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Anthropogenic impact on marine ecosystem health: A comparative multi-proxy investigation of recent sediments in coastal waters



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ABSTRACT

Hazardous substances entering the sea, and ultimately deposited in bottom sediments, pose a growing threat to marine ecosystems. The present study characterized two coastal areas exposed to significant anthropogenic impact - Gulf of Gdańsk (Poland), and Oslofjord/Drammensfjord (Norway) - by conducting a multi-proxy investigation of recent sediments, and comparing the results in light of different available thresholds for selected contaminants. Sediment samples were analyzed for benzo(a)pyrene (B(a)P) and other polycyclic aromatic hydrocarbons (PAHs), nonylphenols (NPs), organotin compounds (OTs), toxic metals (Cd, Hg, Pb), as well as mutagenic, genotoxic and endocrine-disrupting activities (in CALUX bioassays). In general, a declining trend in the deposition of contaminants was observed. Sediments from both basins were not highly contaminated with PAHs, NPs and metals, while OT levels may still give rise to concern in the Norwegian fjords. The results suggest that the contamination of sediments depends also on water/sediment conditions in a given region.

Anthropogenic impact on the health of marine ecosystems is a growing concern in coastal areas, where hazardous substances are more likely to find their way into the sea. An increasing number of such substances are listed by international bodies concerned with environmental protection (HELCOM, 2009; MSFD, 2008; NEA, 2018; OSPAR, 2017a; WFD, 2000). Due to the complexity of anthropogenic releases, potential toxic effects and spreading of chemical contaminants into the marine environment, it is crucial to analyze coastal waters and sediments for a large number of relevant chemical and toxicological variables, which can be assessed in combination to provide information on ecosystem health. Such variables can be termed proxies of environmental health.

Hazardous substances entering the marine environment tend to become associated with suspended particles and are ultimately deposited in bottom sediments. They are persistent and still can be bioavailable as a result of resuspension, diffusion into the water column, decomposition and other transformations. Many indices and/

or assessment criteria exist to help classify sediments as contaminated, or subject to ecological risk, or toxic (SQiRT, 2008; M-608, 2016). However, their use and interpretation are not completely clear, or obvious, and most of them are non-regulatory sediment quality guidelines. Indices and criteria may change depending on the area and the assessment purpose (e.g. environmental management, status screening, health evaluation). Also, different approaches to sediment appraisal may provide significantly different results. In order to contribute to this debate, the present study attempted the characterization of two coastal areas by conducting a multi-proxy investigation of recent sediments, and comparing the results in light of the different available thresholds.

Sediment samples were collected in the Gulf of Gdańsk, in northern Poland, as well as in the Oslofjord/Drammensfjord, in southern Norway (Fig. 1). The sampling took place in the context of a larger Polish-Norwegian Research Programme on “Climate Change Impact on Ecosystem Health – Marine Sediment Indicators” (CLISED, 2014–2017), aiming to study climate change effects in the sedimentary record, and

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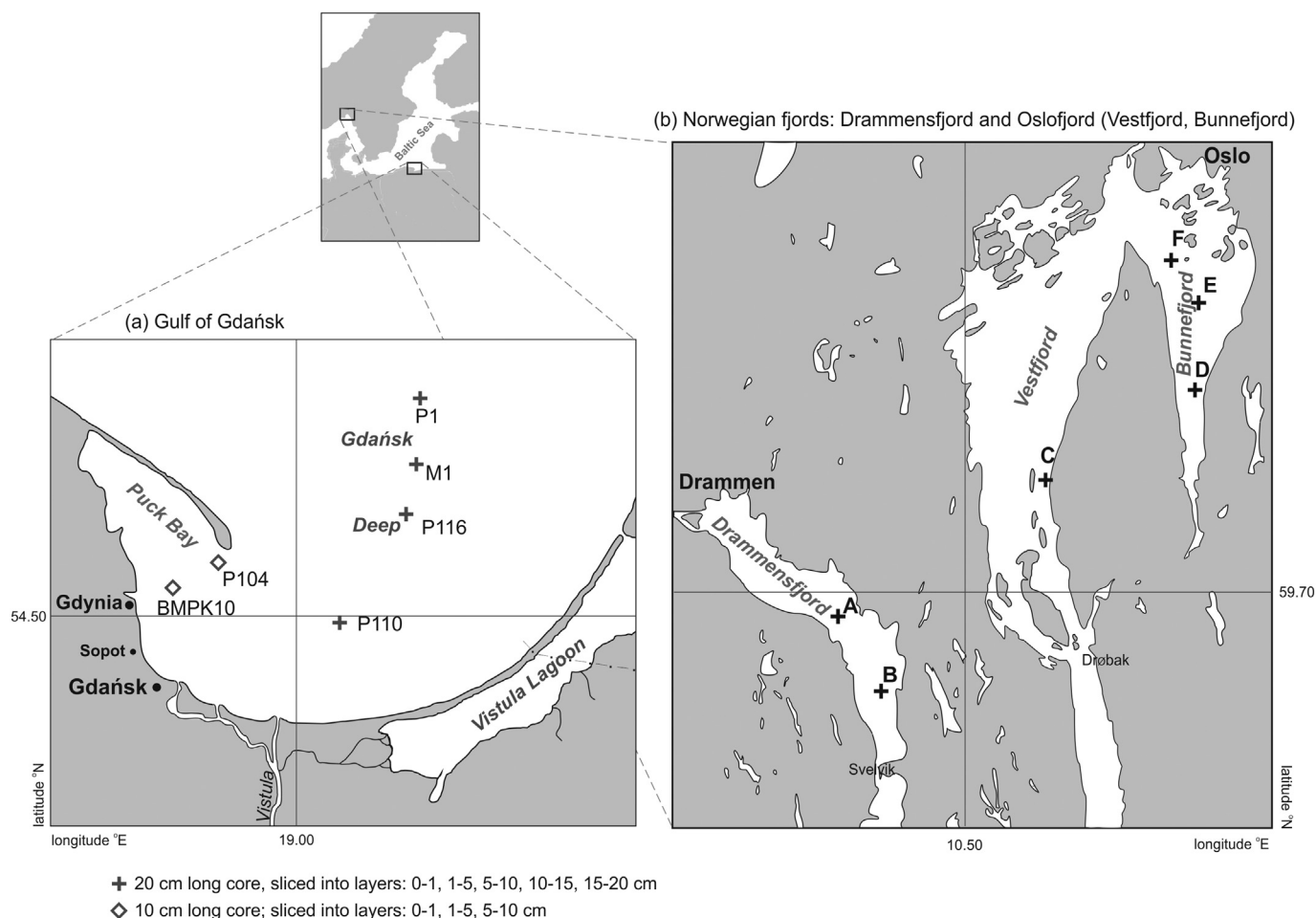


Fig. 1. Sampling location.

connect it to indicators of the marine environment health archived in the sediments. Both basins, albeit different in morphology and boundary conditions, are considered representative of situations not uncommon, in the Northern European Seas, where coastal areas have been heavily affected by significant human activities.

The first study area, the Gulf of Gdańsk, is located in the southern Baltic Sea. The depth of this basin increases seawards, to the Gdańsk Deep (max. depth 118 m) in the north, whereas shallower waters are found in Puck Bay (mean depth 3.1 m) located in the west. Its hydrological conditions are determined by large inflows of freshwater from the Vistula River and infrequent inflows of North Sea water through the Danish Straits. Both the Vistula River and the adjacent Gdańsk-Sopot-Gdynia conurbation (region population ~1.5 million), exert a significant anthropogenic influence on the Gulf of Gdańsk environment via urban pollution, industrial and agricultural effluents, discharges caused by the ship traffic of two large seaports, nutrient inputs from multiple sources. These factors, together with the variability of salinity (4.5–12.5) and oxygen (from well-oxygenated to hypoxic/anoxic waters) conditions, as well as different sediment grain sizes (from gravels to clay), render the Gulf of Gdańsk a well-suited model basin for studying the fate of contaminants in the marine environment (Lubecki and Kowalewska, 2010).

The second study area, the Oslofjord, is a northward inlet of the Skagerrak, which connects the North Sea with the Kattegat and the Baltic Sea. It is divided into an inner and outer fjord by the sill at Drøbak Sound. The inner Oslofjord consists of two main basins: the Vestfjord and the Bunnefjord (for both max. depth ~160 m). The hydrological conditions of these basins are determined by limited deep water exchange and winter renewal. Due to the high population density

(the most populated, ~1.5 million, and industrialized area in Norway) and the immediate proximity of the large seaport, the Oslofjord has been exposed to heavy maritime activities and to the input of large amounts of wastewater and nutrients. On the west side, the outer Oslofjord is connected to the Drammensfjord by a sill at Svelvik. For decades, increasing population and intensive agriculture in the drainage area, as well as industrial and sewage discharges, have contributed to high pollution loads and oxygen depletion. However, in recent years the oxygen levels in the Drammensfjord have improved slightly (NGI, 2010). The water masses of all these fjords are stratified, varying from brackish surface water (salinity 1–10) to saline bottom water (salinity 30.5).

The combination of these two test areas provided a chance to sample a significant spectrum of contaminants' origins and impacts in a wide range of environmental conditions. Sediment samples were collected in 2014, during two cruises of the R/V Oceania, at 12 stations, i.e. 6 stations for each of the test areas above (Fig. 1). The locations of the sampling stations were selected so as to represent both different exposures to contaminants and different environmental conditions (see Supplementary materials – Table A for details). The Gulf of Gdańsk samples were collected in Puck Bay (BMPK10, P104) and along the main spread of Vistula waters in this basin, up to the Gdańsk Deep (P110, P116, M1, P1). The Norwegian fjords samples were collected in the Drammensfjord (A, B) and in the inner Oslofjord (Vestfjord - C, Bunnefjord - D, E, F). The sediment cores were 20 or 10 cm long, depending on the location (Fig. 1). The sediments were taken with a Niemistö core sampler (in the Gulf of Gdańsk) and a GEMAX twin-core sampler (in the Oslofjord/Drammensfjord), then sliced, sub-sampled, and stored at -20°C . The subsamples were analyzed to determine

concentrations of multiple organic and inorganic contaminants, and to investigate sediment toxicity using relevant bioassays. Three different groups of organic contaminants, i.e. benzo(a)pyrene (B(a)P) and other polycyclic aromatic hydrocarbons (PAHs), nonylphenols (NPs) and organotin compounds (OTs), as well as three metals, i.e. cadmium (Cd), mercury (Hg) and lead (Pb), were chosen for this investigation. In addition, mutagenic and genotoxic activities, i.e. the dioxin-like activity (DR CALUX), activity against aryl hydrocarbon (Ah) receptor (PAH CALUX) and the endocrine-disrupting activity (ER α CALUX) of the sediments, were assessed. The concentrations of contaminants were related to environmental parameters of near-bottom waters and selected parameters of bottom sediments. Sediment handling of samples for metal analysis was done under nitrogen protective atmosphere. In addition, at two selected stations, P116 and E (one in each of the two areas), deeper sediment cores (334 and 384 cm, respectively) were also collected, in which background concentrations of metals were determined. These particular samples were taken in 2015, with a vibro corer (station P116) and gravity corer (station E), from the R/V IMOR and the R/V Trygve Braarud, respectively.

The contaminants selected for the present study have different origins but all are considered, and monitored, as priority hazardous substances (i.e. by HELCOM, OSPAR, Norwegian Environment Agency, Marine Strategy Framework Directive). These are both legacy contaminants (natural and anthropogenic: B(a)P and other PAHs, toxic metals), as well as more recent compounds (anthropogenic: NPs, OTs).

The analytical methods used in the present study, for PAHs, NPs, OTs, metals, CALUX bioassays, as well as descriptions of additional measurements and statistical analysis, are included in the Supplementary materials - Methods.

The sampling locations in the two areas showed a high diversity of sediment types (from silty sand to clayey silt) and organic matter content (1.6–8%), as previously described in Szymczak-Żyła et al. (2017). On the basis of the C N⁻¹ ratios, as well as the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, it was concluded that the sediments from the Gulf of Gdańsk and Drammensfjord are under stronger impact of terrestrial organic matter, in comparison to those from the Oslofjord (Szymczak-Żyła et al., 2017). The Gulf of Gdańsk is a brackish area, whereas in the Norwegian fjords bottom water is characterized by salinity typical for ocean water. Deeper parts of both basins suffer from almost permanent hypoxia/anoxia. During the sampling, oxygen deficiency was noticed in near-bottom waters at the three deepest stations of the Gdańsk Deep (0.5–3.9 mg O₂ L⁻¹) and the Norwegian sites (0.2–1.7 mg O₂ L⁻¹), except the Vestfjord (see Supplementary materials – Table A for details).

Contents of B(a)P in the sediment samples from the Gulf of Gdańsk and the Oslofjord/Drammensfjord were comparable, ranging between 21 and 371 ng g⁻¹ dry weight (d.w.) and from 21 to 527 ng g⁻¹ d.w., respectively (Table 1). The highest levels (weighted mean for the individual cores > 200 ng g⁻¹ d.w.) were found at three stations in the Gdańsk Deep (P116, M1, P1), and at two stations in the Oslofjord (C, E). However, the B(a)P profiles along these sediment cores differed. In general, a declining trend in the deposition of B(a)P in the sediments was observed in both areas. Nevertheless, most of the samples of very recent sediments (0–1 cm) taken in the Norwegian fjords were less contaminated by B(a)P than those from the Gulf of Gdańsk (median: 39 and 101 ng g⁻¹ d.w., respectively). Since B(a)P has mainly pyrolytic sources, and is introduced through atmospheric deposition, these downward trends, in both areas, seem to be a result of lower emission of airborne B(a)P due to global climate policy about reducing CO₂ emission (EC, 2007). The lower contamination of the Norwegian sediments (0–1 cm layer) could be related to an emission of CO₂ about seven times lower in Norway than in Poland (EC, 2017). Only one sample, the deepest layer (15–20 cm) at station E, was slightly above T₅₀ = 520 ng g⁻¹, i.e. the concentration that corresponds to 50% probability of toxicity (SQUIRT, 2008). Based on the concentrations and Effects Range Median (ERM) indices of B(a)P and other nine PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene,

chrysene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene; Long et al., 1995; Nasher et al., 2013), the mean ERM quotients were calculated (Fig. 2a). The results indicated that the contamination level of PAHs was generally medium-low (0.1 < mERMq < 0.5), corresponding to 30% probability of toxicity. It is worth emphasizing that sediments deposited in recent years (0–5 cm) were mostly classified as low contaminated (mERMq \leq 0.1; 11% probability of toxicity), except for the stations: P1, M1, P116 (Gdańsk Deep), C (Vestfjord) and F (Bunnefjord), where the sediments were classified as medium-low contaminated with PAHs (0.1 < mERMq < 0.5).

Concentrations of NPs in individual sediment layers varied from 3 to 65 ng g⁻¹ d.w. in the Gulf of Gdańsk, and from 2 to 689 ng g⁻¹ d.w. in the Oslofjord/Drammensfjord (Table 1). The highest NP contents in the Gulf of Gdańsk were recorded at three stations (P1, M1, P116) located in the Gdańsk Deep, as was the case for B(a)P contamination. Based on the sediment accumulation rate (Szymczak-Żyła et al., 2017), it has been estimated that the most contaminated sediments in the Gdańsk Deep, with respect to NPs, accumulated between the 1940s/1950s and 1980s. It is noteworthy that the most contaminated sediments from the Gulf of Gdańsk were about 10 times less contaminated than the sediment from the most NP contaminated site in the Norwegian fjords (station E, 5–10 cm layer). However, the latter sediment layer was also deposited between the 1950s and 1980s. At the stations where the highest NP levels were found (stations D and E in the Oslofjord), a high variability of NP levels was observed in the sediment cores. Only at these two stations, NP levels in some layers were recorded as above the Predicted No Effect Concentration (PNEC) threshold (180 ng g⁻¹ d.w.), established as a tentative guideline to protect benthic communities (EU, 2005). The analysis of NP distribution in the sediment cores from both areas indicates that the fresh input of NPs is generally lower than several decades ago. This may be the result of including NPs on the lists of priority hazardous substances (HELCOM, 2009; NEA, 2018; OSPAR, 2017a), of significant restrictions implemented in the EU since January 2005 (WFD, 2000; EU, 2003b), and of current water policies in general.

Concentrations of OTs (butyltins + phenyltins) in the sediment samples from the Gulf of Gdańsk and the Oslofjord/Drammensfjord ranged between 3 and 60 ng Sn g⁻¹ d.w., and from 1 to 323 ng Sn g⁻¹ d.w., respectively (Table 1). In the Gulf of Gdańsk, only tributyltin (TBT) and its degradation products (dibutyltin (DBT) and monobutyltin (MBT)) were found, whereas phenyltins (PhTs) were below the limit of detection (LOD). In the Oslofjord/Drammensfjord, both butyltins and phenyltins were recorded in the samples, though the percentage of phenyltins in the sum of OTs was low and did not exceed 13%. According to the classification suggested by Dowson et al. (1993), sediments from the Gulf of Gdańsk were ranked as lightly (1–8 ng Sn g⁻¹) or moderately (8–41 ng Sn g⁻¹) contaminated with TBT, whereas one third of the samples from the Oslofjord/Drammensfjord was classified as highly contaminated (41–205 ng Sn g⁻¹). Apparently, the input of OTs into the Oslofjord/Drammensfjord was several times higher than that into the Gulf of Gdańsk, during the last few decades. The highest OT contents were determined at the stations in the Drammensfjord (A, B) and in the Bunnefjord (D, E, F), where severe oxygen deficiency was recorded (< 2 mg O₂ L⁻¹), and the maximum OT concentrations were mainly determined for the 5–10 cm sediment layers, which were formed from the 1950s to 1990s (Szymczak-Żyła et al., 2017). Although a decrease in TBT concentrations has been observed in the Norwegian fjords in recent years (Arp et al., 2014), 52% of the sediment samples can be ranked as bad (20–100 $\mu\text{g kg}^{-1}$) or very bad (> 100 $\mu\text{g kg}^{-1}$) class, according to the Norwegian classification of TBT in sediments (Bakke et al., 2010), defined for management purposes only. It should also be noted that the so-called effects-based classification of TBT in sediments, presented by the Norwegian Environment Agency, defines levels > 0.032 $\mu\text{g kg}^{-1}$ as very bad class (Bakke et al., 2010; M-608, 2016). And this is a very low threshold, relative to the TBT concentrations found in this study. At present, a few years after the use of OTs in antifouling

Table 1

Concentrations of organic contaminants (B(a)P, NPs, TBT, DBT, MBT, ΣPhTs) and metals (Cd, Hg, Pb) in the sediment samples collected in the Gulf of Gdańsk and the Oslofjord/Drammensfjord.

Station/sample		B(a)P [ng g ⁻¹]	NPs [ng g ⁻¹]	TBT [ng Sn g ⁻¹]	DBT [ng Sn g ⁻¹]	MBT [ng Sn g ⁻¹]	ΣPhTs [ng Sn g ⁻¹]	Cd [μg g ⁻¹]	Hg [μg g ⁻¹]	Pb [μg g ⁻¹]
<i>Gulf of Gdańsk</i>										
P1	0–1	100	25	4.0	2.8	5.3	< LOD	1.02	0.032	31.5
	1–5	193	40	4.7	3.7	5.1	< LOD	1.81	0.103	81.1
	5–10	266	45	6.6	4.1	5.4	< LOD	1.63	0.129	96.9
	10–15	256	40	3.6	2.6	3.2	< LOD	1.37	0.128	81.6
	15–20	183	15	2.4	1.0	1.7	< LOD	1.01	0.096	78.9
M1	0–1	135	23	4.3	2.6	5.9	< LOD	0.94	0.044	33.7
	1–5	252	48	7.9	4.6	7.9	< LOD	1.61	0.101	74.7
	5–10	306	62	7.9	4.1	6.9	< LOD	1.62	0.083	73.5
	10–15	296	50	2.4	1.7	3.2	< LOD	1.37	0.121	66.1
	15–20	214	19	1.1	0.5	1.9	< LOD	1.24	0.131	74.0
P116	0–1	143	30	5.6	5.4	8.7	< LOD	1.38	0.140	70.8
	1–5	249	49	9.7	5.2	9.0	< LOD	1.72	0.170	90.0
	5–10	320	65	10.0	5.8	8.8	< LOD	1.56	0.178	89.1
	10–15	371	47	5.5	2.7	3.8	< LOD	1.50	0.140	75.4
	15–20	297	35	1.2	0.7	1.2	< LOD	1.27	0.098	59.0
P110	0–1	101	30	6.8	3.8	8.2	< LOD	0.36	0.011	17.2
	1–5	115	15	6.9	4.7	10.4	< LOD	1.02	0.072	41.9
	5–10	125	21	9.4	6.5	12.0	< LOD	0.96	0.071	40.9
	10–15	193	31	10.9	6.1	11.2	< LOD	0.90	0.150	78.5
	15–20	290	21	4.0	2.3	4.1	< LOD	0.37	0.062	58.4
BMPK10	0–1	77	16	28.5	16.1	15.2	< LOD	0.33	0.033	24.0
	1–5	60	15	17.0	12.3	11.5	< LOD	0.18	0.003	13.0
	5–10	73	58	18.9	18.9	9.9	< LOD	0.18	0.001	11.1
P104	0–1	26	5.2	4.6	3.5	3.8	< LOD	0.22	0.013	9.79
	1–5	21	3.1	0.9	1.7	2.3	< LOD	0.20	0.007	7.04
	5–10	36	5.9	5.0	3.2	4.4	< LOD	0.18	0.003	6.57
<i>Oslofjord/Drammensfjord</i>										
A	0–1	21	17	4.0	3.2	6.5	7.1	0.05	0.007	10.0
	1–5	52	16	32.8	11.5	6.5	6.5	0.22	0.149	35.6
	5–10	58	87	77.7	27.2	14.4	20.9	0.24	0.065	30.4
	10–15	139	99	10.2	25.3	12.2	2.8	0.51	0.195	45.6
	15–20	197	13	< LOD	1.0	0.8	< LOD	0.43	0.341	88.9
B	0–1	28	14	9.6	3.8	5.3	< LOD	0.08	0.013	18.3
	1–5	31	14	44.2	10.3	6.3	2.7	0.08	0.021	16.1
	5–10	58	99	145.0	37.2	19.7	38.9	0.28	0.067	32.8
	10–15	170	130	42.3	41.8	23.8	22.6	0.70	0.195	54.1
	15–20	242	31	0.5	2.1	1.3	< LOD	0.57	0.619	85.4
C	0–1	341	17	15.7	12.6	27.1	4.10	0.05	0.003	30.4
	1–5	232	9.7	23.8	15.3	28.1	3.1	0.11	0.060	61.8
	5–10	204	13	34.1	23.3	35.7	3.7	0.13	0.069	68.5
	10–15	275	16	34.6	16.6	31.8	5.4	0.20	0.150	84.8
	15–20	351	18	20.1	12.4	17.4	4.6	0.13	0.263	102.1
D	0–1	32	27	9.8	8.1	13.0	15.8	0.12	0.019	13.2
	1–5	65	159	55.2	29.2	43.0	18.5	0.37	0.073	27.6
	5–10	98	363	100.6	55.8	71.4	58.5	1.89	0.729	127.7
	10–15	208	231	27.3	17.5	23.9	14.1	0.96	0.867	108.9
	15–20	257	31	2.3	1.7	3.3	5.1	0.47	0.711	98.1
E	0–1	46	42	17.4	11.5	14.2	15.0	0.18	0.038	16.6
	1–5	94	314	96.3	47.1	56.1	24.2	0.71	0.211	57.7
	5–10	192	689	117.1	64.3	78.2	63.0	0.92	0.131	78.8
	10–15	441	219	24.2	15.7	19.4	14.3	1.85	0.372	121.7
	15–20	527	38	4.4	2.0	3.6	< LOD	0.92	0.597	93.1
F	0–1	142	30	53.0	47.5	64.1	29.3	0.54	0.255	81.2
	1–5	228	89	57.6	53.9	67.5	43.0	1.33	1.200	153.5
	5–10	254	31	< LOD	1.2	0.9	< LOD	0.32	0.305	63.7
	10–15	229	4.9	2.2	4.7	6.2	1.7	0.28	0.275	70.4
	15–20	74	1.9	< LOD	1.0	< LOD	< LOD	0.17	0.071	41.6

paints was prohibited (EU, 2003a; IMO, 2001), concentrations of OTs in marine environment are expected to be lower. In many areas, TBT levels in marine sediments have indeed fallen considerably (OSPAR, 2017b). However, harbours, shipping routes and anoxic sediments may still be significantly contaminated with OTs. In this study, concentrations of TBT in very recent sediments (0–1 cm), collected close to the Port of Oslo (station F) and the Port of Gdynia (station BMPK10) were also higher, compared to those from other locations.

Total concentrations of Cd and Pb in the sediments did not differ significantly ($p > 0.05$) between the two basins and ranged: (1) for Cd, 0.18–1.81 $\mu\text{g g}^{-1}$ d.w. in the Gulf of Gdańsk, and 0.05–1.89 $\mu\text{g g}^{-1}$ d.w.

in the Oslofjord/Drammensfjord, (2) for Pb, 6.57–96.9 $\mu\text{g g}^{-1}$ d.w., and 10.0–153.5 $\mu\text{g g}^{-1}$ d.w., respectively (Table 1). A statistically significant difference ($p < 0.05$) was observed only for Hg, where the concentrations varied between 0.001 and 0.178 $\mu\text{g g}^{-1}$ d.w. in the Gulf of Gdańsk, and between 0.003 and 1.200 $\mu\text{g g}^{-1}$ d.w. in the Oslofjord/Drammensfjord. To assess the degree of metal contamination, two indices were applied: the Individual Contamination Factor (ICF) and the Enrichment Factor (EF) (Fig. 2b, c). According to the classification suggested by Zhao et al. (2012), the vast majority of the stations were ranked as highly contaminated with both Cd and Pb (ICF > 6), while the others were recognized as considerably contaminated

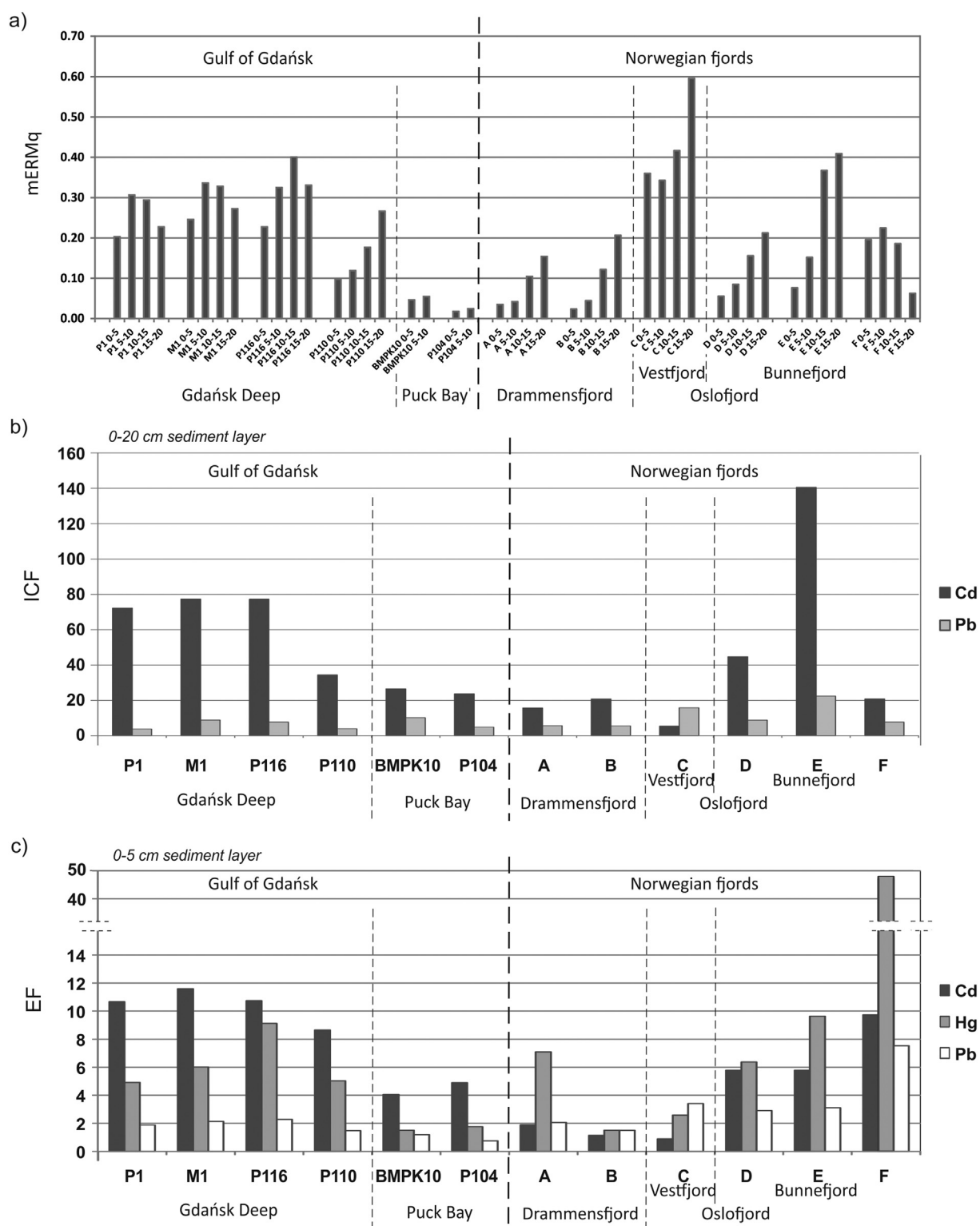


Fig. 2. The mean Effects Range Median quotients (mERMq) based on PAHs (a), individual contamination factors (ICF) (b), and enrichment factors (EF) (c) for the sediment samples in the Gulf of Gdańsk and the Norwegian fjords.

($3 < \text{ICF} < 6$; for Cd – station C; for Pb – stations A, B, P1, P110, P104). The higher the ICF values, the higher is the ecological risk to the environment, due to lower retention time of metal. In this study, ICF values were particularly high at station E in the Bunnefjord, mostly for Cd (up to 140) but also for Pb (22). The ICFs for Hg were not calculated due to the lack of bioavailable fractions of this metal (concentrations < LOD). Based on the total metal content, the EFs were

determined to evaluate changes of metal contamination in the study area, in comparison to the pre-industrial era. For what Cd and Hg enrichment is concerned, the highest anthropogenic input was observed mainly in sediments from the Gdańsk Deep and the Bunnefjord. According to the classification suggested by Zhao et al. (2012), these stations were ranked as considerably ($5 < \text{EF} < 20$) or even highly ($\text{EF} > 20$) (Hg, station F) contaminated with Cd and Hg. As far as Pb is

Table 2

Toxic potential of the sediments in the Gulf of Gdańsk and the Oslofjord/Drammensfjord based on the percentage of stations where appropriate thresholds have been exceeded.

Threshold	PAHs	TBT	NPs	Hg	Pb	Cd
	0.1 ^a	8 ng Sn g ^{-1b}	180 ng g ^{-1c}	0.71 μg g ^{-1d}	218 μg g ^{-1e}	9.6 μg g ^{-1f}
<i>Gulf of Gdańsk</i>						
0–1*	50%	17%	0	0	0	0
1–5*	67%	33%	0	0	0	0
5–10*	67%	50%	0	0	0	0
10–15**	100%	25%	0	0	0	0
15–20**	100%	0	0	0	0	0
<i>Oslofjord/Drammensfjord</i>						
0–1*	33%	83%	0	0	0	0
1–5*	33%	100%	17%	17%	0	0
5–10*	50%	83%	33%	17%	0	0
10–15*	100%	83%	33%	17%	0	0
15–20*	83%	17%	0	17%	0	0

^aThreshold based on mERMq (mean Effects Range Median quotients).

^bThreshold according to Dowson et al., 1993.

^cThreshold based on PNEC (Predicted No Effect Concentration).

^{d, e, f}Thresholds based on ERM (Effects Range Median).

*n = 6.

**n = 3.

None.
Low.
High.
Very high.

concerned, human input seems to have been low ($EF < 2$) or moderate ($2 < EF < 5$). It should be emphasized that a significant source of Cd, Hg and Pb is fossil fuel burning and consequent atmospheric deposition, involving long range transport of these metals, what have an important influence on the contamination level in the two sampling areas (HELCOM, 2017).

Considering all contaminant levels, an attempt to evaluate the toxic potential of the sediments in the Gulf of Gdańsk and the Oslofjord/Drammensfjord was made. Four different groups of contaminants, including six thresholds (for PAHs, NPs, TBT, and metals: Hg, Pb, Cd), were taken into account (Table 2). According to the established thresholds (detailed in Table 2), the sediments in the Gulf of Gdańsk and the Oslofjord/Drammensfjord have not suffered from Pb and Cd pollution. Furthermore, the sediments from the Gulf of Gdańsk were not affected by Hg and NP pollution, while in the sediments from the Norwegian fjords, the Hg and NP thresholds were exceeded only in rare cases. The result that gives rise to concern is the large number of samples from the Oslofjord/Drammensfjord above the TBT threshold. Further, the percentage of results above the mERMq thresholds for PAHs is high in sediments from both test areas, mostly for the deeper sediment layers (10–15 and 15–20 cm). However, the mERMq threshold for PAHs was set at 0.1, i.e. between the low and the medium-low contamination level. A statistically significant difference ($p < 0.05$) between the two basins was observed only for TBT. For the Oslofjord/Drammensfjord the percentage of the samples above the TBT threshold was significantly higher than for the Gulf of Gdańsk.

Another approach to the assessment of sediment toxicity was the use of CALUX bioassays, which measure the combined effects (i.e. the biological response) exerted by complex mixtures of chemicals that have similar modes of toxic actions, even though there are no clear guidelines for the assessment of sediments based on CALUX bioassays (BDS CALUX, 2014; EC, 2014). The results of three kinds of sediment activities are presented in Table 3. The dioxin-like activity was higher

in the Oslofjord/Drammensfjord ($5.4\text{--}67.0\text{ ng TEQ kg}^{-1}$) than in the Gulf of Gdańsk ($2.8\text{--}31.0\text{ ng TEQ kg}^{-1}$), with the highest value recorded at station E (in the Bunnefjord). In contrast, the estrogen-disrupting activity was higher in the sediments from the Gulf of Gdańsk ($0.15\text{--}5.90\text{ ng }17\beta\text{-estradiol eq g}^{-1}$) than in the Norwegian fjords ($0.15\text{--}1.80\text{ ng }17\beta\text{-estradiol eq g}^{-1}$). In both cases, however, these differences do not appear to be statistically significant ($p > 0.05$). The sediments from station BMPK10 (close to Gdynia) and from station D (in the Bunnefjord) were characterized by extremely high activity against the Ah receptor (870,000 and 230,000 ng B(a)P eq g⁻¹, respectively). No correlations between the detected activities and contaminant concentrations (i.e. PAH CALUX vs. B(a)P eq, ERα CALUX vs. NPs) were observed. This result indicates the presence of toxic agents that were not analyzed chemically in the present study, as well as inconstant ratios of these compounds relative to other ligands of the Ah receptor (in case of PAH CALUX) and of the cytosolic estrogen receptor (in case of ERα CALUX) (Windal et al., 2005). It is also worth noting that relative potencies of individual compounds binding to receptors may be very different. These bioassays do not provide information about specific chemical compounds present in the tested samples, but they help characterize them on the basis of their specific activity, and constitute a valuable tool for screening in the risk assessment process.

Using all available data, both on different contaminants accumulated in the sediments and on environmental parameters of near-bottom waters (salinity, temperature, oxygen saturation) and sediments (grain-size, content of pigments and organic carbon), some correlations were identified, and differences between stations and areas impacted by various stressors were pointed out. K-means clustering was applied to show differences between specific locations, based on data for the whole cores, representing the load of contaminants deposited over the last ~100 years (Fig. 3a), and separately for the very surface sediment layers (0–1 cm), to investigate relations for the current contamination status (Fig. 3b) in the two basins.

The results of factor analysis enabled the dataset to be reduced to two factors. The relationships of each variable to these factors, expressed by factor loadings, are presented in Table 4. When considering the factors separately for the 0–1 cm layer, Factor 1 seems to be largely related to contaminants and organic matter, whereas Factor 2 may be associated with parameters of near-bottom water. It is worth noting that oxygen saturation had a negative projection on the second factor. As far as the whole cores are concerned, variables involving contaminants were correlated with both the first or/and second factor. Despite these differences, in both cases three cluster centers were found (Fig. 3a, b): the first contains stations located in the Norwegian fjords,

Table 3

The endocrine-disrupting activity (ERα CALUX), activity against Ah receptor (PAH CALUX) and dioxin-like activity (DR CALUX) in the sediments (0–1 cm) from the Gulf of Gdańsk and the Oslofjord/Drammensfjord.

Location/ sample	ERα CALUX [ng 17β- estradiol eq g ⁻¹]	PAH CALUX [ng B(a) P eq g ⁻¹]	DR CALUX [ng TEQ kg ⁻¹]
<i>Gulf of Gdańsk</i>			
P1	1.40	3000	15.00
M1	5.90	1000	31.00
P116	2.40	5800	21.00
P110	0.87	2400	8.60
BMPK10	0.15	870,000	6.90
P104	0.12	300	2.80
<i>Oslofjord/Drammensfjord</i>			
A	0.19	2300	5.40
B	0.17	900	3.60
C	0.15	6600	48.00
D	1.80	230,000	17.00
E	0.72	900	67.00
F	1.10	5700	29.00

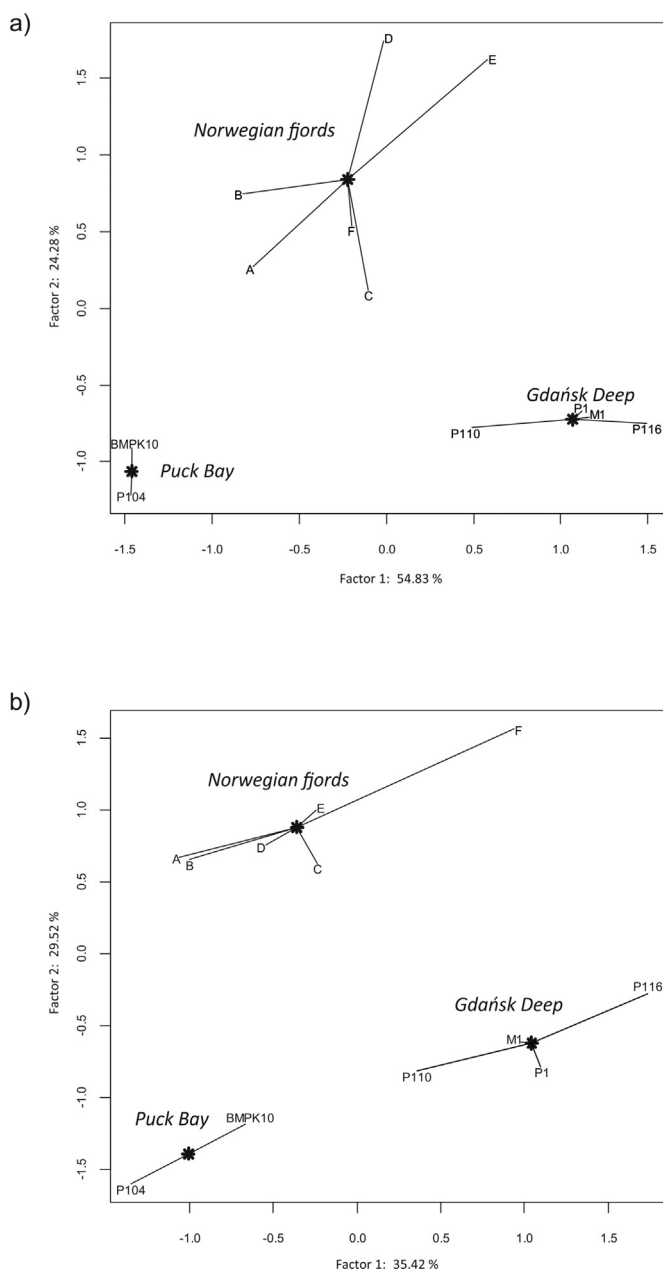


Fig. 3. K-means clustering and differences between specific locations based on all data for the whole cores (a) and for the very surface sediment layers (0–1 cm) (b).

the second consists of two stations in Puck Bay, and the last groups together all the stations from the Gdańsk Deep, which is the main accumulation area for particulate matter and adsorbed contaminants in this part of the Baltic Sea. This 'geographical' outcome, resulting from a combination of both anthropogenic contaminant stressors (very different groups of contaminants originated from different sources) and environmental variables, suggests that water and sediment conditions have a significant impact on the level of contamination in sediments of a particular region. This may be also linked to possible transformation processes of organic contaminants, and to fractionation of metals dependent on environmental conditions.

In conclusion, the variability in contaminant levels of the Gulf of Gdańsk and the Oslofjord/Drammensfjord appears to be comparable, but strong local variations can be observed between sampling stations. The multi-proxy investigation showed a declining trend in the deposition of organic contaminants (B(a)P, NPs, OTs) in the marine sediments

Table 4

Relationship of variables (contaminants and environmental parameters) to the factors defined based on the factor analysis (varimax rotation).

	Whole cores		Layer 0–1 cm	
	Factor 1	Factor 2	Factor 1	Factor 2
BaP	0.86*	0.23	0.42	0.13
BaP eq	0.94*	0.05	0.73*	0.02
OTs	−0.17	0.94*	0.17	0.59*
NPs	0.21	0.80*	0.58*	0.43
Hg	0.13	0.88*	0.60*	0.38
Pb	0.77*	0.56*	0.77*	0.27
Cd	0.91*	−0.02	0.88*	−0.32
Oxygen	−	−	−0.33	−0.66*
Salinity	−	−	−0.27	0.95*
temperature	−	−	−0.07	0.94*
Σchl-a	0.80*	0.20	0.80*	−0.32
Silt	0.78*	0.39	0.77*	0.26
Clay	0.45	0.55*	−0.08	0.85*
Corg	0.94*	−0.25	0.86*	−0.40
Variance [%]	54.83	24.28	35.42	29.52
Cumulative variance [%]	54.83	79.11	35.42	64.94

* Statistically significant at $p < 0.05$.

of both basins. A similar trend was observed for the three metals considered (Cd, Hg, Pb), but only in the Norwegian fjords. The downward trend could be the result of the significant efforts that were made in recent years (e.g. by OSPAR, HELCOM, MSFD) to reduce discharges, emissions and losses of contaminants at sea (OSPAR, 2017c). In general, the stations located in the Norwegian fjords were found to be more contaminated by organic compounds than those in the Gulf of Gdańsk (except for B(a)P, the concentrations of which were comparable in both basins). In addition, phenyltins were detected only in the Oslofjord/Drammensfjord. Finally, no correlations between the results of chemical analyses and CALUX bioassays were observed.

On the basis of the indices applied in the present study, the sediments from the two basins were not highly contaminated with PAHs, NPs and metals, while OT levels may give rise to concern in the Norwegian fjords. This result should not be underestimated, in particular because many countries have stopped monitoring OTs in sediments, after the use of such substances in antifouling paints for ships was prohibited in 2008 (EU, 2003a; IMO, 2001).

Finally, although anthropogenic influence on contamination levels in sediments is indisputable, the results of the statistical analysis presented here indicate that the level of contaminants in marine sediments depends not only on the exposure to contaminants, but also on the water and sediment conditions in particular region.

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