determination limits and the range of errors are given in Table 1.

Normalization

Normalization allows to compare sediments of different grain size and to determine the anthropogenic contribution of different chemical elements to the analyzed material. The starting point of this procedure is the identification of the element to be normalized; usually this component appears as a result of natural processes. There are many methods of normalization that could be used (Ebbing *et al.* 2002; Uścinowicz *et al.* 2011). In addition, sediments should have a linear dependence between the content of a certain element and the content of the element to be normalized. Fe was chosen as a normalizing agent, since it is the most suitable element for the Gdansk Basin, especially when partial digestion was used (Uścinowicz *et al.* 2011). There are only traces of Cu, Zn, Co, Ni and Cr in the composition of bottom sediments of the investigated area. Therefore, the role of mineralogical composition in the distribution of PHEs is not very significant.

Environmental indices

To describe the contamination of toxic substances in the sediments, we may define the contamination factor (C_f) (Hakanson, 1980) accordingly: $C_f = C_{Me}/C_{Background}$, where C_{Me} – the content of the substance, $C_{Background}$ – the background content of the substance. The modified degree of contamination (mC_d) was calculated accordingly: $mC_d = (C_{f1}+C_{f2}\ldots+ C_{fn})/n$, where n – number of analyzed elements (Abrahim 2005; Abrahim, Parker 2008).

The interpretation of results obtained was done according to the C_f classification (Hakanson 1980), where

$C_f < 1$ – low contamination factor (indicating low sediment contamination of the substance in question);
$1 \leq C_f < 3$ – moderate contamination factor;
$3 \leq C_f < 6$ – considerable contamination factor;
$C_f \geq 6$ – very high contamination factor.

For mC_d, the results obtained were analysed using Abrahim (2005) and Abrahim, Parker (2008), where
$mC_d < 1.5$ – very low degree of contamination;

Table 1 Determination limits and the range of errors for the metal’s concentrations

Range of errors	Fe	Cu	Zn	Co	Ni	Cr
Control measurements of the etalon samples	4.60	58	95	20	55	66
Validated values	4.90 ± 0.54	52 ± 7	96 ± 14	18 ± 2	54 ± 6	66 ± 4

$1.5 \leq mC_d < 2$ – low degree of contamination;
$2 \leq mC_d < 4$ – moderate degree of contamination;
$4 \leq mC_d < 8$ – high degree of contamination;
$8 \leq mC_d < 16$ – very high degree of contamination;
$16 \leq mC_d < 32$ – extremely high degree of contamination;
$mC_d \geq 32$ – ultra high degree of contamination.

Selection of the background value

We decided not to use pre-industrial PHEs concentrations in the cores of muddy sediment (Carvalho Gomes *et al.* 2009; Uścinowicz *et al.* 2011; Zahra *et al.* 2014; Zalewska *et al.* 2015) or their Clarke values for the crust. This approach cannot fully reflect the regional characteristics of the south-eastern part of the Baltic Sea. To assess the contribution of any potential source of PHEs, it is sufficient to identify changes in their concentration and compare the results with the background value.

To calculate PHEs background values after normalization, the median obtained for the entire set of samples was used. The median reflects the so-called typical value and is not so much dependent on the maximum and minimum values, as well as on statistical outliers. This approach does not contradict the methodology used in the study (Tomlinson *et al.* 1980) and was also used in Krek *et al.* (2018).

Statistical data

Microsoft Excel 2007 and Statistical Package for the Social Sciences (SPSS) 10 software were used to perform statistical analyses. For the entire data set, descriptive statistics and correlation coefficients between the elements were calculated. Cluster analysis was also used for investigating the similarities between heavy metals from the sediment samples. A hierarchical cluster analysis was performed based on the complete linkage amalgamation rule.

RESULTS

In the coarse sediments, the silty clay fraction did not exceed 3.69% (at point 31), with an average value of 0.29%. For silts, the fraction >0.063 was close to 100%. Point 57 (offshore the Vistula Spit) at a depth of 60 m was the place of transition from fine grained to coarse grained sediments (83.3% silty-clay). In the middle part of the Vistula Spit, the boundary of the distribution of silty-clayey sediments is located slightly shallower than in the rest of the Russian part of the Baltic Sea. Basically speaking, silty-clayey sediments occur at depths exceeding 70 m. In the transit zone, a fluffy layer was found on coarse-grained sediment.

The content of Fe, Cu, Zn, Co, Ni, and Cr in the silty-clayey sediments was an order of magnitude higher than in the coarse-grained sediments (Table 2, Fig. 2). The Fe normalization procedure use allowed for the first time to reliably compare the level of pollution in different types of sediments in the Russian sector the south-eastern part of the Baltic Sea. It revealed that coarse grained sediment was much more contaminated primarily due to an increase in the PHEs maximum concentration in single points (see Fig. 2). This can be explained by the impact of point sources of PHEs located in the sampling area. Only the normalized Co concentration in coarse sediment was much higher than that in silty-clayey sediments; the concentration of other PHEs was the same in both types of sediments. Increased values of Co in some samples corresponded to the increased values of Cr. The concentration of Ni correlated very weakly with other PHEs, which can probably be explained by its genesis (Fig. 3).

The calculation of the environmental indices (C_f and mC_d) allowed assessing the impact of individual sources of pollution on bottom sediments. Higher values of environmental indices are typical of coarse-

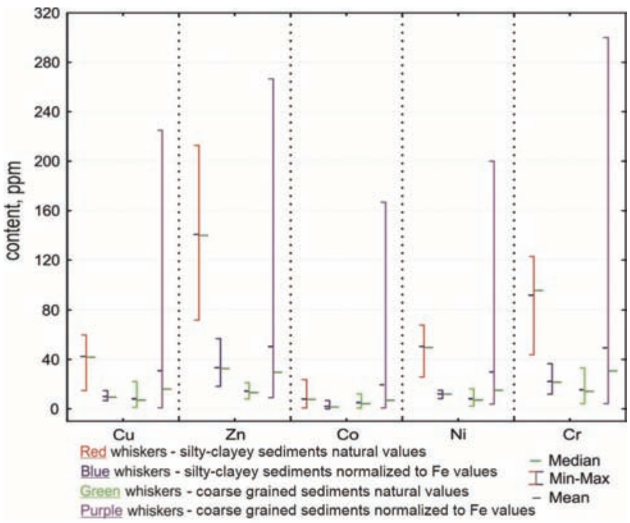

Fig. 2 The average content of Cu, Zn, Co, Ni and Cr: silty-clayey sediments of the Gdansk Basin (31 samples), coarse grained sediments (37 samples)

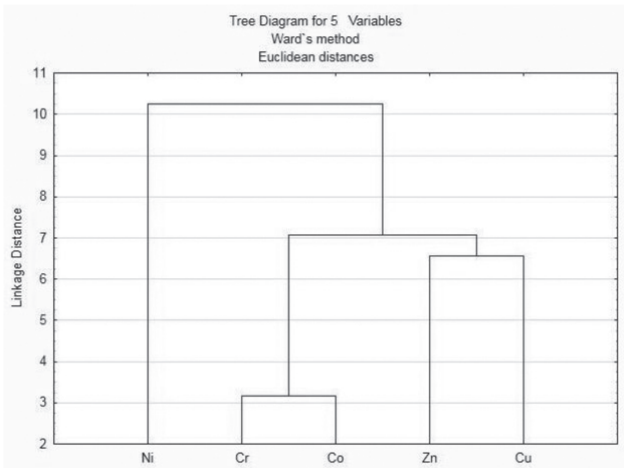

Fig. 3 Interrelations between the elements normalized to Fe

Table 2 C_f and mC_d for sediments normalized to Fe (south-eastern part of the Baltic Sea)

Point	Sediment type	Elements / Cf					mCd
		Cu	Zn	Co	Ni	Cr	
1	fine silt	0.79	*1.08*	0.29	0.83	0.75	0.75
2	very fine silt	0.69	0.79	0.13	0.98	0.79	0.67
3	fine silt	0.71	0.93	0.25	0.89	0.73	0.70
4	fine silt	0.96	*1.29*	0.31	*1.09*	0.98	0.93
5	coarse silt	0.75	0.98	0.33	0.91	0.73	0.74
6	fine silt	0.83	*1.06*	0.17	0.83	0.70	0.72
7	coarse silt	0.90	*1.17*	0.06	0.97	0.70	0.76
8	coarse silt	*1.22*	*1.65*	0.08	*1.05*	0.92	0.99
9	very fine silt	0.92	*1.03*	0.59	0.99	0.71	0.85
10	coarse silt	*1.29*	*1.98*	0.94	*1.16*	0.79	1.23
11	fine silt	0.77	0.71	0.44	0.76	0.57	0.65
12	very fine silt	0.96	0.81	0.41	*1.20*	*1.13*	0.90
13	coarse silt	*1.23*	*1.44*	0.68	0.95	*1.16*	1.09
14	fine silt	0.94	*1.24*	0.78	*1.12*	*1.04*	1.02
15	fine silt	0.85	0.96	0.78	*1.07*	0.97	0.93
16	fine silt	0.88	*1.06*	0.59	0.90	0.88	0.86
17	coarse silt	*1.13*	*1.57*	0.82	*1.07*	0.95	1.11
18	coarse silt	*1.06*	*1.48*	0.64	*1.15*	*1.14*	1.09
19	fine silt	0.78	*1.03*	0.58	0.87	*1.02*	0.86
20	coarse silt	0.91	*1.27*	0.15	*1.13*	*1.31*	0.95
21	coarse silt	*1.02*	*1.52*	0.45	*1.24*	*1.25*	1.10
22	coarse silt	0.98	*1.17*	0.16	*1.11*	*1.43*	0.97
23	fine silt	0.94	*1.22*	0.63	*1.11*	*1.29*	1.04
24	coarse silt	*1.36*	*1.62*	0.25	*1.18*	*1.35*	1.15
25	coarse silt	*1.17*	*1.74*	0.08	*1.23*	*1.48*	1.14
26	coarse silt	*1.47*	*2.18*	0.18	*1.24*	*1.73*	1.36
27	coarse silt	*1.07*	*1.41*	0.63	*1.24*	*1.37*	1.14
28	slightly gravelly sand	*2.63*	*1.27*	**8.92**	*2.37*	0.94	***3.23***
29	slightly gravelly sand	***5.92***	***3.44***	**14.87**	***4.44***	***3.76***	**6.49**
30	gravelly sand	0.53	0.54	0.20	0.42	0.64	0.47
31	sand	0.81	*1.07*	*1.46*	*1.74*	*1.77*	1.37
32	sand	**6.28**	***3.82***	**10.81**	**9.68**	**6.41**	**7.40**
33	gravelly sand	*1.69*	*1.42*	0.85	0.76	*1.08*	1.16
34	sandy gravel	0.69	0.50	*1.49*	0.62	0.19	0.70
35	sandy gravel	**9.05**	***3.50***	***4.96***	***5.17***	***3.53***	**5.24**
36	slightly gravelly sand	*1.41*	*2.00*	0.71	*1.69*	*1.79*	*1.52*
37	sand	**13.16**	**10.20**	**49.55**	**17.74**	**14.11**	**20.95**
38	sandy gravel	*2.30*	*1.66*	*2.97*	*1.48*	*1.41*	*1.96*
39	slightly gravelly sand	*2.30*	*1.27*	*2.97*	***3.55***	0.94	***2.21***
40	sandy gravel	**22.20**	**9.56**	**14.87**	**11.09**	**11.76**	**13.90**
41	sandy gravel	***3.04***	***3.82***	**18.30**	***3.41***	*2.89*	**6.29**
42	slightly gravelly sand	***5.31***	***3.24***	***4.57***	*2.73*	***3.62***	***3.89***
43	gravelly sand	***4.93***	***3.19***	**7.43**	***4.44***	***3.14***	**4.62**
44	slightly gravelly sand	0.37	0.79	***5.61***	0.50	0.98	*1.65*
45	slightly gravelly sand	0.07	0.46	*1.55*	0.33	*1.16*	0.71
46	sandy gravel	*1.48*	*1.91*	*2.23*	*2.00*	*1.76*	*1.88*
47	sand	0.99	*1.53*	**11.89**	*2.37*	*1.72*	***3.70***
48	slightly gravelly sand	0.42	0.86	***3.35***	0.50	0.53	1.13
49	gravelly sand	*1.64*	*1.78*	**6.94**	0.59	*1.88*	***2.57***
50	mud	0.98	*1.27*	*1.42*	*1.20*	0.96	1.17
51	sandy gravel	*2.57*	0.75	***3.88***	*1.16*	*1.33*	*1.94*
52	mud	*1.24*	*1.89*	*1.30*	*1.00*	*1.45*	1.38
53	mud	0.96	0.91	*1.27*	*1.16*	*1.08*	1.07
54	mud	*1.17*	*1.36*	*1.41*	*1.04*	*1.11*	1.22
55	sand	0.93	0.78	*1.61*	0.84	*1.46*	1.12

Point	Sediment type	Elements / Cf					mCd
		Cu	Zn	Co	Ni	Cr	
56	slightly gravelly sand	0.23	*1.18*	*2.12*	*2.11*	*1.79*	1.49
57	sandy mud	0.87	*1.61*	*2.09*	*1.35*	*1.21*	1.42
58	sand	0.90	0.65	*1.16*	0.69	*1.10*	0.90
59	sand	*1.77*	0.98	*1.52*	*1.82*	*1.81*	*1.58*
60	slightly gravelly sand	*1.73*	0.83	*1.21*	*1.08*	*1.59*	1.29
61	sand	***3.17***	*1.91*	*1.06*	*1.90*	*2.69*	***2.15***
62	slightly gravelly sand	*1.16*	0.54	*1.16*	0.62	0.88	0.87
63	slightly gravelly sand	*1.26*	0.56	0.81	0.81	0.98	0.88
64	sand	0.89	0.46	0.71	0.58	0.65	0.66
65	sand	*2.15*	0.79	*1.77*	0.70	0.70	1.22
66	slightly gravelly sand	*1.04*	0.50	*1.93*	0.72	0.61	0.96
67	sand	0.46	0.51	*1.77*	0.70	0.62	0.81
68	gravelly sand	0.31	0.35	*1.74*	0.75	0.78	0.79
D6: points 33–43, 51		*1.77*	*1.45*	**8.42**	*1.38*	***3.73***	***3.35***

Note: Contamination factor C_f: normal font – low, italic – moderate, bold italic – considerable, bold – very high. Modified degree of contamination mC_d: normal font – nil to very low, italic – low, bold italic – moderate, bold – high, bold brown – very high, bold purple – extremely high.

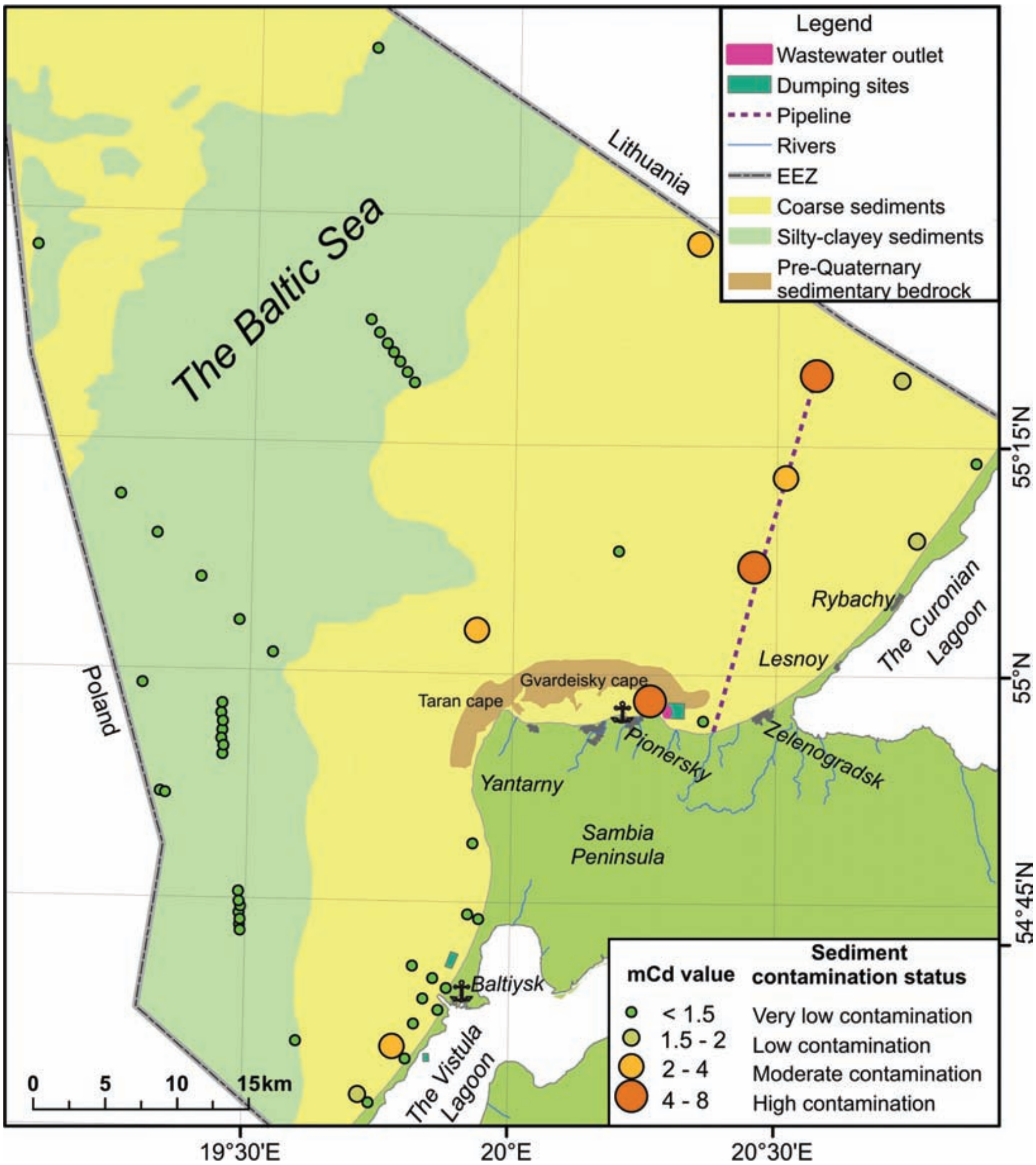

Fig. 4 Modified degree of sediments contamination in the south-eastern part of the Baltic Sea. The mC_d classification by Abrahim (2005) and Abrahim, Parker (2008) was used

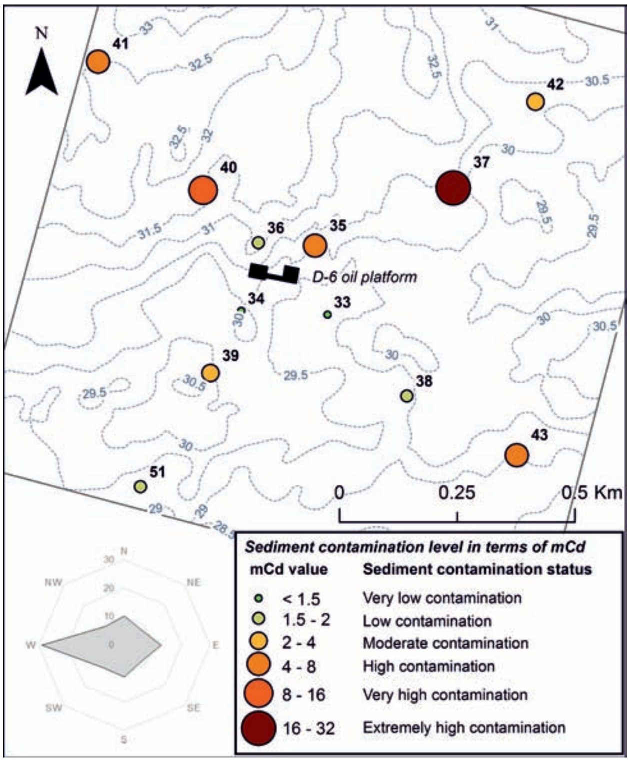

Fig. 5 Modified degree of contamination in the area of the D6 oil platform. The location of the platform is shown at Fig. 1. The wind rose is shown in the inset

grained sediments; it can be explained by a more intensive use of the shallow part of the sea. The mC_d values, ranging from a high to an extremely high degree of contamination, were characteristic of bottom sediments near the oil platform, pipeline and Cape Gvardeisky (see Table 2, Fig. 4). It was hold that the extraction of oil and oil infrastructure are major sources of PHEs. It was the first time such high values were recorded.

DISCUSSION

The impact of the oil platform

In the bottom sediments near the D6 oil platform, there are signs of PHEs coming not from the derrick footing, but from the sea surface or the water column. The maximum content of PHEs is registered at some distance from the platform (about 500 m) along all the axes of sampling. This may be due to the arrival of technogenic suspended matter in the water column appeared, for instance, during maintenance works (repair and painting). This suspended matter is further transported by currents until it falls down to the sea bottom.

The main transport of suspended matter in the bottom layer, to north-north-east, is characterized by the maximum values of mC_d (Meier 2007). The direction of the transport of suspended matter corresponds to the direction of atmospheric transport according to the data provided by a meteostation installed on the platform (Fig. 5). Higher mC_d values for areas to the south of the platform are markers of hydrodynamic activity in the area and reveal the tendency of PHEs sedimentation and accumulation at some distance from the platform.

The change in mC_d values near the oil platform in the direction of the main transport of suspended matter from points 37 and 40 to points 41 and 42 ($\Delta\ mC_d$ = 6.1 per km) allows to state that the radius of the direct impact of the oil platform on bottom sediments is at least 3.5 km. It should be noted that contaminants from the platform do not spread linearly. The impact of the oil platform can still be measured at point 44, which is located at a distance of 10 km away from the oil platform. The correlation coefficient between the concentrations of Cu, Zn, Co, Ni, and Cr at this point and the average content of these metals near the oil platform is 0.71. Unfortunately, the existing system of ecological monitoring near the oil platform and other oil infrastructure does not allow to more accurately assess the actual zone of impact. The area of impact depends on the conditions of the propagation of anthropogenic suspended matter. In a shallow area, given the absence of a gradient layer, the main factors affecting the transport of pollutants are the depth of the sea, the currents and the topography of the underwater slope (Fredsøe, Deigaard 1992).

Pipeline

Parts of the oil pipeline lying on the sea bottom (from the platform to a depth of 15 m) are exposed to the dynamic impact of sand sediments. The impact of the pipeline is reflected in an increased mC_d index – from the moderate to the high degree of contamination at points 47 and 32. In the coastal zone, where the pipeline is buried below the sediments, no impact was registered.

Port Pionersky and the sewage discharge system

Key sources of pollution in the area of Cape Gvardeisky are the seaport of Pionersky, dumpings and the sewage discharge system (combined sewage and water treatment facilities of resort towns). Previous environmental assessments recorded various levels of contamination in these areas (Krek *et al.* 2018). Presumably, the discharge of treated sewage water plays a major role in this anomaly, since the town of Pionersky is much smaller in size and has a much weaker impact compared with the city of Baltiysk where the values of environmental indices were significantly lower.

The Curonian Spit National Park and the Vistula Spit

Near the village of Rybachy (point 46), located offshore the Curonian Spit National Park, no sources

Table 3 Comparison of PHEs in the Russian and Polish sectors of the south-eastern Baltic Sea normalized to Fe

Metal	Polish sector					Russian sector, ** all types of sediments	
	Szefer *et al.* 2009* Points 27–30		Uścinowicz *et al.* 2011* intervals of values were taken from the integrated map	Recalculated from Belzunce Segarra *et al.* 2007*, Points K1–K6			
	mean	med	mean	mean	med	mean	med
Co	2.2	2.0		4.6	4.5	10.8	3.9
Cu	9.8	10.4	5–15	15.6	15.5	20.5	10.5
Zn	40.1	41.2	25–75	54.2	54.6	42.3	32.2
Cr	23.8	23.4	<20	34.4	37.1	36.5	23.8
Ni				11.8	11.3	20.9	12.4

* ICP-OES method; ** AAS method.

of pollution were found. The area has a low degree of contamination caused by episodic pollution. Here, increased concentrations of Cu, Ni, Zn, Cd, and oil products were detected in 2014–2015 (Krek *et al.* 2018). The latest data show that the level of pollution has decreased, and yet, pollutants are still distinguishable. In this area, the decrease in the PHEs concentration was confirmed by the data of the environmental monitoring in 2016–2017. It is hardly possible to relate this pollution to the activity of the platform and oil infrastructure. Gravitational processes play a major role in the transport of sediment on the underwater coastal slope. The transport of sediment 20 m up the underwater slope is an unlikely scenario. Traces of contamination may be a result of alongshore sediment drift. Similar alongshore transport of sediment (Babakov 2003) causes pollution of the underwater coastal slope of the Vistula Spit from the port of Baltiysk.

Transition zone (the depth approx. 50 m)

Points 28 and 49, located in the so-called transition zone, have a minimal sedimentation rate. Here, the influence of the coastal zone and compensating currents is reduced to a minimum and modern coarse-grained material is practically not received here. Here, the velocity of bottom currents is still high for a continuous deposition of silty-clayey sediments (Emelyanov *et al.* 2002). However, the absence of stable conditions for the accumulation of silty-clayey sediments does not mean that silty particles cannot temporarily accumulate in one place in calm water. When sampling, we noticed a grey suspended layer at the above-mentioned points. This fluffy layer can form and grow during the period of hydrodynamic equilibrium.

Comparison with the neighbouring water areas

The average values of PHEs for the Russian sector of the south-eastern part of the Baltic Sea were very close to the values obtained in the Polish sector of the Baltic Sea. Only the Co content was significantly higher and the median value was identical. This is due to the high Co values in some sand samples (Table 3).

CONCLUSION

The research has clearly shown the contribution of different anthropogenic factors to the contamination of bottom sediment in the Russian sector of the south-eastern part of the Baltic Sea. The most significant contamination was registered in coarse grained sediments typical of shallow areas, which are used much more intensively for different types of economic activity. Contrary to previous studies (Emelyanov *et al.* 2012; Emelyanov, Konovalova 2013), we hold that the oil platform and its infrastructure and the sewage water discharge are the main contributing factors to the contamination of bottom sediments by heavy metals. The distribution of heavy metals along the Curonian Spit is associated primarily with alongshore bed load transport as there are no potential sources of pollution due to the absence of any industrial objects. The heightened concentrations of heavy metals near the Vistula Spit may be explained by the outflow from the Vistula Lagoon, which carries pollutants from the Pregolya River, Kaliningrad Sea Channel, and Baltiysk port. In the transition zone (depths of 40–60 m), the periodically appearing fluffy layer may be the determining factor in the spread of contamination caused by fine-grained and dispersed material coming from the coasts. However, this assumption requires a more detailed study as there are only a few samples from these depths and they were taken during similar conditions. The silty-clayey sediments of the Gdansk Deep are not directly affected by anthropogenic sources of heavy metals. PHEs in the silty-clayey sediments determine the prevailing natural-anthropogenic situation in the studied area of the Baltic Sea.

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