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Risk of heavy metals and their compounds pollution in Port Gdynia waters

Keywords

heavy metals and their compounds, environmental pollution, port area

Abstract

The Baltic Sea is one of the world's largest brackish water areas and an ecologically unique ecosystem. The Port of Gdynia is a universal modern port specializing in handling of general cargo, mainly unitized cargo transported in containers and in a ro-ro system. Ships traffic in the Port of Gdynia has increased in recent years. Many of ships carry cargo that could severally impact coastal ecosystems if accidentally released. The sea water is influenced by heavy metals and their compounds that originate from both natural and anthropogenic origins. This paper discusses the concentration of heavy metals and their compounds in the Gdynia Port waters. It is based on data collected during the period from 2000 to 2019. The samples were tested and analyzed to find concentration of cadmium, lead and zinc. The level of contamination is lower than the Polish standards. Samples taken from the port area water are non-polluted, and the analysis shows that all metals are within the limits.

1. Introduction

The impacts of human activity on the aquatic systems have been reported for over 200 years.

However, coupled with fast population growth, industrialization, as well as some agricultural activities, the risks of pollution in natural environments like river, sea and ocean increased in the last 150 years (Santoyo et al., 2000).

Chemical pollution is one of the most critical threats to human populations and aquatic ecosystems. Many substances from industrial activities are released into natural waters without knowledge of the potential environmental risk.

Water is the vital resource, necessary for all aspects of human and ecosystem survival and health. The quality of sea water can vary widely depending on the quality of rivers, treated and untreated municipal loads and treated and untreated industrial loads. Pollutants are being added to the sea water through human and natural processes.

Problems of contamination with toxic metals started in the Middle Age, with the mining activities, but were accelerated in the beginning of the nineteenth century with the processing of metals in chemical and foundry plants (Souza et al., 2015).

Many metallurgic, chemical and petrochemical industries are located in the river banks and on the sea coasts. In addition, other sources of pollution as residential sewage waters, storm water, and leachate from illegal solid waste dumps also contribute to pollution of waters (Magdaleno et al., 2014).

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Heavy metals and their compounds are toxic elements released by some types of industrial effluents (Tarley & Arruda, 2003). Many metals form stable complexes with biomolecules, and their presence, even at low quantities, can be harmful to plants and animals. The free metal ion is the most toxic form to aquatic life (Florence & Batley, 1980).

A lot of studies are abounding in literature on heavy metal contamination of sea water (Bastami et al., 2015). Such works include evaluation of water quality pollution indices for heavy metal contamination monitoring and its impact on the receiving environment (Zohra & Habit, 2016).

All these researchers concluded that there is need to monitor sea water quality on a regular basis.

The Baltic Sea Area is highly sensitive due to limits in the water exchange, which is very slow. Water remains in the Baltic Sea for about 30 years.

Expanding urban populations, traditional and developing technologies, and intensive agricultural production have greatly increased the amount waste water generated. Levels of contaminants have also grown: these contaminants include both organic (e.g. pesticides, petroleum hydrocarbons) and inorganic (e.g. metals) chemicals. Heavy metal pollution is a worldwide environmental problem. Heavy metals and their compounds deposited into sea water by human activities are not only toxic to animals and plants, but can also affect human health as they are broken down and may travel up the food chain.

Thus, the accumulation of heavy metals and their compounds will affect the quality of aquatic ecosystems, and the ecological risk of heavy metals and their compounds in sea water should be assessed to effectively manage these ecosystems.

Baltic Sea has received considerable loads of heavy metals due to industrialization in Eastern Europe. Concern for the Baltic's ecological health eventually led to the legislation and voluntary measures to limit pollution during the last decades of the 20th century (Vallius, 2014). Currently, almost all heavy metal species have declined to levels approaching the safe limits for humans and environment.

The data suggest that the Szczecin Lagoon appear to be the most polluted with heavy metals and their compounds within the Polish Exclusive Economic Zone (EEZ) of the Baltic Sea.

The Gulf of Gdansk is relatively shallow with intensively populated costal area. The renewal of its waters is very slow. These factors adversely affect the aquatic environment. The discharge of freshwater into Gulf of Gdansk is dominated by the Vistula River.

In order to evaluate the quality of Port Gdynia water, systematic monitoring of the presence of heavy metals and their compounds in surface water is carried out.

The concentration of three heavy metals and their compounds (Cd, Zn and Pb) in surface water between 2011–2020 were measured to assess the potential contamination level.

The chapter is organized into 4 parts, this Introduction as Section 1, Sections 2–3 and Conclusions as Section 4. Section 2 is devoted to Baltic Sea pollution problems, source of water contamination by heavy metals and their compounds and consequences for ecosystem. In Section 3, the concentration of heavy metals and their compounds in the Gdynia Port is discussed. It is based on data collected during the period from 2000 to 2019. Finally, the evaluation of results is discussed. The level of contamination is compared with Polish standards. As conclusion, it can be said that samples taken from port area water are non-polluted, and the analysis shows that all metals are within the limits.

2. Gulf of Gdansk waters pollution

2.1. Source of contamination

The Baltic Sea is an inland sea with an area of 374,000 km^2, the drainage for which is about four times greater. The Baltic Sea is almost totally surrounded by land and therefore more endangered by pollution than other marine areas.

It is one of the largest brackish water bodies worldwide and surrounded by nine countries, with 85 million inhabitants living in the drainage basin (Haseler et al., 2020). Limited water exchange take place with the North Sea (HELCOM, 2010). The special hydrological and geographical conditions of the Baltic Sea make it very sensitive to adverse impact from anthropogenic inputs (Szlinder-Richert et al., 2009). As one the most sensitive marine ecosystems, the Baltic Sea has been classified as Particularly Sensitive Sea Area by the Marine Environment Protection Committee of the International Maritime Organization.

Vistula River supplies about 7% of fresh water to the Baltic Sea. The source of the Vistula River is in Silesia in Poland. These areas form part of socalled black triangle of Poland, Czech Republic and Germany. The main industries in this region are coal mining, metal mining and metal smelting. Industrial activity has resulted in heavy metal pollution and the concentration of these metals in Vistula River is very high (Glasby et al., 2004).

The Vistula River was very polluted in the past, and although some improvements have been observed in the last decade, it remains heavily polluted especially in its upper course. This pollution has entered to reservoir and part of it has settled, in the form of toxic sediments (Majewski, 2013).

The general sources of heavy metals and their compounds deposits are well recognised. Usually, their presence in a fluvial environment is linked with mining activities within the river basin (Martin, 2015), the highly industrialization (Santos Bermejo et. al., 2003), intensive agriculture (Martin, 2004) the functioning of urban agglomerations and remobilisation of older, strongly polluted deposits (Kałmykow-Piwińska & Falkowska, 2020).

In the fluvial environment, the transportation volume of heavy metals and their compounds depends on their physicochemical properties and on the dynamics and chemical properties of the river water environment (Miller, 1997). These metals are transported in a dissolved form as aggregates precipitated from solution and bound with mineral and organic components and more than 90% of the transported elements are bounded to particles that are less than 0.063 mm in size (Horowitz, 1991).

Heavy metals and their compounds in surface water have traditionally been subdivided into two fractions: *dissolved* and *particulate* according to an operationally defined limit – usually 0.45 mm. Knowledge of the chemical forms of metals is essential to understand their interaction with living organisms, as a metal speciation controls its mobility, bioavailability and toxicity (Guéguen & Dominik, 2003). Thus, determining the total concentration of a heavy metal in a water sample provides relative information about its toxicity (Evans, 1989). Contaminating metals are present in various forms: as free metals, complex ions, metals bound to a variety of ligands, forming molecules of various dimensions and chemical characteristics, which may further be bound to larger entities of colloidal size, both organic and inorganic.

Cadmium is primarily sourced from anthropogenic activities (e.g. phosphate fertilizers) and partially from lithogenic components. The lead concentration could be influenced by different source due to increasing human activities, economic and social development (e.g. mining, coal burning), use (batteries, pigments, plastics), recycling and disposal of compounds containing lead, and use of mineral fertilizers (Zaborska, 2014). Lead is one of the most important metals influencing the Baltic Sea Environment.

Zinc is predominantly sourced from lithogenic components (Xu et. al., 2016).

The more recent municipal, industrial and agricultural activities in the Pomerania Region resulted in a high level of contamination by metals and organic compounds in coastal area for the past 50 years (Nikulina & Dullo, 2009).

The Port of Gdynia is the third largest port in Poland and consist of the West Port (inner port) and the East Port (outer port). The port is protected year-round by a 2.5 km breakwater and never freezes over during winter. The value of water salinity ranges from 7.94 to 8.12 PSU, while pH ranges from 7.48 to 8.35 (Radke et al., 2013).

Although the Port of Gdynia is protected year-round by the outer breakwater, which prevents mixing form currents or high waves in the port, during strong easterly winds it can decrease by as much as 0.6 m and during sustained strong westerly winds the water level can rise by up to 0.6m. This phenomenon may cause intensive movement of water and lead to direct and consistent distribution of water toward individual docks. The individual docks of the Port of Gdynia provide easy access to the water mass from the sea. Taking into account this fact it may be assumed that storms and winds may play natural role in the transport of water mass in the port channels (Radke et al., 2012).

The source of Port Gdynia contaminants derives from both natural (physical and chemical weathering of parent rocks) and anthropogenic sources. Wastewater discharge, harbour activities, urban effluent and fertilizer application constitute the major anthropogenic inputs (Gao & Chen, 2012).

2.2. Consequence of ecosystem contamination by heavy metals and their compounds

Heavy metal pollution is one of the most important issues due to the harmful effect on the human body. When present in aquatic system, heavy metals and their compounds are a threat to human health due to their impact on the quality of the water, food and ecosystems.

Lead at concentration above the maximum allowed is considered as neurotoxicant, causing damage to the central nervous system. Zinc can cause irritation and corrosion of the intestinal tract. Exposure to cadmium causes symptoms similar to food poisoning. High concentration accumulated in organisms destroys the testicular tissue and red blood cells and can lead to mutagenic and teratogenic effects (Almeida et al., 2011).

Ingestion of significant amounts of drinking water containing metals will harm human health, resulting in several types of cancers (Yu at al., 2010).

Harmful substances like heavy metals and their compounds released by anthropogenic activities will be accumulated in marine organisms through the food chain; as a result, human health can be at risk because of consumption of fish contaminated by the toxic chemicals (Copat et al., 2012). The pollution of seafood with heavy metals and their compounds is a problem from both hygienic and ecotoxicological points of view. Fish absorb heavy metals and their compounds from the sea water depending on a variety of factors such as the characteristics of the species under consideration, the exposure period, concentration of the elements, as well as abiotic factors such as temperature, salinity, pH and seasonal changes (Ginsberg & Toal, 2009).

Prior to the mind-1960s, metal contamination of the aquatic environment could not be addressed as analyses, and the toxicity and fate of metals in the aquatic environment were poorly understood (Meybeck, 2013). In addition, contamination was not routinely assessed for the lack of analytical techniques and survey methodologies.

Currently, it is well known that to register any changes undergoing in environment it is necessary to monitor specific elements corresponding to the anthropogenic pressure. Implementation of legal acts on the international scale is one of the main drivers leading to the improvement of the environmental status.

The HELCOM Baltic Sea Action Plan is an example of voluntary initiative of countries wishing to have a healthy sea back (Zalewska et. al., 2015).

To reduce pollution and improve the situation in the Baltic Sea, surrounding countries organized the Convention on the Protection of the Marine Environment of the Baltic Sea Area, known as Helsinki Convention, which come into force in 1980. The Helsinki Commission (HELCOM) founded in 1974 acts as coordinator and is responsible for the enforcement of the Baltic monitoring program and international research project.

In Europe, there are recent examples of even wider and more restrictive legal acts like: Water Framework Directive (WFD), a major field of water policy. And the Marine Strategy Framework Directive (MSFD) – establishing a framework for community action in field of marine environmental policy (Zalewska & Danowska, 2017).

Increasing public awareness of environmental pollution influences search and development of technologies that help in cleanup of contaminants such as heavy metals. Heavy metal contamination of ecosystem is a major environmental concern. In order to reduce the level of metal contamination, several remediation technologies have been implemented. These techniques include immobilization methods with the help of low-cost absorbent, application of some chelating agent and biology-based technique, i.e., phytoremediation

The heavy metal from aqueous solution can be removed by passive binding with non-living biomass through biosorption process. The technique of using microorganism to reduce level of metal contamination is better than conventional separation techniques. The biosorption process is a new technology, which can easily use as a refining treatment in shallow bodies of water.

3. Experimental

3.1. Location of water sampling points

Samples of water were collected in 2011–2019 from the selected locations of the Port of Gdynia. Table 1 and Figure 1present the sampling points of surface waters for the testing. Two locations were designated for each of the docks.

Table 1. Location of sampling points in the port of Gdynia

Sample number	Location
1, 2	South Channel
3, 4	Dock I – Presidental Dock
5, 6	Dock II – Wendy Dock
7, 8	Dock III – Coal Dock
9, 10	Outer harbour
11, 12	Dock IV –Marshal Pilsudski Dock
13, 14	Dock V – Minister Kwiatkowski Dock
15, 16	Dock VI
17, 18	Dock VII
19, 20	Harbour Channel

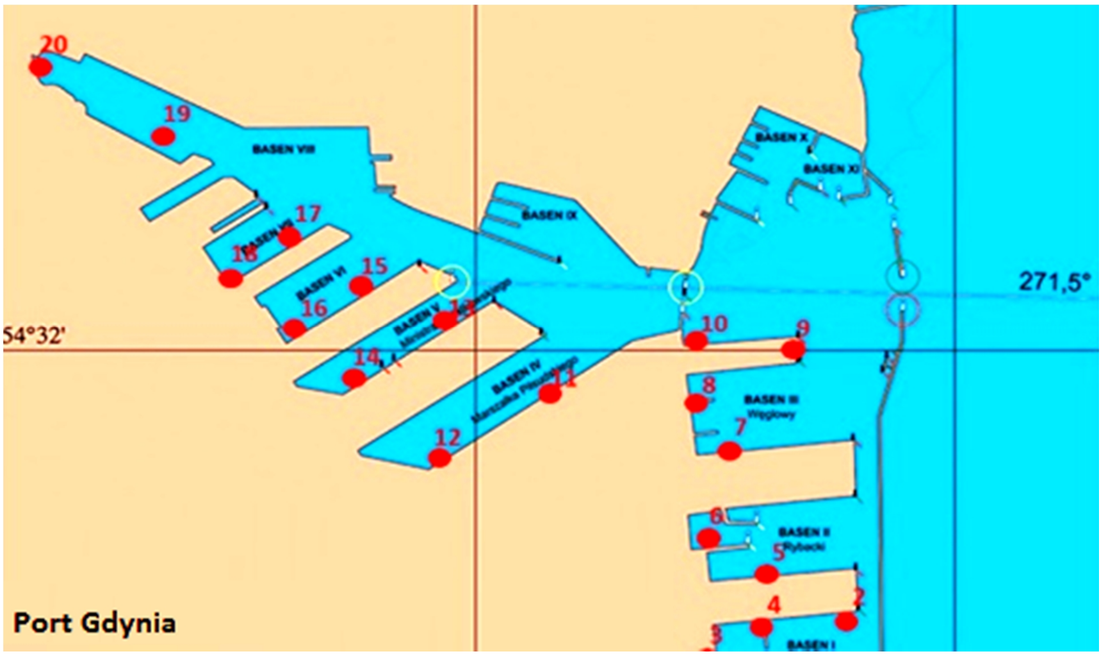

Figure 1. Port Gdynia – sampling points.

The samples were collected in the spring–summer and autumn–winter seasons.

3.2. Methods

Samples of surface water for the study of the level of contamination with heavy metals and their compounds were obtained in accordance with the standard PN-ISO 5667-9:2005.

The heavy metal contamination level was measured using the methods presented in Table 2.

Table 2. Methods of used in the research

Number	Parameter	Method
1	Pb	Mass spectroscopy method (ICP-MS), standard PN-EN ISO 17294-2:2016
2	Cd	Mass spectroscopy method (ICP-MS), standard PN-EN ISO 17294-2:2016
3	Zn	The method of atomic emission spectroscopy, standard PN-EN ISO 11885:2009

The total content of metals was measured by means of atomic absorption spectroscopy (AAS). The investigation and analysis of Pb, Cd and Zn, was performed by atomic emission spectrometry with excitation in inductively coupled plasma ICP-OES) according PN-EN ISO 11885:2009: Water quality – Determination of selected elements by optical emission spectrometry with inductively coupled plasma using the spectrometer Optima 2000DV, PERKIN-ELMER. The lower limit of quantification of the analyzed elements (ICP-OES) was:

- Pb – 0.005 mg · dm^{-3},
- Cd – 0.0005 mg · dm^{-3},
- Zn – 0.022 mg · dm^{-3} / 0.001 mg · dm^{-3}.

After the change in the regulations on limit values in surface waters, the method of mass spectrometry with inductively coupled plasma (ICP-MS) – NexION 350D spectrometer by PERKIN-ELMER was used to determine metals in waters taken from port canals.

The lower limit of quantification for the analyzed elements (ICP-MS method) is:

- Pb – 0.01 μg · dm^{-3},
- Cd – 0.01 μg · dm^{-3},
- Zn – 1.0 μg · dm^{-3}.

3.3. Results and discussion

The concentrations of heavy metals and their compounds detected in the sea water at all twenty sampling locations during 2010 to 2019 are summarized in Tables 3–8.

Table 3. Zinc concentration in the study areas (spring–summer seasons)

Sample number	Concentration of Zn [mg Zn/dm^3]								
	year								
	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	BDL	BDL	0.023±0.003	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	0.023±0.003	BDL	BDL	BDL	BDL	BDL
6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	BDL	BDL	0.091±0.014	BDL	BDL	BDL
8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
11	BDL	BDL	BDL	BDL	BDL	0.066±0.01	BDL	BDL	BDL
12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13	BDL	BDL	BDL	0.023±0.003	BDL	0.027±0.004	BDL	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	0.062±0.009	BDL	BDL	BDL
15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
19	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL – below detection limit.

Table 4. Zinc concentration in the study areas (autumn–winter seasons)

Sample number	Concentration of Zn [mg Zn/dm^3]								
	year								
	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
5	BDL	BDL	0.024±0.004	BDL	BDL	BDL	BDL	BDL	BDL
6	BDL	BDL	0.035±0.005	0.03±0.004	BDL	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	0.041±0.006	BDL	BDL	BDL	BDL	BDL
8	BDL	BDL	BDL	0.042±0.006	BDL	BDL	BDL	BDL	BDL
9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
16	BDL	BDL	BDL	0.023±0.004	BDL	BDL	BDL	BDL	BDL
17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
19	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL – below detection limit.

Table 5. Lead concentration in the study areas (spring–summer seasons)

Sample number	Concentration of Pb [μg Pb/dm^3]								
	year								
	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	BDL	BDL	BDL	BDL	BDL	BDL	0.318±0.064	0.423±0.85	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.293±0.059	0.010±0.002
3	BDL	BDL	BDL	BDL	BDL	BDL	0.085±0.017	0.317±0.063	0.010±0.002
4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.71±0.14	0.03±0.01
5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.360±0.072	0.010±0.002
6	BDL	BDL	BDL	BDL	BDL	BDL	4.6±1.0	0.48±0.01	BDL
7	BDL	BDL	BDL	BDL	BDL	BDL	0.162±0.032	0.51±0.01	BDL
8	BDL	BDL	BDL	BDL	BDL	BDL	0.204±0.041	0.428±0.086	BDL
9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.458±0.092	0.010±0.002
10	BDL	BDL	BDL	BDL	BDL	BDL	0.241±0.048	0.71±0.14	BDL
11	BDL	BDL	BDL	BDL	BDL	BDL	0.014±0.003	0.57±0.11	BDL
12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.7±0.14	BDL
13	BDL	BDL	BDL	BDL	BDL	BDL	0.267±0.053	0.54±0.11	0.010±0.002
14	BDL	BDL	BDL	BDL	BDL	BDL	0.2±0.04	0.85±17	0.010±0.002
15	BDL	BDL	BDL	BDL	BDL	BDL	0.055±0.011	1.17±0.23	0.010±0.002
16	BDL	BDL	BDL	BDL	BDL	BDL	0.204±0.041	0.66±0.13	0.010±0.002
17	BDL	BDL	BDL	BDL	BDL	BDL	0.116±0.00.023	1.19±0.24	0.010±0.002
18	BDL	BDL	BDL	BDL	BDL	BDL	1.37±0.3	1.03±0.21	0.010±0.002
19	BDL	BDL	BDL	BDL	BDL	BDL	1.26±0.28	1.03±0.23	0.010±0.002
20	BDL	BDL	BDL	BDL	BDL	BDL	0.441±0.088	1.27±0.28	0.010±0.002

BDL – below detection limit.

Table. 6. Lead concentration in the study areas (autumn–winter seasons)

Sample number	Concentration of Pb [μg Pb/dm^3]								
	year								
	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	BDL	BDL	BDL	BDL	BDL	0.093±0.019	0.98±0.20	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	0.43±0.086	1.06±0.21	BDL	0.1±0.02
3	BDL	BDL	BDL	BDL	BDL	0.101±0.02	0.241±0.048	BDL	BDL
4	BDL	BDL	BDL	BDL	BDL	0.318±0.064	0.188±0.038	BDL	0.01±0.002
5	BDL	BDL	BDL	BDL	BDL	0.055±0.011	0.218±0.44	BDL	BDL
6	BDL	BDL	BDL	BDL	BDL	0.076±0.015	0.244±0.049	BDL	BDL
7	BDL	BDL	BDL	BDL	BDL	0.033±0.007	0.159±0.3	BDL	0.24±0.04
8	BDL	BDL	BDL	BDL	BDL	0.139±0.028	0.187±0.039	BDL	BDL
9	BDL	BDL	BDL	BDL	BDL	0.048±0.01	0.135±0.027	BDL	0.85±0.15
10	BDL	BDL	BDL	BDL	BDL	0.127±0.025	0.184±0.037	BDL	BDL
11	BDL	BDL	BDL	BDL	BDL	0.051±0.01	0.285±0.057	BDL	BDL
12	BDL	BDL	BDL	BDL	BDL	0.022±0.004	0.61±0.12	BDL	0.51±0.09
13	BDL	BDL	BDL	BDL	BDL	0.111±0.022	0.149±0.03	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	BDL	0.151±0.03	BDL	0.19±0.03
15	BDL	BDL	BDL	BDL	BDL	0.134±0.027	0.32±0.064	BDL	BDL
16	BDL	BDL	BDL	BDL	BDL	0.0.99±0.02	0.329±0.066	BDL	BDL
17	BDL	BDL	BDL	BDL	BDL	0.033±0.007	0.290±0.058	BDL	BDL
18	BDL	BDL	BDL	BDL	BDL	0.086±0.017	0.237±0.047	BDL	0.09±0.02
19	BDL	BDL	BDL	BDL	BDL	0.101±0.02	0.185±0.037	BDL	0.03±0.05
20	BDL	BDL	BDL	BDL	BDL	0.58±0.012	0.289±0.059	BDL	BDL

BDL – below detection limit.

Table 7. Cadmium concentration in the study areas (spring–summer seasons)

Sample number	Concentration of Cd [µg Cd/dm^3]								
	year								
	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	BDL	BDL	BDL	BDL	BDL	BDL	0.043±0.009	BDL	0.010±0.002
2	BDL	BDL	BDL	BDL	BDL	BDL	0.035±0.008	BDL	0.010±0.002
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.010±0.002
4	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.010±0.002
5	BDL	BDL	BDL	BDL	BDL	0,9±0,2	0.03±0.007	BDL	0.03±0.01
6	BDL	BDL	BDL	BDL	BDL	BDL	0.064±0.014	BDL	0.010±0.002
7	BDL	BDL	BDL	BDL	BDL	BDL	0.023±0.005	BDL	0.010±0.002
8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.010±0.002
9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.010±0.002
10	BDL	BDL	BDL	BDL	BDL	BDL	0.034±0.007	BDL	0.010±0.002
11	BDL	BDL	BDL	BDL	BDL	BDL	0.025±0.005	BDL	0.010±0.002
12	BDL	BDL	BDL	BDL	BDL	BDL	0.033±0.007	BDL	0.010±0.002
13	BDL	BDL	BDL	BDL	BDL	BDL	0.031±0.007	BDL	0.010±0.002
14	BDL	BDL	BDL	BDL	BDL	BDL	0.003±0.007	BDL	0.010±0.002
15	BDL	BDL	BDL	BDL	BDL	BDL	0.036±0.008	BDL	0.010±0.002
16	BDL	BDL	BDL	BDL	BDL	BDL	0.035±0.008	BDL	0.010±0.002
17	BDL	BDL	BDL	BDL	BDL	BDL	0.02	BDL	0.010±0.002
18	BDL	BDL	BDL	BDL	BDL	BDL	0.027±0.006	BDL	0.010±0.002
19	BDL	BDL	BDL	BDL	BDL	BDL	0.036±0.008	BDL	0.010±0.002
20	BDL	BDL	BDL	BDL	BDL	BDL	0.038±0.008	BDL	0.010±0.002

BDL – below detection limit.

Table. 8. Cadmium concentration in the study areas (autumn–winter seasons)

Sample number	Concentration of Cd [µg Cd/dm^3]								
	year								
	2011	2012	2013	2014	2015	2016	2017	2018	2019
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	0.394±0.087	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
4	BDL	BDL	BDL	BDL	BDL	BDL	0.111±0.024	BDL	BDL
5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
7	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.03±0.03
10	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
12	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
13	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	BDL	0.091±0.020	BDL	BDL
15	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
16	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
17	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.06±0.01
18	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
19	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

BDL – below detection limit.

The metal concentrations in the water were compared with the limit values presented in Table 9.

Table. 9. The concentration limits of heavy metals and their compounds

Time period [year]	Class of water	Zn [mg/dm^3]	Cd [µg/dm^3]	Pb [µg/dm^3]
2012–2014	I–II	≤1	≤ 0.45-1.5	7.2
	III–V	limits not determined	maximum allowable concentration	maximum allowable concentration
2015–2019	I–II	≤1	≤1.5	14
	III–V	limits not determined	maximum allowable concentration	maximum allowable concentration

Source: Regulation ME 2016.

Physicochemical parameters of surface waters in the Port of Gdynia fall within the values specified for class II of the quality of surface water bodies.

The concentration of zinc in the tested waters of the port basins of the Port of Gdynia was in almost all cases below the limit of quantification of the analytical method used (< 0.022 mg/dm^3).

At several points (between 2013 and 2016), the concentration exceeded the limit of quantification and ranged from 0.023 mg/dm^3 to 0.091 mg/dm^3. These values are lower than the limit values specified in the Polish Regulation of the Minister of the Environment.

Between 2011 and 2016, the concentration of lead in the tested waters of the port basins of the Port of Gdynia was in all cases below the limit of quantification of the analytical method used.

Between 2016 (autumn–winter season) and 2019 the concentration of this metal was in almost all case points exceeding the limit of quantification and ranged from 0.03 µg/dm^3 to 0.58 µg/dm^3. These values are lower than the limit values specified in the Regulation of the Minister of the Environment.

The concentrations of cadmium are in most cases lower than the limit of quantification of the analytical method used. In 2017, the metal concentration exceeded the limit of quantification in almost all measuring points and ranged from 0,023 µg/dm^3 to 0.394 µg/dm^3. These values are lower than the limit values specified in the Regulation of the Minister of the Environment.

The concentration of the mean metal concentration on significant differences between 2011 and 2019 showed that only lead concentration had changed. Zinc and cadmium did not show any changes through time.

Port of Gdynia has a variety of industrial and commercial activities, its primary source of contamination derives from urban and harbor activities. It is a reason why the heavy metals concentration does not increase at the same time at the same rate. The largest contamination by lead was found in samples collected from West port (docks VI and VII). There are two large shipyards in the vicinity of the West Port where vessels are built and undergo renovation. In this area, one of the largest shipping terminals in the Baltic Sea – the Baltic Container Terminal – is located.

4. Conclusion

In recent years more attention has been devoted to pollution in the environment due to increase in anthropogenic contribution by heavy metals and their compounds. Although some natural discharges of metal occur, pollution and the consequential environmental and ecological degradation are predominantly anthropogenic. The source of marine pollution is municipal and industrial waste directly into the sea or via rivers.

The investigation of Port of Gdynia surface water indicates that the concentrations of heavy metals and their compounds are lower than the maximum allowed values established by national legislation. Many years of research suggest that the concentration of cadmium and lead and their compounds in water Gdynia Port is in almost all cases below the detection limit.

The concentrations of zinc, which is an indicator of water quality from the group of substances harmful to the natural environment, in the waters of the port of Gdynia are below the limit values for surface waters.

These results indicate that the heavy metal concentration in surface water of Port Gdynia generally meet the Polish Standards criteria and suggest that the overall water quality has not been significantly impacted by heavy metal pollution. The result of this study will be useful for marine environment managers for the remediation of pollution source.

Greater attention should be paid to anthropogenic sources of heavy metals and their compounds because of further industrialization and economic development in the northern part of Poland.

Heavy metals and their compounds may be non-uniformly distributed in ports water. Zones characterized by industrial activity are directly subject to sources of anthropogenic pollution. Because of the variability of the concentration of heavy metals in the various port section, it is imperative to make a differentiated assessment of the polluted water. Due to the fact that, that the largest contamination load was found in samples collected from West Port, it may be said that is area of potentially high concentration of pollution. Water sampling from selected points and testing should be more frequent.

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