Original Research

Pollution of Klaipeda Port Waters

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Abstract

Twelve consecutive seasonal surveys were carried out in Klaipeda port, Lithuania, in 2006-08. Water parameters such as temperature, pH, salinity, dissolved oxygen, particulate material, nutrients (N/NH_4^+, N/NO_2^-, N/NO_3^-, P/PO_4^{3-}), petroleum hydrocarbons, and heavy metals (Cu, Zn, Ni, Pb, Cr, Cd, Hg) were determined in both the surface and near-bottom water horizons. Total contamination of port waters was evaluated and the patterns of seasonal and spatial contamination patterns revealed. It was determined that the level of water contamination in Klaipeda and its separate water areas depends on the input of pollutants from the Curonian Lagoon basin and local sources, water circulation patterns, and seasonal dynamics of water parameters. As Klaipeda is in a zone of circulation and maximal interface of fresh (from Curonian Lagoon) and saline (Baltic Sea) waters, its water pollution is associated with the dominant type of water. The highest levels of pollution, in combination with the highest water temperatures, highest concentrations of particulate material and smallest concentrations of O_2, occur in summer, when heavy metals, lead in particular, are the dominant pollutants in the water.

Keywords: contaminants, heavy metals, nutrients, petroleum hydrocarbons, pollution, salinity

Introduction

Contaminants are introduced into aquatic environments from different anthropogenic sources. Marine ports are significant hubs of economic activity and major sources of pollution [1-2]. Equipment and activities at ports together with stormwater runoff and effluent discharge cause an array of serious environmental effects. A large share of oil contamination is a result of permanent pollution from such sources as unloading and loading of oil tankers and the removal of bilge water. Dredging, a routine activity of ports, causes resuspension of bottom sediments contaminated with toxic chemicals, including mercury and other heavy metals, oil products, etc. [2]. When a water body is overloaded with nitrogen and phosphorus, a process of eutrophication can rapidly increase and become a serious pollution problem [3]. Multiple contaminants from ports disperse in the surrounding water basins and may seriously affect the condition of river and sea water ecosystems [2-4]. As sea ports often are established in the lower reaches, the water quality in the port basins depends on another very important factor: the inflow of dissolved and particulate material from the river basins [2]. Every port is distinguished for specific natural and anthropogenic factors responsible for water contamination levels, spectrum of pollutants, and dynamic patterns [2-4].

Klaipeda is situated in the Klaipeda Strait, an artery of permanent water circulation between the freshwater Curonian Lagoon and the Baltic Sea. Continental freshwater runoff into the sea is dominant. The river water is collected from a catchment's area of 100,500 km^2. In the Klaipeda port basin, the continental materials are supplemented with pollutants from the port and from Klaipeda city and diluted by cleaner saline water from the Baltic Sea.

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The character of water circulation in the Klaipeda Strait depends on the throughput of the strait, which increases after every dredging of the port basin. In 1976, the navigation channel was 12 m deep. In 1999, the depth in the northern part of the channel reached 14 m [4]; today it is 14.5-15.5 m. According to the research data published in 1996 [5], 5.55 km^3 of water from the Baltic Sea reached the Curonian Lagoon every year, i.e. 11% more than three decades before. Today, the inflow of sea water into the Klaipeda Strait and reciprocal saline water flows into the sea have acquired the character of a permanent process [6].

There have been few attempts of complex evaluation of Klaipeda port water [4, 7, 8]. More frequently, hydrochemical indices of Klaipeda Port (Strait) water quality have been discussed in scientific publications devoted to the Curonian Lagoon with brief surveys of the port [9-12]. The water column of the port is characterized by complicated interrelations of its main physical and chemical parameters and their especially intensive temporal and spatial dynamics, which makes their recording, analysis, and generalization of research results not an easy task. An attempt is made to solve this task, taking into account the differences of composition and properties of saline and fresh water types and seasonal influence on the dynamics of water indices. The main objective of the present article is to examine the port water for contamination with nutrients, petroleum hydrocarbons and heavy metals, to evaluate the total level of multiple pollution, and to discover the seasonal and dynamic patterns of pollution.

Materials and Methods

The length of the Klaipeda Strait is about 12 km and its width Kiaules Nugara Isle is 1.5 km, and in the mouth area 0.4 km. The quays and embankments are concentrated in the eastern bank of the strait. The largest semi-closed water areas used for the port needs are Malku Bay and local ports: Baltija Shipbuilding Yard (Baltija SY) and Winter Port (Fig. 1).

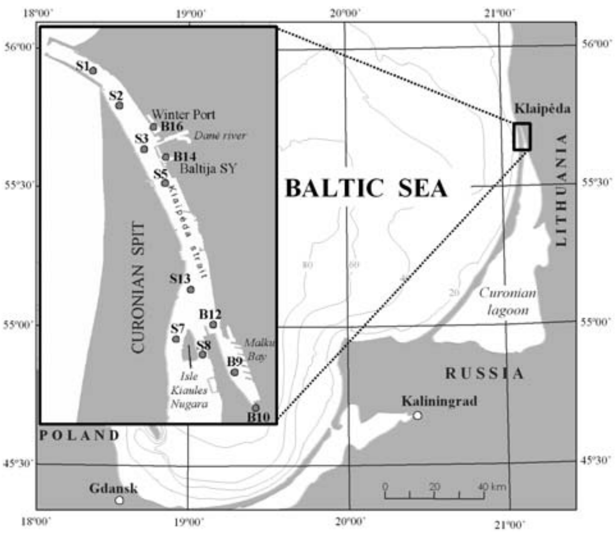

Fig. 1. Klaipeda port water area and sampling stations.

Table 1. Location and depth of stations in the Klaipeda port basin.

Station	Location	Distance from port gate, km	Depth, m
*S1	55º43'41N 21º04'52E	0.3	15.5
S2	55º42'57N 21º06'24E	2.4	14.6
S3	55º42'18N 21º07'04E	3.9	14.0
S5	55º41'49N 21º07'31E	4.9	14.1
S13	55º40'15N 21º08'11E	7.7	13.5
S7	55º39'33N 21º08'00E	9.4	9.0
S8	55º39'25N 21º08'32E	9.5	9.2
**B9	55º39'12N 21º09'13E	10.1	11.4
B10	55º38'43N 21º09'43E	11.1	10.0
B12	55º39'45N 21º08'50E	8.9	12.0
B14	55º42'12N 21º07'33E	4.6	6.9
B16	55º42'41N 21º07'14E	3.6	9.1

* stations located in Klaipeda Strait – S;
** stations located in the semi-closed bays – B

Field investigations were carried out during 12 seasonal expeditions (4 surveys per year) in the winter (February 8-13), spring (May 9-17), summer (August 7-10), and autumn (October 24-November 8) seasons of 2006-08. Seven stations were situated in the Klaipeda Strait (index S) and 5 stations (index B) in the semi-closed bays (Fig. 1, Table 1). The water was recovered from the surface (0-0.5 m) and near-bottom (0.5-1 m above the bottom) water layers. In winter 2006, samples could not be taken from 6 stations in the port bays and at the Kiaules Nugara Isle (St. S8) due to unstable ice cover. The depth at the observing stations was measured with a sea-gauge to accuracy of 0.05 m. Water transparency was determined by the maximal depth of Sekki disc visibility in the water. The water temperature (ºC), salinity (‰), pH, and concentration of dissolved oxygen (mg/L) were measured using express device Multi 340I. The velocity (cm/s) and direction (azimuth, º) of water flow were measured using AANDERAA INSTRUMENTS multifunctional sound RCM 9. The concentration of particulate material was determined in laboratory by water filtration through membrane filters with mesh diameter 0.5 μm, drying filters to stable weight and weighing to accuracy of 0.1 mg.

Inorganic nitrogen (N/NH_4^+, N/NO_2^-, N/NO_3^-) and phosphorus (P/PO_4^{3-}) compounds in the water were determined by the international (ISO) and European (CEN) standard methods approved by Lithuanian normative documentation. Phosphates were determined by spectrometric method [13], ammonium nitrogen – manual spectrometric detection [14], nitrite nitrogen – molecular absorption spectrometric method [15] and nitrate nitrogen – spectrometric method using sulfosalicylic acid [16].

The concentration of total petroleum hydrocarbons (TPH) was determined by infrared spectroscopy [17], heavy metals (HM) Pb, Cu, Ni, Cr, Zn, and Cd by atomic absorption spectrometry using graphite furnace [18], and Hg by atomic fluorescence spectrometry method [19].

The spatial structure of obtained data in the water column of Klaipeda port was analyzed by GIS methods. For discovering the interrelations between water quality parameters (pH, O_2, N/NH_4^+, N/NO_2^-, N/NO_3^-, P/PO_4^{3-}, TPH, Cu, Zn, Ni, Pb, Cr, Cd, and Hg) and also between these parameters and water salinity, Pearson's correlation coefficient (r) was calculated for separate seasons and for the whole research period. Each data set was checked for normality using Kolmogorov-Smirnov test and evaluated according to the form of the histograms [20]. For higher homogeneity, the analyzed data of three years from the same 12 observation stations were grouped by seasons and water horizons. The linkage of significant correlation coefficients (significance level $p<0.01$) between two variables was estimated using the commonly accepted gradation: when $r \leq 0.5$ the link between the variables is poor, when $0.5< r<0.7$ it is relatively fair, and when $r \geq 0.7$ it is strong [21, 22].

For description of total pollution of a body of water, various water quality indices of different spectrum, season of measuring, and limit values were used [22-27]. The environmental impact of an individual pollutant is reflected by the ratio (C_i/L_i) between its measured (C_i) value and maximal concentration limit (L_i). The L_i values are given in the normative documentation [23, 28, 29]. The values of maximal concentration limit (MCL) of N/NH_4^+, N/NO_2^-, N/NO_3^-, P/PO_4^{3-}, TPH, Cu, Zn, Ni, Pb, Cr, Cd, and Hg used in the Lithuanian Water Quality Standards for dangerous and other controlled substances discharged into the aquatic environment [28] were taken as a point of departure for evaluation of water contamination (Table 2). The water contamination level was determined by calculating the Nemerov [30] water pollution multi-factor index (PI), which reflects the effect of each investigated pollutant on water, and also highlights the influence of the high concentration pollutants on water and water quality. PI is calculated according to the equation (1):

$$\mathrm{PI} = \sqrt{\frac{\max(C_i/L_i)^2 + avg(C_i/L_i)^2}{2}} \tag{1}$$

...where C_i – measured concentration of chemical (i), L_i– MCL.

According to Nemerov index, the effects of chemical pollutants on the water environment can be classified and described by a few levels:
PI<1 – no effect,
1<PI<2 – slight effect,
2<PI< 3 – moderate effect,
3<PI< 5 – strong effect, and
PI>5 – serious effect [23].

For evaluation of contamination level with nutrients (n), we calculated PI_n, and evaluation of contamination level with total petroleum hydrocarbons (TPH) and heavy metals (HM) – PI_p in the following way.

Average seasonal concentrations and pollution indices of chemicals under consideration were calculated for seasonal evaluation of surface and near-bottom water pollution in each measuring station. The seasonal pollution indices for nitrates, nitrites, ammonium, and phosphates (surface and near-bottom water horizons) were calculated in each station using equation (1) serving as a basis for calculation of pollution indices PI_n showing the level of water pollution with nutrients at each station. In the same way, seasonal indices of total water pollution with heavy metals (Cu, Zn, Ni, Pb, Cd, and Hg) and total petroleum hydrocarbons (PI_p) were calculated for each station. When the concentration of an analyzed chemical in any of the stations throughout the investigation period in more than 50% cases was lower than the limit value of the method and the determined maximal concentration was twice as low as MCL, the pollution index was equall to 0. In the same way, using equation (1), total pollution indices PI_t were calculated for surface and near-bottom water layers of each station based on the seasonal values of pollution indices of nutrients, metals, and petroleum hydrocarbons. The total seasonal and annual pollution index PI_T representing the whole water column in each station was calculated as an arithmetic mean of indices (PI_t) for the surface and near-bottom water layers.

Results

Indices Describing the Properties of Water Column

At the times of measuring, the water flow in the upper part of the strait water column as a rule was oriented from the Curonian Lagoon toward the Baltic Sea. The flow included both fresh and brackish water. The velocity of water flow reached 0.2-0.5 m/s. In the near-bottom (thickness 2-3 m) horizon, saline water flew from the sea into the lagoon (except in February 2007 and October 2007 and 2008) at lower velocities. In the semi-closed port water areas, the directions of water flow were rather variable and velocities minimal (0.01-0.08 m/s).

According to our data, the water salinity in the port of Klaipeda fluctuated within a wide spectrum: from 0‰ to 7.5‰ (Table 2). The amount of saline water in the Klaipeda Strait usually increases in times of reduced continental runoff: from July until October (these were the cases in 2006 and 2008). By May, the month of spring measuring, the continental run-off had slackened and the average water salinity values in the Klaipeda Strait had become rather high: 5‰ near the bottom, 1.7‰ at the surface. In autumn, when salinity is more evenly distributed in the water column, it reaches its maximal values in the upper water horizon (Fig. 2). The maximal average salinity values in the longitudinal profile of Klaipeda Strait were recorded in the closest proximity to the Klaipeda Strait mouth (St. S1): 4‰ (0-7.5‰) in the near-bottom horizon and 2‰ (0-6.3‰) in the surface horizon. Closer to the Curonian Lagoon, average salinity is slowly reduced, reaching its minimal values at Kiaules Nugara Isle (Fig. 1, St. S7): 2.5‰ (0-6.6‰) in the near-bottom horizon and 1‰ (0-6.2‰) in the surface horizon. During the propagation of saline marine water into the strait, the water of bays stays fresh for some time, yet during the backflow it becomes saline as well.

The water temperature is the best index of seasonal fluctuations (Table 2). In cold seasons, the difference between the water temperatures in the surface and near-bottom horizons is small, in summer it is greater. This becomes especially evident when saline cool Baltic Sea water flows in the near-bottom horizon.

The water transparency in the Klaipeda Port basin in most cases approximates 1 m. Transparency values become higher with increasing salinity of the surface water horizon (Fig. 2). The strongest fall of transparency values are observed in summer (Fig. 2).

The average concentration of particulate material in the port water reaches its maximal value (19.3 mg/L) in summer (Fig. 2), due to the abundance of living plankton and dispersed plankton detritus, when the concentration of biogenic material in it increases to 63% [2]. In terms of abundance of particulate material, summer is followed by winter (15.2 mg/L) and spring (15 mg/L) (Fig. 2, Table 2). In all seasons, the concentration of suspended and resuspended particles is slightly higher near the bottom than in the surface horizon (Fig. 2, Table 2).

The values of pH varied from 6.8 to 9.3 (Table 2). Values slightly exceeding pH 9 were recorded in spring due to disturbance of CO_2 equilibrium by photosynthesis processes. The values of pH measured in the bays were even smaller.

In autumn, the measured average value of dissolved oxygen in the water column reached 10 mg/L O_2. In winter and spring, the values were slightly higher, in summer considerably smaller (Table 2). The minimal values of dissolved oxygen (down to 4.8 mg/L O_2) were recorded in the surface and near-bottom water horizons of the southern part of Malku Bay (MCL is 4 mg/L O_2 [29]).

Nutrients

Nitrates. Winter concentrations of nitrates reach maximal values (not exceeding the MCL: 2.26 N/NO_3^- mg/L) in Klaipeda Strait. In some cases in the backwaters of the port, their concentrations exceeded MCL. In the time span between spring and autumn, the concentrations of nitrates in the water were considerably smaller (Table 2).

Nitrites. In winter (both horizons) and spring (surface horizon), the average values of nitrites approached 0.010-0.012 N/NO_2^- mg/L. In autumn (both horizons) and spring (near-bottom horizon), the average values of nitrites were considerably smaller: 0.004-0.005 N/NO_2^- mg/L. In summer the average nitrite concentration in the water column of Klaipeda port basin was highest (Table 2). Nitrite concentrations exceeded MCL (0.03 N/NO_2^- mg/L) mainly in the semi-closed water areas.

The highest average ammonium concentrations in the water, as in the case with nitrites, were observed in summer, but in the near-bottom horizon in winter (Table 2).

The highest average concentrations of phosphates were observed in winter (Table 2). In spring and summer the concentrations of phosphates in the water column were considerably lower (Table 2). In autumn the average phosphate concentration in the water doubled in the central part of the strait and in the water area in front of Malku Bay (Fig. 1). In the lower water layer of this bay, it slightly (<1.1×) exceeded the MCL values.

Total Petroleum Hydrocarbons and Heavy Metals

In 2006-08, the concentrations of total petroleum hydrocarbons (TPH) in the water column fluctuated between the limit value for the method (35 μg/L) and 139 μg/L, i.e. they were almost thre times as high as the MCL value (50 μg/L). The concentrations of TPH exceeding the MCL values were determined in all seasons (Table 2). In winter, when degradation of petroleum hydrocarbons is especially slow, the TPH concentration in the port water is highest. Even the average TPH concentration in the surface water horizon slightly (1.1×) exceeded the MCL values. In spring, summer and autumn, the average values of petroleum hydrocarbons did not exceed MCL (Table 2).

Hg concentration in the port water reached the highest average value in spring and all other heavy metals (Cu, Zn, Ni, Pb, Cr, Cd) in summer (Table 2). In all seasons, the average concentration of heavy metals as a rule was higher in the near-bottom horizon (Table 2). In spring (Pb), summer (Cu, Cr, Pb), and autumn (Pb) average concentrations of some heavy metals exceed MCL (Table 2).

Fresh Continental and Saline Marine Water Indices

Seasonal fluctuations of fresh continental and saline marine water indices are noticeably different. For demonstration of these differences, two groups of data representing fresh and brackish water masses were chosen. The analysis of fresh continental water was performed based on the measuring data from stations S7 and S8 situated farthest from the sea (Fig. 1). The measured salinity value in these stations did not exceed 0.5‰. Saline water samples were

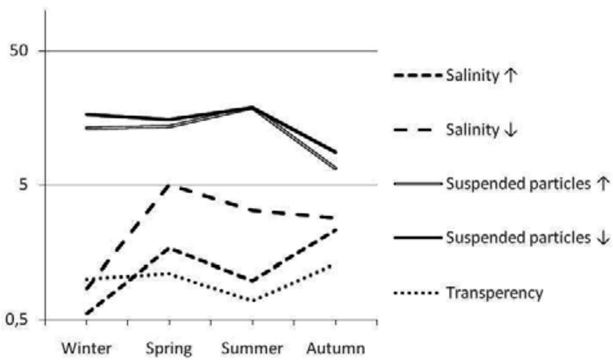

Fig. 2. Average values of water salinity (‰), concentration of particulate material (mg/l) and water transparency (m) in the surface (↑) and near-bottom (↓) water horizons in 2006-08.

Table 2. Seasonal water indices in the port of Klaipeda and concentration values of pollutants in the surface (A) and near-bottom (B) horizons (2006-08).

A)

	Parameters	T	S	pH	O_2	PM	N/NH_4^+	N/NO_2^-	N/NO_3^-	P/PO_4^{3-}	TPH	Cu	Zn	Ni	Pb	Cr	Cd	Hg
		ºC	‰		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Winter	Average	1.1	0.5	8.2	10.8	13.4	0.094	0.012	1.91	0.045	53.2	1.6	<20	<1	1.4	4.7	<0.1	<0.001
	Standard Deviation	1.0	0.7	0.4	0.9	7.8	0.091	0.016	0.80	0.014	23.5	0.5	0.0	0.0	0.6	3.2	0.0	0.00
	Min	-0.3	0.0	7.0	9.7	5.0	<0.028	0.002	0.60	0.027	<35	0.8	<20	<1	<1	<0.5	<0.1	<0.001
	Max	3.2	2.1	8.9	12.6	44.0	0.357	0.063	3.07	0.070	139	2.9	24.5	<1	2.6	9.1	0.12	<0.001
Spring	Average	12.0	1.7	8.6	10.2	14.1	0.076	0.012	0.45	0.010	43.2	4.7	<20	1.0	4.9	8.4	0.10	0.003
	Standard Deviation	2.0	1.0	0.4	0.9	3.4	0.043	0.014	0.22	0.007	13.5	4.2	0.0	0.2	4.3	3.7	0.03	0.008
	Min	3.1	0.0	7.5	7.1	7.0	<0.028	<0.0015	0.14	<0.006	<35	1.1	<20	<1	<1	2.0	<0.1	<0.001
	Max	14.9	3.8	9.3	11.2	21.0	0.215	0.055	0.96	0.027	83.0	18.5	24.4	1.8	15.0	14.5	0.20	0.030
Summer	Average	20.0	0.9	8.5	7.0	19.0	0.099	0.014	0.30	0.014	44.7	12.0	20.0	2.3	21.9	12.1	0.14	<0.001
	Standard Deviation	0.8	1.5	0.4	1.3	3.9	0.104	0.013	0.12	0.008	9.2	4.4	1.9	1.5	9.8	3.7	0.03	0.00
	Min	16.8	0.0	7.3	4.8	10.0	<0.028	<0.0015	0.11	<0.006	<35	5.1	<20	<1	9.5	6.1	<0.1	<0.001
	Max	20.8	5.1	9.0	9.1	30.0	0.395	0.042	0.59	0.028	69.0	20.2	25.2	4.9	41.4	18.7	0.18	<0.001
Autumn	Average	7.8	2.0	8.4	9.8	6.6	0.036	0.005	0.41	0.023	46.9	5.7	20.0	1.5	9.1	7.5	0.12	<0.001
	Standard Deviation	1.3	2.6	0.4	0.9	2.7	0.011	0.006	0.27	0.010	14.8	4.5	1.5	1.0	8.5	3.9	0.03	0.00
	Min	5.9	0.0	6.8	7.2	3.0	<0.028	<0.0015	0.09	0.011	<35	1.2	<20	<1	<1	<0.5	<0.1	<0.001
	Max	10.0	6.3	8.8	11.2	17.0	0.063	0.014	1.18	0.051	104	17.4	24.0	3.9	28.4	15.5	0.19	0.010
MCL – maximum concentration limit							0.78	0.03	2.26	0.065	50	10	100	10	5	10	5	0.3

Temperature (T), salinity (S), pH, dissolved oxygen (O_2), particulate material (PM), nutrients (N/NH_4^+, N/NO_2^-, N/NO_3^-, P/PO_4^{3-}), total petroleum hydrocarbons (TPH), heavy metals (Cu, Zn, Ni, Pb, Cr, Cd, Hg).

Table 2. Continued.

B)

	Parameters	T °C	S ‰	pH	O_2 mg/L	PM mg/L	N/NH_4^+ mg/L	N/NO_2^- mg/L	N/NO_3^- mg/L	P/PO_4^{3-} mg/L	TPH µg/L	Cu µg/L	Zn µg/L	Ni µg/L	Pb µg/L	Cr µg/L	Cd µg/L	Hg µg/L
Winter	Average	1.4	0.9	8.2	10.8	16.9	0.108	0.010	2.19	0.046	46.2	1.9	20.3	<1	2.0	5.5	0.10	<0.001
	Standard Deviation	1.0	1.9	0.3	1.1	10.6	0.059	0.011	0.97	0.016	11.5	0.8	3.3	0.0	1.1	3.3	0.03	0.00
	Min	0.0	0.0	7.4	9.0	2.5	0.038	0.002	0.66	0.023	<35	0.9	<20	<1	<1	<0.5	<0.1	<0.001
	Max	2.7	6.3	8.7	13.2	48.0	0.250	0.036	3.53	0.074	76.0	3.8	32.2	<1	4.0	10.4	0.20	<0.001
Spring	Average	10.2	5.0	8.5	10.2	15.8	0.090	0.005	0.35	0.008	45.1	5.0	20.3	1.0	5.4	8.6	0.13	0.008
	Standard Deviation	1.6	1.9	0.2	0.8	4.5	0.054	0.003	0.17	0.004	13.5	4.3	2.7	0.3	5.0	4.9	0.05	0.012
	Min	5.6	0.0	8.0	7.0	9.0	0.030	0.002	0.12	<0.006	<35	<0.5	<20	<1	<1	1.0	<0.1	<0.001
	Max	13.6	6.8	9.1	11.3	30.0	0.230	0.011	0.95	0.019	83.0	18.0	31.2	2.6	16.2	16.4	0.20	0.040
Summer	Average	18.7	3.4	8.4	7.0	19.6	0.099	0.014	0.40	0.014	43.2	13.1	20.9	2.6	25.0	13.1	0.15	<0.001
	Standard Deviation	1.4	3.4	0.4	1.3	8.2	0.100	0.016	0.15	0.008	11.2	5.8	3.5	1.6	13.0	4.5	0.06	0.00
	Min	15.9	0.0	6.9	4.8	8.0	<0.028	<0.0015	0.16	<0.006	<35	4.8	<20	<1	7.5	5.0	<0.1	<0.001
	Max	20.3	7.5	8.8	8.8	35.0	0.374	0.051	0.71	0.032	62.0	22.5	28.7	5.0	46.8	20.3	0.29	0.03
Autumn	Average	8.0	2.5	8.4	10.1	8.8	0.072	0.004	0.34	0.028	44.5	5.9	20.7	1.6	8.9	8.0	0.13	<0.001
	Standard Deviation	1.3	2.6	0.3	1.1	3.7	0.043	0.004	0.18	0.017	13.2	5.4	3.1	1.1	9.5	4.6	0.06	0.00
	Min	6.0	0.0	6.8	8.0	3.0	<0.028	<0.0015	0.06	0.013	<35	1.4	<20	<1	<1	<0.5	<0.1	<0.001
	Max	10.2	6.5	8.9	11.5	25.0	0.183	0.014	0.74	0.070	69.0	23.6	30.5	4.6	34.3	20.2	0.30	0.02
MCL – maximum concentration limit							0.78	0.03	2.26	0.065	50	10	100	10	5	10	5	0.3

Temperature (T), salinity (S), pH, dissolved oxygen (O_2), particulate material (PM), nutrients (N/NH_4^+, N/NO_2^-, N/NO_3^-, P/PO_4^{3-}), total petroleum hydrocarbons (TPH), heavy metals (Cu, Zn, Ni, Pb, Cr, Cd, Hg).

taken from stations S1 and S2 (closest to the sea, Fig. 1) where salinity values exceeded 3‰. The generalized data revealed differences of the port water quality indices predetermined by genetic features of water masses (Table 3). It was determined that in winter, spring, and summer, the fresh water mass in the port is distinguished by higher temperatures. In autumn, the shallow Curonian Lagoon water cools faster so that the mass of saline water remains warmer by 1.1ºC (Table 3). In all seasons, the concentration of dissolved oxygen and pH values in the fresh water mass exceeded the values in the saline water (Table 3). Higher concentrations of particulate material and nitrates (in all seasons), nitrites, and phosphates (except in autumn) are characteristic of fresh Curonian Lagoon water. The autumn concentrations of nitrites and phosphates often are higher in saline water. Meanwhile, concentrations of ammonium ions are higher in saline water mass in all seasons (Table 3).

The concentration of TPH is higher in the fresh lagoon water in all seasons except spring. The concentrations of Cu, Zn, and Ni in the fresh and saline water masses differ slightly. Fresh water is distinguished for the highest concentrations of lead in summer and saline water in autumn. In contrast to all other metals, the concentration of chromium in saline water always is higher than in the fresh water.

Dependences of the water indices on salinity are on view in Table 4.

Klaipeda Port Water Pollution Levels

The concentrations of contaminants in components of the natural environment are the main indicator of the levels of pollution of different objects. The present work is based on the calculated (in 2006-08) seasonal and annual values of the pollution index (PI) [30]. Seasonal contamination with nutrients (PI_n), heavy metals and petroleum hydrocarbons (PI_p), and total pollution (PI_t) were evaluated separately for surface and near-bottom water horizons (Table 5). The total contamination of port water column (index PI_T) is subject to obvious seasonal fluctuations. Slight levels of pollution in winter and spring only are characteristic of port bays (Figs. 3 and 4). In summer, water pollution levels reach their maximum (PI_T>5 in Winter Port and Malku Bay) and the contaminated water spreads over the entire port basin (Fig. 5). The autumn values of PI_T are smaller but contaminated zones (1<PI_T<1.6) also persist in the open strait (Fig. 6).

The annual PI_T values for each station represent arithmetic means derived from average seasonal PI_T values. The average annual spectra of pollutants in all semi-closed water areas (and St S13 of the Klaipeda Strait) are comparable: they are predominated by heavy metals (about 70%), especially by lead (Fig. 7, Sts B9, B10, B12, B14, B16, and S13). Nutrients (24%) and TPH (21-23%) account for the

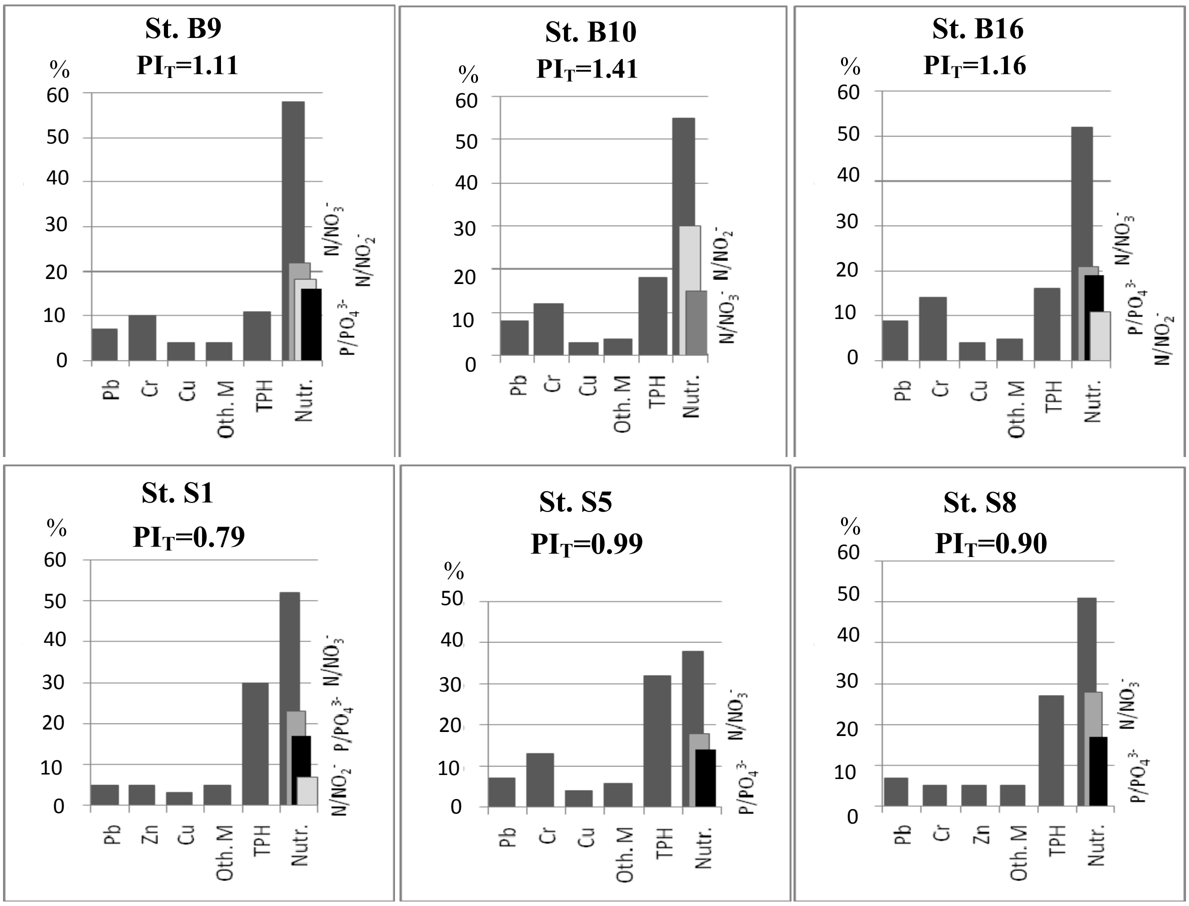

Fig. 3. Structure of winter PI_T components in slightly affected (Sts B9, B10, and B16) and clean (Sts S1, S5, and S8) water.

major part of the spectrum in relatively clean ($PI_T<1$) strait water (Fig. 7, Sts S1, and S2).

Discussion

Seasonal Fluctuations

The values of Klaipeda Port water indices (temperature, pH, concentrations of particulate material, dissolved oxygen) and concentrations of contaminants (particularly nutrients) markedly change depending on the season. Though the highest concentrations of nitrates, phosphates, and TPH in Klaipeda occur in winter (Table 2), winter water is the cleanest according to multiple contaminants (PI_T=0.96). Comparable average values also occur in spring (PI_T=0.99). The maximal contamination effect is reached when, under the conditions of rising temperatures, the nutrients are consumed by organisms. In warm seasons, the water of Curonian Lagoon and Klaipeda Strait is distinguished for an especially high abundance of bacterioplankton and phytoplankton. The emergence of some specific varieties of plankton implies that anthropogenic eutrophication continues [31, 32]. In summer, contrary to nitrates and phosphates, the concentrations of nitrites and ammonium (in the surface horizon alone) rise. The elevated concentrations of nitrites imply that the nitrification process is interrupted, i.e. the self-cleaning process is disturbed and water pollution values are high. Summer was the only season when direct dependence between ammonium and nitrite concentrations was significant ($p<0.01$): r=0.67 for the surface water horizon and r=0.72 for the near-bottom horizon. The inverse dependence between dissolved oxygen and ammonium concentrations was even better than in the case with nitrites: r=-0.82 for the surface water horizon and r=-0.85 for the near-bottom horizon. The calculated correlation between the summer concentrations of nitrites and the dangerous pollutant lead was relatively fair in the near-bottom water horizon (r=0.57) and strong in the surface horizon: r=0.72 (for Ni r=0.65, for Cu r=0.57, for Cr r=0.56). This allows assuming that seasonal increases of Pb and less marked increases of other metals are related to biosorption.

In the seasonal pattern of port water quality fluctuations, summer stands for the highest pollution levels and widest range of fluctuations of pollution values: $1.37<PI_T<5.45$ (Table 5, Fig. 5). In terms of the structure of pollutants, the most strongly affected autumn water (Fig. 6, Sts B10 and B14) resembles the cleanest summer water (Fig. 5, Sts S1 and S2).

Dependence of Water Indices on Water Genesis

The values of port water indices largely depend on the type of water (marine saline, continental fresh, or mixed) dominant at the time of measuring. Water dynamics in the Klaipeda Strait were predetermined by hydro-meteorological factors, though seasonal influence remained.

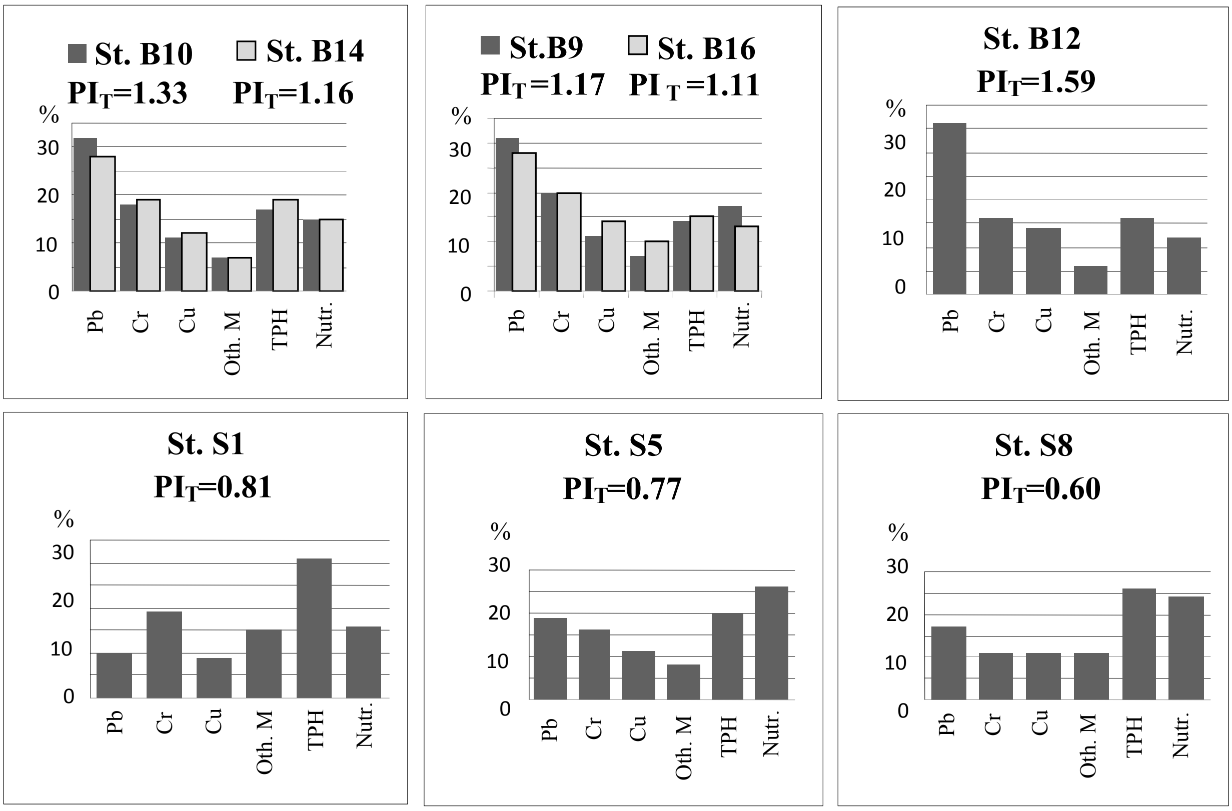

Fig. 4. Structure of spring PI_T components in slightly affected (Sts B9, B10, B12, and B16) and clean (Sts S1, S5, and S8) water.

Table 3. Seasonal water indices and concentration values of pollutants in the fresh and saline waters of Klaipeda port (2006-08): temperature (T), salinity (S), pH, dissolved oxygen (O_2), particulate material (PM), nutrients (N/NH_4^+, N/NO_2^-, N/NO_3^-, P/PO_4^{3-}), total petroleum hydrocarbons (TPH), and heavy metals (Cu, Zn, Ni, Pb, Cr, Cd, Hg).

	Season	Water mass	T °C	S ‰	pH	O_2 mg/L	PM mg/L	N/NH_4^+ mg/L	N/NO_2^- mg/L	N/NO_3^- mg/L	P/PO_4^{3-} mg/L	TPH µg/L	Cu µg/L	Zn µg/L	Ni µg/L	Pb µg/L	Cr µg/L	Cd µg/L	Hg µg/L
Winter	Average	Fresh	**1.3**	**0.2**	**8.4**	**11**	**11.3**	**0.048**	**0.005**	**2.27**	**0.045**	**44.4**	**1.2**	**<20**	**<1.0**	**1.1**	**1.7**	**<0.1**	**<0.001**
	Min		0	0.0	8.2	9.6	7	<0.028	0.002	2.02	0.028	<35	0.8	<20	<1.0	<1.0	**<0.5**	<0.1	<0.001
	Max		2.7	0.5	8.7	12	15	0.098	0.080	2.68	0.060	76.0	1.6	<20	<1.0	1.80	4.2	<0.1	<0.001
	Average	Saline	**0.1**	**4.7**	**8.3**	**10.8**	**9**	**0.160**	**0.003**	**0.69**	**0.017**	**44.0**	**1.3**	**<20**	**<1.0**	**0.90**	**2.8**	**<0.1**	**<0.001**
	Min		0	3.0	8	10.4	5	0.150	0.002	0.66	<0.006	<35	0.9	<20	<1.0	<1.0	<0.5	<0.1	<0.001
	Max		0.2	6.3	8.6	11.1	13	0.168	0.005	0.72	0.028	54.0	1.8	<20	<1.0	<1.0	5.2	<0.1	<0.001
Spring	Average	Fresh	**12.9**	**0.0**	**8.8**	**10.5**	**22.5**	**0.044**	**0.006**	**0.51**	**0.018**	**36.9**	**1.7**	**<20**	**<1.0**	**1.4**	**1.8**	**<0.1**	**<0.001**
	Min		10	0.0	8.2	9.3	18	<0.028	0.004	0.45	<0.006	<35	1.2	<20	<1.0	<1.0	1.0	<0.1	<0.001
	Max		14.1	0.0	9.1	11.2	30	0.052	0.009	0.55	0.027	42.0	2.3	<20	<1.0	2.0	2.5	<0.1	<0.001
	Average	Saline	**10.5**	**5.6**	**8.5**	**9.7**	**16**	**0.124**	**0.005**	**0.31**	**0.005**	**45.5**	**2.6**	**<20**	**<1.0**	**1.2**	**7.9**	**<0.1**	**<0.001**
	Min		9.1	3.1	8.1	7.1	13	0.082	0.002	0.12	<0.006	35.0	1.2	<20	<1.0	<1.0	1.2	<0.1	<0.001
	Max		12.3	6.8	8.9	11.3	22	0.215	0.010	0.62	0.007	83.0	7.5	<20	<1.0	5.2	12.4	<0.1	0.020
Summer	Average	Fresh	**20.2**	**0.1**	**8.7**	**8.3**	**23.5**	**0.030**	**0.007**	**0.33**	**0.023**	**43.6**	**7.0**	**<20**	**<1.0**	**12.9**	**7.9**	**<0.1**	**<0.001**
	Min		19.7	0	8.1	7.7	14	<0.028	<0.0015	0.25	0.020	35.0	6.5	<20	<1.0	7.1	6.3	<0.1	<0.001
	Max		20.5	0.5	9	8.8	35	0.042	0.011	0.39	0.024	50.0	8.0	<20	<1.0	15.7	9.6	<0.1	<0.001
	Average	Saline	**17.2**	**6.2**	**8.4**	**6.9**	**17.4**	**0.091**	**0.004**	**0.27**	**0.0132**	**35.5**	**7.6**	**<20**	**<1.0**	**9.6**	**8.4**	<0.1	**<0.001**
	Min		15.9	4.3	8.2	5.8	9	<0.028	0.002	0.10	<0.006	**<35**	4.8	<20	<1.0	7.5	5.0	<0.1	<0.001
	Max		19.5	7.5	8.7	8.7	33	0.154	0.006	0.37	0.026	40.0	9.4	<20	<1.0	10.8	11.8	0.11	<0.001
Autumn	Average	Fresh	**8.2**	**0**	**8.5**	**11.2**	**6.3**	**0.052**	**0.003**	**0.36**	**0.018**	**38.0**	**2.3**	**<20**	**<1.0**	**1.8**	**2.0**	**<0.1**	**<0.001**
	Min		8	0	8.4	10.8	4	<0.028	<0.0015	0.33	0.016	<35	2.0	<20	<1.0	1.2	1.8	<0.1	<0.001
	Max		8.5	0	8.6	11.5	8	0.080	0.004	0.39	0.022	49.0	2.8	<20	<1.0	2.5	2.3	<0.1	<0.001
	Average	Saline	**9.1**	**5.6**	**8.3**	**10.1**	**12.8**	**0.081**	**0.006**	**0.26**	**0.032**	**37.2**	**2.7**	**<20**	**<1.0**	**5.2**	**3.2**	**<0.1**	**<0.001**
	Min		6.7	3.4	8.1	9.2	9	0.003	<0.0015	0.12	0.018	<35	1.2	<20	<1.0	1.5	<0.5	<0.1	<0.001
	Max		10.2	6.5	8.5	10.9	25	0.160	0.014	0.51	0.063	42.0	5.9	<20	<1.0	10.1	10	<0.1	<0.001
Annual		Fresh	**10.6**	**0.1**	**8.6**	**10.2**	**15.9**	**0.043**	**0.005**	**0.867**	**0.026**	**40.7**	**3.1**	**<20**	**<1.0**	**4.3**	**3.4**	**<0.1**	**<0.001**
		Saline	**9.2**	**5.5**	**8.4**	**9.3**	**12**	**0.114**	**0.004**	**0.382**	**0.017**	**40.5**	**3.6**	**<20**	**<1.0**	**4.2**	**5.5**	**<0.1**	**<0.001**
		Port Area	**9.9**	**2.1**	**8.4**	**9.5**	**14.3**	**0.084**	**0.009**	**0.794**	**0.023**	**45.9**	**6.3**	**20.0**	**1.5**	**9.8**	**8.5**	**0.12**	**<0.001**

Table 4. Variability of Pearson correlation coefficients (r) between water quality parameters and water salinity.

Season	Horizons	pH	O_2	PM	N/NH_4^+	N/NO_2^-	N/NO_3^-	P/PO_4^{3-}	TPH	Cu	Zn	Ni	Pb	Cr	Cd	Hg
		Correlation coefficients (r)														
Winter	Surface	0.14	-0.07	-0.44	0.49*	-0.02	**-0.72***	**-0.55***	0.09	0.01	-0.25	0.00	-0.46*	0.07	-0.23	0.00
	Near bottom	0.04	-0.02	-0.46*	0.21	-0.17	**-0.76***	**-0.60***	0.02	0.05	-0.20	-0.11	**-0.58***	0.11	-0.18	0.00
Spring	Surface	0.10	0.01	-0.27	0.38	-0.05	-0.38	**-0.71***	-0.05	-0.04	-0.26	-0.34	-0.16	0.43*	-0.31	0.34
	Near bottom	0.06	0.03	-0.50*	0.27	-0.44*	-0.16	-0.46*	0.27	0.07	-0.28	-0.25	-0.10	0.34	-0.11	0.21
Summer	Surface	-0.40	**-0.53***	-0.03	0.34	0.05	-0.31	**-0.73***	-0.19	-0.14	-0.35	-0.15	-0.20	0.11	-0.22	0.00
	Near bottom	-0.18	**-0.64***	-0.48*	0.40	0.35	**-0.51***	**-0.78***	**-0.62***	-0.41	**-0.56***	-0.23	-0.26	-0.29	-0.41	0.00
Autumn	Surface	-0.25	0.26	0.22	0.11	0.48*	**-0.56***	0.37	-0.36	**-0.53***	-0.41	-0.36	-0.44*	0.05	-0.28	0.00
	Near bottom	-0.36	0.17	0.23	0.13	0.27	**-0.75***	0.48*	-0.25	-0.39	-0.37	-0.38	-0.43*	0.14	-0.47*	0.00

*Significant at $p<0.01$; $r>0.5$ are in bold.

In comparison with fresh Curonian Lagoon water, saline sea water is distinguished by lower temperatures (except in autumn), smaller values of pH, and smaller O_2 concentrations (Table 3). Baltic Sea water contains considerably smaller amounts of particulate material [2, 4, 11] (Table 3). The bulk of particulate material is carried into the Klaipeda Port from the Curonian Lagoon [11]. Particulate material is one of the indices reflecting the water quality in the Klaipeda Port basin. Fine particles absorb the larger part of toxins in the water, protecting the water ecosystem from critical pollution [33].

Concentrations of nitrites, nitrates, and phosphates (except near-bottom horizon in autumn) in the continental water is 1.2-3.3 times as high as their concentration in the sea water, whereas the continental water contains a smaller concentration of ammonium (Table 3). Comparison of annual average values for 2006-08 (Table 3) with the long-term dynamics of nutrients in the adjoining water areas [34, 35] showed that nitrate concentration in the saline port water mass by 1.5-7 and in the fresh by 2-6 times exceeded the respective values for the Baltic Sea offshore and Curonian Lagoon. The average concentration of nitrates (0.794 mgN/L) in the Port water determined for 2006-08 by 1.5 times exceeded the value determined in 2004-06 [34]. The average concentration of phosphates (0.023 mgP/L) in the port water determined for 2006-08 is comparable with the average values of recent years [34, 35].

Comparison of the values of fresh and saline water indices and concentrations of contaminants showed that in the majority of cases the autumn average values in the near-bottom saline water horizon exceed the ones in the continental fresh water (Table 3). In the context of the present study, the untypical properties were characteristic of saline water that invaded the Curonian Lagoon. In October 2007 and 2008 the studied saline near-bottom water flew (returned) from the lagoon into the sea. Meanwhile, in other cases saline water flew from the sea into the lagoon.

The impact of saline water on various water indices is proved by calculated seasonal correlation coefficients r (Table 4). The most pronounced inverse linear dependences are characteristic of nitrates, phosphates and dissolved oxygen ($r>0.5$). Meanwhile the concentrations of petroleum hydrocarbons and heavy metals were almost independent of salinity values ($r\leq0.5$).

Water salinity is decisive for many aspects of water quality in the saline-fresh water interface zones. Salinity gradients predetermine the distribution of dissolved and solid phases of metal concentrations [36-38] and affect the composition of the complex of metals in the water column and other geo-chemical features [39-41]. Variations of salinity values affect the distribution of nutrients and dynamics of other water indices [42, 43]. Fresh-saline water interfaces are characterized by especially high fluctuations of metals and other pollutants [44]. The impurities of sea water not only show the content of dissolved salts but also indirectly imply other possible water qualities: transparency, concentration of particulate material, degree of saturation with nitrogen and phosphorus compounds, etc.

Table 5. Values of pollution indices for surface and near-bottom water horizons (total pollution PI_t, nutrients PI_n, petroleum hydrocarbons and heavy metals PI_p) in the stations of Klaipeda Strait (S) and semi-closed water areas (B).

Season Area	Station	PI_t		PI_n		PI_p		Season Area	Station	PI_t		PI_n		PI_p	
		Surface	Near bottom	Surface	Near bottom	Surface	Near bottom			Surface	Near bottom	Surface	Near bottom	Surface	Near bottom
Winter – S	S1	0.77	0.81	0.58	0.71	0.76	0.79	Summer – S	S1	**1.45**	**1.29**	0.25	0.14	**1.47**	**1.31**
	S2	0.95	0.73	0.63	0.77	0.94	0.64		S2	**1.67**	**1.48**	0.16	0.16	**1.69**	**1.50**
	S3	0.83	0.72	0.71	0.63	0.82	0.72		S3	**2.07**	**2.06**	0.15	0.17	**2.10**	**2.09**
	S5	**1.30**	0.69	0.59	0.70	**1.30**	0.68		S5	**2.19**	**2.27**	0.23	0.21	**2.22**	**2.31**
	S13	1.00	0.60	0.68	0.44	0.99	0.60		S13	**3.23**	**4.09**	0.51	0.74	**3.27**	**4.13**
	S7	0.90	0.78	0.73	0.82	0.89	0.49		S7	**1.82**	**2.08**	0.19	0.25	**1.84**	**2.10**
	S8	0.95	0.87	0.85	0.92	0.98	0.62		S8	**2.16**	**2.25**	0.25	0.28	**2.18**	**2.28**
	Average	0.96	0.74	0.68	0.71	0.95	0.65		Average	**2.08**	**2.22**	0.25	0.28	**2.11**	**2.25**
Winter – B	B9	**1.05**	**1.16**	**1.18**	**1.20**	0.57	**1.12**	Summer – B	B9	**4.27**	**5.20**	0.61	0.49	**4.31**	**5.25**
	B10	**1.89**	0.92	**1.97**	**1.01**	**1.24**	0.67		B10	**5.14**	**5.75**	0.56	0.41	**5.18**	**5.81**
	B12	0.69	0.83	0.59	0.87	0.68	0.67		B12	**3.49**	**4.37**	0.35	0.30	**3.53**	**4.42**
	B14	**1.22**	**1.09**	**1.31**	**1.13**	0.69	0.80		B14	**4.63**	**5.77**	0.55	0.66	**4.68**	**5.82**
	B16	**1.02**	**1.04**	**1.08**	**1.12**	0.64	0.83		B16	**4.79**	**5.42**	0.60	0.73	**4.84**	**5.47**
	Average	**1.17**	**1.01**	**1.23**	**1.07**	0.76	0.82		Average	**4.46**	**5.30**	0.53	0.52	**4.51**	**5.36**
Spring – S	S1	0.78	0.84	0.20	0.16	0.80	0.85	Autumn – S	S1	**1.01**	0.68	0.24	0.37	**1.02**	0.69
	S2	0.64	0.74	0.21	0.13	0.66	0.76		S2	0.61	0.53	0.25	0.32	0.62	0.54
	S3	0.60	0.57	0.16	0.13	0.62	0.59		S3	**1.26**	**1.06**	0.19	0.22	**1.29**	**1.08**
	S5	0.92	0.62	0.92	0.15	0.80	0.64		S5	0.93	0.77	0.29	0.39	0.95	0.79
	S13	0.82	0.93	0.20	0.21	0.84	0.96		S13	**1.75**	**1.43**	0.28	0.28	**1.77**	**1.45**
	S7	0.56	0.80	0.23	0.18	0.57	0.81		S7	**1.19**	**1.02**	0.20	0.21	**1.21**	**1.04**
	S8	0.58	0.62	0.22	0.18	0.58	0.60		S8	0.85	0.75	0.28	0.39	0.87	0.76
	Average	0.70	0.73	0.31	0.16	0.69	0.75		Average	**1.09**	0.89	0.25	0.31	**1.10**	0.91
Spring – B	B9	0.91	**1.42**	0.64	0.17	0.92	**1.46**	Autumn – B	B9	**1.44**	**1.67**	0.27	0.35	**1.47**	**1.70**
	B10	**1.27**	**1.39**	0.33	0.23	**1.29**	**1.41**		B10	**2.32**	**2.80**	0.38	0.27	**2.35**	**2.84**
	B12	**1.19**	**1.99**	0.24	0.17	**1.22**	**2.04**		B12	**1.74**	**1.55**	0.41	0.44	**1.76**	**1.58**
	B14	**1.02**	**1.31**	0.20	0.16	**1.06**	**1.35**		B14	**1.83**	**2.35**	0.28	0.32	**1.87**	**2.38**
	B16	**1.05**	**1.17**	0.33	0.19	**1.07**	**1.21**		B16	0.75	**1.07**	0.36	0.34	0.77	**1.09**
	Average	**1.09**	**1.46**	0.35	0.18	**1.11**	**1.49**		Average	**1.61**	**1.89**	0.34	0.34	**1.64**	**1.92**

Spatial Distribution of the Klaipeda Port Water Pollution Indices

Analysis of the spatial distribution patterns of contamination indices in the Klaipeda port basin revealed the areas with the highest pollution levels, paths of dispersion of pollutants and cleanest areas of port basin. It was established that the levels of water contamination are higher in the semi-closed water areas in the neighbourhood of industrial objects. Additionally, the fluctuation patterns of salinity demonstrate slower renewal of the water in the bays than in the open areas of Klaipeda Strait. This is the substantial cause of higher concentrations of pollutants in semi-closed water areas. Local reductions of pH values in the bays are characteristic of strongly affected port areas where hydrogen ions are emitted in the process of organic matter degradation and reduce pH values [45].

In winter, when the Klaipeda Strait is mainly clean, semi-closed water areas are slightly affected by contamination with nutrients (Fig. 3, Table 5). In contrast to winter, heavy metals (lead standing out among them) account for the greater part of spring pollution in slightly affected semi-cloused water areas (Fig. 4, Sts B). Considerably lower concentrations of lead are the main cause of pollution index PI_T reduction to the values identifying clean water in Klaipeda Strait (Fig. 4, Sts S).

In summer the concentrations of nitrites in the semi-closed water areas of the port are twice as high as in the open strait. This implies elevated contamination of bays. The inverse dependence between the concentrations of dissolved oxygen and nitrites was relatively fair in both the surface (r=-0.57) and the near-bottom (r=-0.63) water horizons (in other seasons significant at (p<0.01) correlation coefficients not found out).

From spring to autumn the degree of pollution with heavy metals and petroleum hydrocarbons of semi-closed bays exceeds the total value for the strait (Table 5). In summer, there is no port area that could be classified as absolutely clean (Fig. 5). Heavy metals, lead in particular, are the main pollutants in the port water area situated in the closest proximity to the sea (37-41% of the total pollution) (Fig. 5, Sts S1 and S2). PI_T values gradually rise moving towards the south (Fig. 5, Sts S3, S5 and S13). Though in the southernmost part of the strait the PI_T values again are lower (Fig. 5, Sts S7 and S8). In the semi-closed water areas of the port the spectrum of pollution is almost identical (Fig. 5, Sts B9, B12, B14, B16). The contribution of Pb reaches its maximal value (56%) in the most strongly affected part of Malku Bay (PI_T=5.45), where the role of nutrients is reduced (7%) (Fig. 5, St. B10). In summer, the average value of pollution for the near-bottom water horizon of semi-closed water areas even exceeds the limit of serious pollution (PI_t=5.30) (Table 5). Analysis of pollution patterns in the port water column show that in all seasons, the near-bottom water horizon of semi-closed water areas is more strongly affected with petroleum hydrocarbons and heavy metals than the surface horizon. Conversely, the surface horizon is more often contaminated with nutrients (except in autumn). In the Klaipeda Strait, seasonal pollution patterns in the near-bottom and surface water horizons are more variable (Table 5).

The distribution pattern of PI_T>1 areas allows assuming that in autumn, slightly affected water masses flood from the Curonian Lagoon and Dane River. Evidence of pollution and local sources persist: the PI_T index reaches its maximal values in the semi-cloased areas of intensive economic activity – southern part of the Malku Bay and Baltija SY quay (Figs. 1 and 6). In contrast to other seasons, the autumn spectrum of pollutants is similar both in open and semi-closed water areas of the strait: Sts S5, S8, and B16; Sts S3, S7, and B9 (Fig. 6). In autumn, the differentiation disappears due to the active water dynamics and horizontal and vertical water mixing. This process is proved by a marked reduction of the vertical salinity gradient in autumn (Fig. 2).

Analysis of distribution patterns of the annual PI_T values in the Klaipeda Strait allowed determining the group of potentially maximally polluted water areas (Fig. 7). This group includes Malku Bay (particularly the southern part), Baltija SY, and winter port (Fig. 1). The water remains relatively clean (annual PI_T<1) only at that part of the strait close to the entrance channel of the port permanently washed by sea waves (Fig. 7).

As in the earlier years [4, 8, 46], stable clearly defined areas with high concentrations of petroleum hydrocarbons

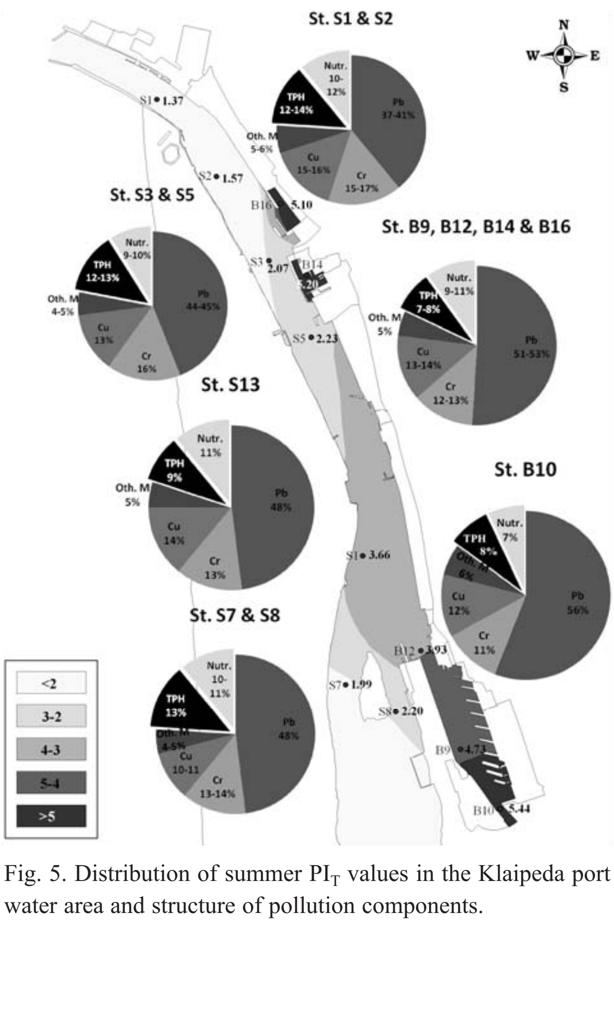

Fig. 5. Distribution of summer PI_T values in the Klaipeda port water area and structure of pollution components.

were not detected in the port water area. The concentrations of heavy metals depend on the strength and distribution of their sources. The correlation coefficients calculated for the whole research period for finding the links between heavy metals and TPH showed that the closest link existed between Pb and Cu, Pb, and Ni, and Cu and Ni concentrations ($r \geq 0.7$), implying their common sources in the port. The correlation between Ni and Cr, Pb and Cr, Zn and Cd, Ni and Cd, and Cu and Cd was relatively fair ($0.5 < r < 0.7$). The link between concentrations of petroleum hydrocarbons and investigated heavy metals was poor ($r \leq 0.5$).

Conclusions

The level of water pollution in Klaipeda and its separate water areas is predetermined by the input of pollutants from the Curonian Lagoon basin and local sources, water circulation patterns, and seasonal dynamics of water parameters.

In winter, the water of the port is least polluted with total multiple contaminants. This is predetermined by a minimized biosorption process during the slowdown of vital activity of organisms and by lower concentrations of heavy metals, lead in particular. In winter, nutrients become the major contaminants.

In spring, total water pollution is the same as in winter, with the difference that the weight of heavy metals – lead in particular – in the spectrum of pollutants in bays rises considerably. The pollutants of the cleaner open strait water, where organisms develop with a time lag, are predominated by petroleum hydrocarbons and nutrients.

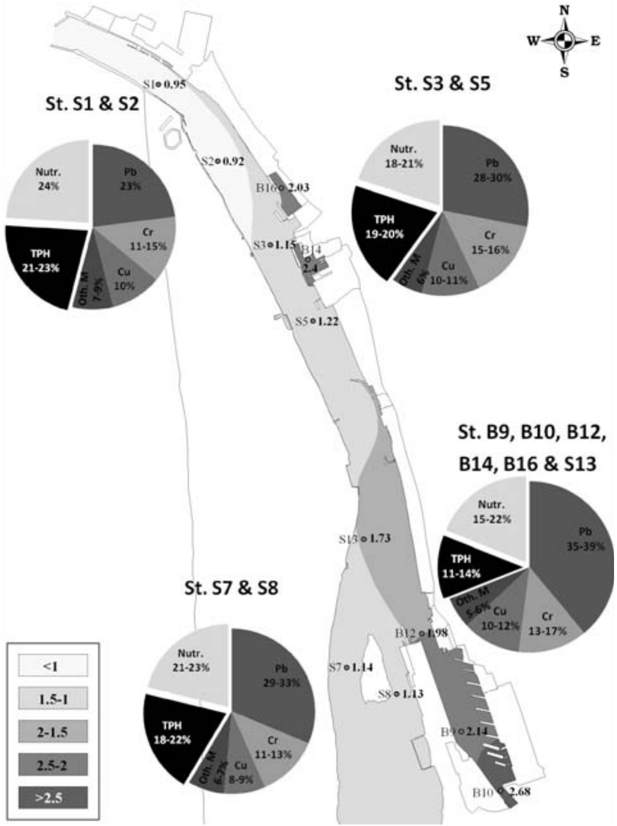

Fig. 7. Distribution of annual PI_T values in the Klaipeda port water area and structure of pollution component.

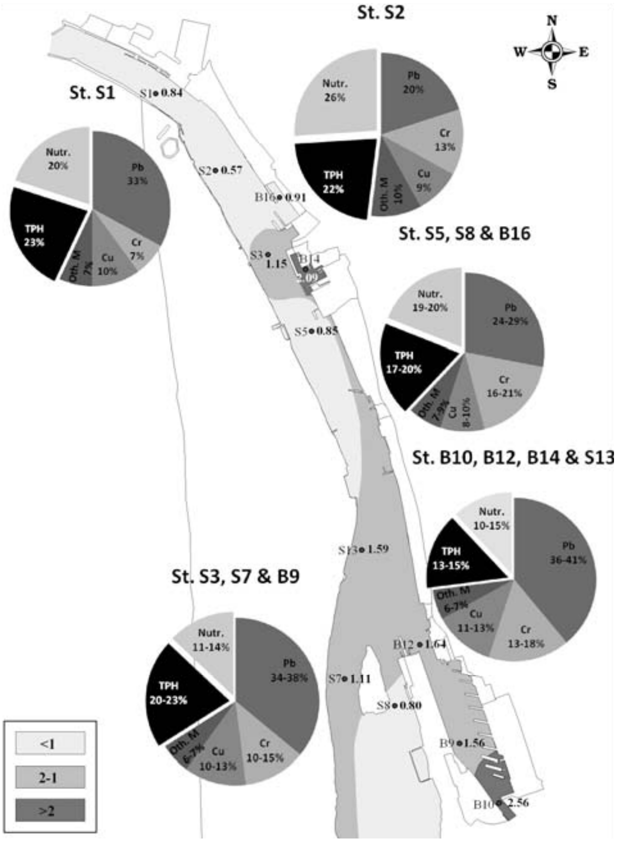

Fig. 6. Distribution of autumn PI_T values in the Klaipeda port water area and structure of pollution components.

The highest levels of pollution, in combination with the highest water temperatures, highest concentrations of particulate material and smallest concentrations of O_2, occur in summer when no clean water remains in the entire port basin and in its semi-closed areas the water is seriously affected. Heavy metals, lead in particular, are the dominant pollutants in summer. The increase of Pb and less marked increase of Cr, Cu, and other metals presumably is related to biosorbtion.

In autumn, the total water contamination level, including heavy metals in the spectrum of pollutants, becomes half as low. The role of continental runoff in contamination of Klaipėda Port basin becomes especially evident.

The pollution dynamics of Klaipeda port water are indirectly reflected by fluctuations of water indices: pollution tends to increase with higher values of temperature and concentrations of particulate material and lower values of salinity, pH, and transparency. Dissolved oxygen in summer and concentrations of nitrates and phosphates in all seasons are in closest inverse dependence with salinity. The concentrations of petroleum hydrocarbons and heavy metals are almost independent of salinity values.

The average values of petroleum hydrocarbons and heavy metals are less dependent on seasonal variations and are considerably higher in the port water than in the saline marine or fresh lagoon water. This implies that the port is the source of these chemicals. In all seasons, the levels of pollution with petroleum hydrocarbons and heavy metals of the near-bottom water in semi-closed port water areas are higher than those of the surface horizon. Among investigated heavy metals, the closest mutual links exist between Pb and Cu, Pb and Ni, and Cu and Ni. Presumably pollutants with similar concentration dynamics have common sources.

The most strongly affected water in the port of Klaipeda is characteristic of semi-closed water areas where intensive economic activity of the port companies takes place and renewal of the water is slow. From these water areas, the contaminated water flows into the open Klaipėda Strait. Analysis of annual distribution patterns of the water pollution showed that the water remains relatively clean only in those water areas close to the entrance channel of the port permanently washed by sea waves.

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