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Studies on Intercorrelation between Selected Persistent Organic Pollutants (POPs) and Ions in Sea Water from the Coastal Zone of the Baltic Sea, Gdańsk Bay Region

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Abstract

The Baltic Sea is a semi-enclosed brackish sea with only limited water exchange with the North Sea and, thus, the North Atlantic. This salty water reservoir with water residence time of approximately 25 years is contaminated with many inorganic and organic pollutants: VOCl (*Volatile Organohalogen Compounds*), HC (*Petroleum Hydrocarbons*), OPNP (*Organophosphorus and Organonitrogenous Pesticides*), OCP (*Organochlorine Pesticides)*, PAH (*Polycyclic Aromatic Hydrocarbons*) and heavy metals. Our paper presents monitoring results and sea environmental pollution assessment of the Southern Baltic coastal zone- the area of the Gdańsk Bay, based on the analysis of sea water samples. A set of various analytes were determined: PAH (16 analytes), VOCl (6 analytes), HC (9 analytes), OPNP (8 analytes), OCP (5 analytes), heavy metals (Zn, Cd, Pb, Cu). The results were subjected to full statistical evaluation. An assessment of sea environment contamination was made by characterization of pollution sources and the definition of intercorrelations between them. The characterization of major statistically important correlations between 45 variables was performed with the use of principal component analysis technique. From the performed PCA it arose that the factor configuration was similar for all sampling points and in all cases 5 factors explain over 60% of the data variance, and the statistically significant loading factors are higher than 0.7 (with $p=0.05$). Additionally, analysis of variance and time series analysis were applied to define important differences between chemical species' concentration levels in time and in accordance with sampling points' geographical location. As a result of time series analyses carried through with consideration to sampling points, there were no statistically important differences discovered in trends of changes from 1996 up to 1999 for any of examined groups of compounds.

Keywords: Baltic Sea, sea water, persistent organic pollutants, volatile compounds, heavy metals, time series analysis, correlations

Introduction

The Baltic Sea is a semi-enclosed brackish sea with only limited water exchange with the North Sea, and,

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thus the North Atlantic [1]. This salty water reservoir with water residence time of approximately 25 years [2] is contaminated with many inorganic and organic pollutants. Minor sea pollution sources (also for the Baltic Sea) are rivers and smaller water-courses, sea transport, urban impurities and industrial sewage, agricultural wastes, and oil residues after catastrophes on the sea. Solid industrial waste is a serious problem, and because of troublesome utilization and storage, it is very often sunk in the sea. Sunk radioactive substances and chemical weapons remaining after activities of World War II are also treated as industrial waste. Additionally, due to the nearness of land, pollutants emitted to the atmosphere in the form of technological gases or dust can integrate with steam and fall into the sea with rain and snow [3,4].

A lot of compounds originating from agricultural fertilizers are washed out from soil and carried into the sea. An estimation has been made that about 40% of total phosphates and 35% of total nitrates getting into the sea come from central and northern Poland. The source of phosphates, which are playing a meaningful role in eutrophication of the coastal Baltic Sea water, is urban waste containing washing powder components [5].

A peculiar category of sea water pollutants is a group of heavy metals. These pollutants are getting into water not only with river flow but also from shipyard installations and ships. Moreover, they are carried by dry and wet precipitation. As published before, Cu, Zn and Ag are introduced to the Gulf of Gdańsk principally from the Vistula River, whereas Cd and Pb are getting there as a result of atmospheric and riverine transport of these elements [6]. With regard to Cd, annual input via atmosphere is approximately 77 Gg, whereas the input from rivers and other sources is about 56 Gg a year [7].

Persistent organic pollutants (POPs) are an extremely important group of hazards. Most commonly known and recognized as sea environment pollutants are petroleum hydrocarbons (PH) and polycyclic aromatic hydrocarbons (PAHs) [7-9]. On terrestrial areas PAHs come from abrading of asphalt surface and tires, scavenge of pistons and crankcases, and also from oil evaporation. PHs infiltrate ecosystem as a result of incomplete liquid fuel combustion. Another important source of petroleum hydrocarbons is the so-called "cold engine effect". Under low temperatures, especially during winter , engines require longer times before they reach an appropriate work temperature. Petroleum light fractions' evaporation from the tank and the carburettor, leakage from the lubrication system or the feeding system, emissions from the crankcase in case of starting older types of cars are also important sources of PHs occurring in run-off waters. One should keep in mind that most of these compounds reach the sea through rivers, storm-water drains, sewage or with deposition (dry or wet), and only 10% of the total amount is getting there in consequence of emergency overlaps, ballast and bilge water dumps and from drilling platforms. Another hazardous group is pesticides, and the most dangerous among them are organochlorine compounds. Many organic compounds containing chlorine are more or less toxic. Representatives of this group are the pesticides DDT (but in this case it is only slightly toxic), lindan, methoxychlor and polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [7-15].

As a result, in the Baltic Sea (water, bottom sediments, fauna and flora) it can be seen that most typical atmospheric pollutants are present in surface, ground and run-off waters [10, 16-17].

Gdańsk Bay is an important part of the Baltic Sea, and due to the amount of pollutants introduced (mostly with the Vistula River waters) the level of water and total ecosystem pollution is elevated.

In this work results of research concerning analyses of 45 components (various organic and inorganic compounds) in water samples, collected in the area of the Baltic sea coastal zone within a 4-year period (from 1996 to 1999), are presented. An assumption has been made that there are groups of pollutants whose presence in sea water samples can be explained by characteristics of terrestrial water pollution sources [18], and also by explanation for statistically important differences in correlations among them. Therefore, obtained results for chosen analyte concentrations are presented in multidimensional intercorrelation form. In this work an attempt to interpret the co-occurence of particular compounds or ions together with the statistic importance of the correlations has been made.

Experimental

Sampling Sites

The Gdańsk Bay (the Baltic Sea) coastal zone is located in the northern part of Poland (18°56'E, 54°40'N). The Vistula River presence, with a highly expanded tributary system, is a cause of untreated run-off waters inflowing directly to Gdańsk Bay.

The research was performed from 1996 to 1999, and samples were collected in quarter intervals. Seawater samples were collected in two selected locations in the Gdańsk Bay zone. Bay water samples coming from the Tricity region were collected close to the Sopot pier and Gdynia-Orłowo cliff territory – typical recreation regions. Additional samples were collected in two locations in direct vicinity of Gdańsk Bay, but placed at the open sea (Władysławowo and Hel). Władysławowo is a resort placed in the root of Hel Sandbar, where the open sea fishery is highly developed due to the presence of the fishing harbour. Moreover, there is a beach and a recreation centre placed in Władysławowo. The Hel is located in the southeastern end of Hel Sandbar, in Puck Bay, and plays the role of seashore recreation centre (hotels and private accommodations, beach), inshore navigation, fishing harbour and fish processing agency. Samples were also collected in the vicinity of Puck city, located on the edge of the Kepa Pucka cliff, in the Puck Bay area (the infrastructure of the fishing harbour, the yacht harbour and the yacht haven). The results of the examined samples (collected in specified locations) comparison provided the basis for the impact assessment of pollution loads (present and changing with time) on Gdańsk Bay, thus on the Baltic Sea. Fig. 1 presents the scheme of sampling point locations.

Analytical Procedures

Samples of seawater were collected from a depth of 1 m and stored in glass bottles. The bottles were filled to the brim, closed with a glass stopper and transported to the laboratory. Before the isolation and preconcentration step, samples were stored in the refrigerator at 4°C [17].

Using developed and described analytical procedures [17-30] analytes from the following groups were determined in collected samples: petroleum hydrocarbons, volatile organohalogen compounds, polycyclic aromatic hydrocarbons, pesticides (organochlorine, organophosphorus and organonitrogenous), polichlorinated biphenyls, several heavy metal ions. In papers presented before [17-30] the detailed reference materials application and equipment calibration procedures description have been specified.

Fig. 1. Location of sampling points.

Compounds analyzed within this research project come mostly from anthropogenic sources. Table 1 presents a list of analytes divided into groups mentioned above and due to the applied analytical technique.

In the case of organohalogen volatile compounds, the determination limit has been considerably lowered thanks to the pre-treatment technique application (isolation and preconcentration) – TLHS (thin layer head space) with the automatically generated liquid sorbent stream [21, 24-28, 30]. For determination of petroleum compounds, purge and trap (PT) technique has been performed. Pesticides and PAHs have been analyzed with the use of the SPE Bakerbond C_{18}, 500 mg and the SPE Bakerbond SDB columns after on-column solid-phase extraction preconcentration.

Table 2 presents the analytical conditions applied for determining analytes in seawater using chromatographic methods.

Zn, Cd, Pb, Cu content in seawater analyses have been performed by electrothermal atomic absorption spectrometry (ET AAS), using BUCK Scientific Spectrophotometer 210 VGP [31-34]. Table 3 presents the work parameters of this apparatus.

Data Processing

As a result of the broad research subject, large series of concentration values have been obtained, which sometimes causes difficulties in evaluation. In this case, the application of multivariate techniques proves to be a very useful tool for the interpretation of such a large data set. These techniques help to reduce the dimensionality and to explain the relationships between measured variables. Moreover, chemometrical treatment of data allows extracting the maximum information from analytical results.

A commercial statistics software package, Statistica 5.0 for Windows (StatSoft Inc., Tulsa, USA) was applied for the chemometrical data mining.

Results and Discussion

The presence of various organic compounds and selected heavy metals in examined sea water samples was observed. The same analytes have been determined in sea water samples collected in other parts of the Baltic Sea [2-5]. These pollutants have been determined on a very low concentration level or, in some cases, have not been found at all in any of the investigated sampling points (isooctane, nonane, chlorobenzene). Most of the analyzed compounds (heavy metals, pesticides, PCBs and selected compounds from PAHs) are biocumulated by living organisms, especially the marine kind, and bioenriched

Table 1. The set of organic compounds determined in seawater samples.

Chemical group of compounds	Analytes	Sample pretreatment	Determination technique
Polycyclic aromatic hydrocarbons (*PAH*)	Naphthalene, Acenaphthalene, Acenaphthene, Fluoren, Fenantrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd)pyrene, Dibenzo(ah)anthracene, Benzo(ghi)perylen	SPE	Gas chromatography with use of various detectors (NPD, ECD, MSD)
Organophosphorus and organonitrogenous pesticides (*OPPs* and *ONPs -OPNPs)*	Simazine, Atrazine, Fenitrothion Propazine, Bromphos-ethyl, Malathion Chlorfenvinfos, Tertbuthylazine	SPE	
Organochlorine pesticides (*OCPs*)	p,p'-DDT, Metoxychlorine, Lindan Heptachlor epoxide, o,p'-DDE	SPE	
Volatile organohalogen compounds (*VOCl*)	$CHCl_3$, $CHBrCl_2$+C_2HCl_3, $CHBr_2Cl$, $CHBr_3$, C_2Cl_4, CCl_4	DAI	Gas chromatography with direct aqueous injection and electron capture detection (DAI-GC- ECD)
Volatile organohalogen compounds *(VOCl)*	Chlorobenzene	PT	Purge and trap technique with thermal desorption and gas chromatography with flame ionization detection (PT-TD – GC-FID)
Petroleum hydrocarbons (*HC*)	Pentane, Hexane, Heptane, Nonan, Isooctane, Benzene, Toluene, Xylene, Undekane, Dekane, Ethylobenzene	PT	

SPE = solid phase extraction; PT = purge and trap technique; DAI = direct aqueous injection

Table 2. Chromatographic parameters for the determination of pesticides, volatile organohalogen compounds and petroleum hydrocarbons.

Parameter	Organochlorine pesticides	Organonitrogen and organophosphorus pesticides	Volatile organohalogen compounds	Volatile petroleum hydrocarbons	Polycyclic Aromatic Hydrocarbons (PAHs)
Chromatograph	GC 6180 VEGA, Carlo Erba - Fisons	GC 8000, Fisons	GC 6180 VEGA, Carlo Erba - Fisons	GC-8000, Fisons	GC-8000, Fisons
Detector	ECD	NPD	ECD	FID	MSD-800 detector in SIM mode
Detector temperature	320°C	270°C	350°C	280°C	
GC column (length x I.D. x film thickness)	60 m x 0.25 mm x 0.25 µm RTx-5 , precolumn - 2 m x 0.32 mm	30 m x 0.25 mm x 0.25 µm Rtx-35, precolumn - 2 m x 0.32 mm	30 m x 0.32 mm x 5 µm DB–1, 2 m x 0.32 mm fused silica precolumn	60 m x 0.32 mm x 1.8 Fm , Rtx-624	30 m x 0.25 mm x 0.25 Fm DB-5
Injector	Cold on-column	Splitless	Cold on - column	Direct PT	On - column
Carrier gas	Hydrogen	Hydrogen	Hydrogen	Helium	Helium
Oven temperature program	60°C → 30°C/min. → 180°C → 10°C/min → 280°C (10 min)	60°C (1 min) → 40°C/min. → 180°C → 30°C/min → 200°C → 7°C/min → 600°C	Isothermal, 104°C	2 min at 35°C; from 35°C to 100°C at 5°C/min, then to 250°C at 10°C/min and 10 min at 250°C	40°C to 120°C at 40°C/min, then to 280°C at 5°C/min and 10 min at 280°C
Injector temperature	60°C	100°C	104°C	-	40^{o}C

within the food chain. It happens very often that the metabolites of chemical compounds are even more toxic to living organisms than their precursors [35-37]. Therefore, water analyses directed on the determination of these compounds are very important and should be performed systematically.

It was necessary to limit the number of tables presenting data. This is why there was only the summary of the data descriptive statistics of seawater analyses shown in Table 4. Moreover, the large number of discovered dependences with division into 5 sampling points (Hel, Władysławowo, Puck, Orłowo, Sopot) were presented in the text and on the figures.

Table 3. Conditions of seawater analysis using atomic absorption spectrometry.

Analyte	Zn	Cd	Pb	Cu
Apparatus type	AAS BUCK Scientific –210 VGP Auto Sampler BUCK Scientific –220 AS			
Method	Flame Atomic Absorption Spectrometry (FAAS)	Graphite Furnace Electrothermal Atomic Absorption Spectrometry (GF ETAAS)		
Wavelength	213.86 nm	228.8 nm	283.2 nm	324.7 nm
Slit	0.2 nm	0.7 nm	0.7 nm	0.7 nm
Lamp current	20 mA	20 mA	20 mA	20 mA
Matrix modifier	-	-	1000 ppm $Mg(NO_3)_2$ + 1000 ppm $(NH_4)_3PO_4$	-

In sporadic cases, when the analytes' concentrations determined in water from particular sampling points were lower than the determination limit of the applied analytical technique, the concentration values have been changed for chemometrical needs into 1/3rd of the detection limit of the applied analytical technique.

Most of the analyzed variables (except for Cd, naphthalene, acenaphthalene, hexane and xylene) have a characteristic data distribution, which is considerably different from the normal type. The skewness factor for these values oscillates between 2 and 8. This arises from the fact that analytes present in water samples are at a very low concentration level, and the biggest population of data have these values very close to applied analytical methods' determination limits.

Correlation Analysis

Bivariate correlation analysis is based on examining relationships between pairs of variables. These correlation coefficients range between –1 and +1 according to the statistical significance of the estimated correlation. Coefficients higher that 0.50 are statistically significant at 95% of the confidence level, after application of the hypothesis test for the correlation coefficient, being the null hypothesis stating that no relationship exists between each pair of analytes.

First correlation study was done for sums of analytes belonging to each group, because in whole data set plenty of intercorrelations have been found between various species in domains of organochlorine pesticides, organonitrogen and organophosphorus pesticides, volatile organohalogen compounds, volatile petroleum hydrocarbons and especially polycyclic aromatic hydrocarbons. As can be seen in Table 5, there are various types of correlations present between groups of analytes for each sampling point.

Correlations for samples collected in Sopot (Gdańsk Bay) were found for the sum of petroleum hydrocarbons and Cd^{2+} (0.79), and also for volatile organohalogen compounds and Pb^{2+} (0.82). Whereas for samples coming from Orłowo (Gdańsk Bay), correlations between Zn^{2+} and Cu^{2+} (0.61) were found, and also between polycyclic aromatic hydrocarbons and Pb^{2+} (0.60). The presence of these substances in Gdańsk Bay is a result of domestic human activity (fireplaces, transport, urban sewage, waste) and of industrial enterprises close neighbouring (emission, sewage, waste, transport). These pollutants are introduced also with the river tributary (the Vistula River, the Kacza River and the Rozwojka River) [18].

Similar correlations were found also for samples coming from sampling points located at the open sea area and in Puck Bay. For Sopot, as for Hel, the correlation between volatile organohalogen compounds and Pb^{2+} was found (0.64). Correlations for the sampling point located in the vicinity of Puck were found between volatile organohalogen compounds and polycyclic aromatic hydrocarbons (0.50). Whereas for Władysławowo, correlations between metal ions were found (Pb, Cu – 0.88). Pb and Cd ions are introduced to the Baltic Sea water in 60% as a result of atmospheric deposition [7].

In order to perform the compounds (or ions) co-occurring analysis and the significance of their influence in particular sampling points interpretation, the principal component analysis (PCA) was applied.

Factorial Analysis

PCA as a multivariate statistical method is used to find a small number of factors from a data set of many correlated variables. Factor analysis is a useful tool for extracting latent information such as underlying (not directly observable) relationships between variables. Factor analysis is based on the mathematical model of the reduced factor analytical solution. The original data matrix is decomposed into the product of factor loading matrix and a matrix of factor scores plus a residual matrix. The residual matrix contains the part of data set variance that cannot be explained by common factors, e. g. analytical uncertainties or feature-own variances. On the basis of the correlation matrix orthogonal factors are extracted solving an eigenvalue problem. In general, the number of extracted factors is lower than the number of measured features. So the dimensionality of the original data space can be decreased by means of factor analysis [38]. In this

Table 4. Descriptive statistics showing mean, minimum, maximum, standard deviation and skewness factor for metals, polycyclic aromatic hydrocarbons (PAHs), volatile organohalogen compounds, volatile petroleum hydrocarbons, chlorine, phosphorous and nitrogen containing pesticides.

	N	Mean value	Min value	Max value	Standard deviation	Skewness Factor
Zn [ug/dm^3]	80	257.5	12.00	1720	280.6	2.69
Cd [ug/dm^3]	80	2.414	0.300	16.00	3.228	1.96
Pb [ug/dm^3]	80	62.69	4.000	500.0	71.41	3.50
Cu [ug/dm^3]	80	55.24	2.000	433.0	72.68	3.24
Naphtalene [ug/dm^3]	80	0.031	0.001	0.187	0.035	2.00
Acenaphtalene [ug/dm^3]	80	0.015	0.001	0.310	0.043	5.14
Acenaphtene [ug/dm^3]	80	0.013	0.001	0.082	0.017	1.69
Fluorene [ug/dm^3]	80	0.018	0.001	0.246	0.035	4.33
Phenantrene [ug/dm^3]	80	0.052	0.001	1.212	0.145	6.90
Anthracene [ug/dm^3]	80	0.023	0.001	0.692	0.082	7.27
Fluoranthene [ug/dm^3]	80	0.022	0.001	0.217	0.039	3.48
Pyrene [ug/dm^3]	80	0.019	0.001	0.290	0.040	4.88
Benzo(a)anthracene [ug/dm^3]	80	0.011	0.001	0.259	0.036	5.84
Chryzene [ug/dm^3]	80	0.010	0.001	0.196	0.028	5.49
Benzo(b)fluoranthene [ug/dm^3]	80	0.008	0.001	0.238	0.027	8.25
Benzo(k)fluoranthene [ug/dm^3]	80	0.007	0.001	0.238	0.029	6.93
Benzo(a)pirene [ug/dm^3]	80	0.004	0.001	0.051	0.009	4.29
Indeno(1,2,3-cd)pirene [ug/dm^3]	80	0.002	0.001	0.033	0.004	5.29
Dibenzo(ah)anthracene [ug/dm^3]	80	0.004	0.001	0.152	0.0201	6.59
Benzo(ghi)perylene [ug/dm^3]	80	0.003	0.001	0.079	0.010	6.60
$CHCl_3$ [ug/dm^3]	80	0.060	0.001	0.587	0.110	3.50
$CHBrCl_2$+C_2HCl_3 [ug/dm^3]	80	0.022	0.001	0.453	0.073	4.11
$CHBr_2Cl$ [ug/dm^3]	80	0.028	0.001	1.872	0.209	8.91
$CHBr_3$ [ug/dm^3]	80	0.003	0.001	0.113	0.013	7.61
C_2Cl_4 [ug/dm^3]	80	0.010	0.001	0.321	0.045	5.78
CCl_4 [ug/dm^3]	80	0.037	0.001	1.163	0.159	5.95
Pentan [ug/dm^3]	80	0.033	0.010	0.230	0.058	2.38
Heksan [ug/dm^3]	80	0.107	0.010	0.700	0.139	2.03
Heptan [ug/dm^3]	80	0.120	0.010	3.000	0.509	5.00
Benzen [ug/dm^3]	80	0.307	0.010	9.700	1.327	6.33
Toluen [ug/dm^3]	80	0.228	0.010	4.410	0.563	5.84
Ksylen [ug/dm^3]	80	0.179	0.010	0.940	0.215	1.48
Undekan [ug/dm^3]	80	0.014	0.010	0.160	0.021	5.63
Dekan [ug/dm^3]	80	0.218	0.010	15.80	1.765	8.93
Etylobenzen [ug/dm^3]	80	0.015	0.010	0.150	0.021	4.68
Simazine [ug/dm^3]	80	0.009	0.001	0.109	0.021	3.40
Atrazine [ug/dm^3]	80	0.003	0.001	0.084	0.011	6.23
Fenitrothion [ug/dm^3]	80	0.004	0.001	0.109	0.017	5.38
Propazine [ug/dm^3]	80	0.012	0.001	0.454	0.054	7.37
Bromphos-ethyl [ug/dm^3]	80	0.017	0.001	0.474	0.063	5.76
Malation [ug/dm^3]	80	0.018	0.001	0.815	0.092	8.36
Chlorfenvinphos [ug/dm^3]	80	0.005	0.001	0.120	0.017	5.62
Tertbutyloazine [ug/dm^3]	80	0.009	0.001	0.174	0.026	4.28
p,p’-DDT [ug/dm^3]	80	0.030	0.001	0.045	0.008	4.16
Metoxychlor [ug/dm^3]	80	0.003	0.001	0.101	0.012	7.30
Lindan [ug/dm^3]	80	0.115	0.001	1.045	0.231	2.98
EpoksydHeptachlor [ug/dm^3]	80	0.003	0.001	0.101	0.012	6.84
o,p’-DDE [ug/dm^3]	80	0.002	0.001	0.101	0.011	8.56

Table 5. Correlation analysis results for sums of analytes belonging to each group for samples collected in five sampling points

Hel									
	Zn	Cd	Pb	Cu	PAH	VOCl	HC	OPNPs	OCPs
Zn	1.00								
Cd	-0.14	1.00							
Pb	0.08	-0.06	1.00						
Cu	0.21	-0.01	-0.17	1.00					
PAH	-0.01	-0.18	-0.16	0.01	1.00				
VOCl	0.00	0.27	**0.64**	0.39	-0.19	1.00			
HC	-0.10	0.08	0.01	-0.18	0.00	-0.09	1.00		
OPNPs	-0.21	-0.21	0.02	0.10	-0.12	-0.12	-0.38	1.00	
OCPs	-0.19	-0.08	-0.09	-0.04	0.26	-0.19	-0.05	0.46	1.00
Władysławowo									
	Zn	Cd	Pb	Cu	PAH	VOCl	HC	OPNPs	OCPs
Zn	1.00								
Cd	-0.20	1.00							
Pb	0.40	0.04	1.00						
Cu	0.48	0.04	**0.88**	1.00					
PAH	-0.38	-0.06	-0.33	-0.44	1.00				
VOCl	0.21	0.10	0.49	0.22	-0.42	1.00			
HC	-0.01	-0.08	0.07	-0.01	-0.13	0.05	1.00		
OPNPs	-0.18	-0.18	-0.09	-0.15	0.03	-0.15	0.10	1.00	
OCPs	-0.33	**0.67**	-0.17	-0.17	0.32	-0.21	-0.07	0.14	1.00
Puck									
	Zn	Cd	Pb	Cu	PAH	VOCl	HC	OPNPs	OCPs
Zn	1.00								
Cd	-0.33	1.00							
Pb	0.05	-0.03	1.00						
Cu	0.31	-0.24	0.36	1.00					
PAH	0.30	0.19	-0.24	0.03	1.00				
VOCl	-0.01	-0.17	0.27	-0.11	**-0.50**	1.00			
HC	-0.15	-0.14	0.08	-0.18	-0.15	-0.16	1.00		
OPNPs	-0.21	0.02	0.33	0.25	-0.06	-0.08	-0.23	1.00	
OCPs	-0.21	-0.07	-0.12	-0.06	-0.03	-0.02	-0.10	-0.13	1.00
Orłowo									
	Zn	Cd	Pb	Cu	PAH	VOCl	HC	OPNPs	OCPs
Zn	1.00								
Cd	-0.28	1.00							
Pb	0.00	-0.08	1.00						
Cu	**0.61**	-0.26	0.41	1.00					
PAH	0.16	-0.04	0.19	0.11	1.00				
VOCl	-0.26	-0.03	-0.31	-0.24	-0.21	1.00			
HC	-0.24	-0.06	**0.62**	0.28	-0.06	0.03	1.00		
OPNPs	-0.21	0.04	0.07	-0.01	-0.07	-0.19	0.14	1.00	
OCPs	-0.26	0.24	-0.16	-0.32	0.18	-0.20	-0.25	-0.14	1.00

continued Table 5.

Sopot									
	Zn	Cd	Pb	Cu	PAH	VOCl	HC	OPNPs	OCPs
Zn	1.00								
Cd	-0.09	1.00							
Pb	-0.11	-0.09	1.00						
Cu	0.19	0.09	-0.24	1.00					
PAH	0.02	0.32	0.12	-0.15	1.00				
VOCl	0.05	-0.18	**0.82**	-0.07	-0.30	1.00			
HC	0.04	**0.79**	-0.11	0.00	0.38	-0.09	1.00		
OPNPs	0.32	-0.18	-0.12	0.32	0.04	-0.07	-0.12	1.00	
OCPs	0.07	-0.19	-0.20	-0.09	-0.16	-0.10	-0.04	-0.16	1.00

work, factor analysis, including varimax rotation [39] has been applied in order to achieve interrelationships between measured variables.

The table containing factor loadings for data, with consideration to location of 5 sampling points, has been created thanks to the PCA application. To obtain higher readability of the results only the first 5 factors for each category are presented in Table 6. In all cases these 5 factors explain over 60% of the data variance, and the statistically significant loading factors are higher than 0.7 (with p=0.05). After rotation (the purpose of rotation is to point a factor at a group of variables, so the factor may be easier to interpret) of the factor loading matrix, the factors can often be interpreted as origins or common sources. From the performed PCA it arose that the factor configuration was similar for all sampling points. It is very hard to separate these factors that are representing specific groups of pollutants in an unique way. In all cases first factor (the most important and explaining the greatest part of variance) is representing PAHs (Hel – 34.37%, Władysławowo – 22.77%, Puck – 19.79%, Orłowo – 26.62%, Sopot – 24.00%). In the case of Hel station a few variables ($CHBr_2Cl$, $CHBr_3$, undekane, athrazine, fenithrotione, propazine, metoxychlorine, heptachlor epoxide, o, p'-DDE) have been removed from chemometrical analysis because of their constant values. PC1 has the highest factor loading (13.40) and the greatest contribution to the total variance of the data set (accounted for the variance percentage of 34.37%). Next, PCs provide a contribution of 12.60%; 10.55%; 8.41% and 6.95% to total variance, respectively. As mentioned before in the case of Hel station, the first PC has a very high factor loading for variables from the PAH group. Additionally, PC2 in general represents the same group (with influence of Zn) but it has been observed that between PC1 and PC2 inversely proportional relationship occurred. These results indicate that PAHs and heavy metals, such as zinc or lead, are coming from similar sources. As mentioned before [40], the pattern of lead and zinc distribution could indicate motor vehicle traffic and major sources of PAH contamination near urban regions and could also originate from combustion processes such as motor vehicle exhausts. Similar results have been presented previously [41, 42]. The residual factors have factor loadings from 4.21 to 2.71 and explain approximately 8% of the total variance each. In the case of Władysławowo a few variables (C_2Cl_4, pentane, undekane, athrazine, p,p'-DDE, metoxychlorine) have been removed from chemometrical analysis because they had constant values, and only five major factors explaining more than 67% of total variance have been taken into account. For these samples first factor (PAHs) has the highest factor loading 9.56 and the greatest contribution to the total variance of the data set (22.77%). This factor can be considered as a PAH, but it has to be noted that a few compounds within this group have their influence in PC4. The second PC has 6.12 factor loading and explains 14.57% of the total variance. In this factor Pb is highly correlated with volatile organohalogen compounds ($CHBr_2Cl$, $CHBr_3$, CCl_4) and may be attributed to decomposition of tetraethyl lead, which is added to gasoline in order to improve the resistance to piston slapping incineration.

The residual factors have factor loadings from 5.02 to 3.14 and explain approximately 10% of the total variance each. In the case of Puck, C_2Cl_4, fenitrothion, propazine, tertbuthyloazine and metoxychlorine were removed from chemometrical analysis because they had constant values, and also in this situation five major factors explained more than 62% of the total variance. Besides the first factor (eigenvalue 8.49), residual factors are very difficult to explain and they have comparable contribution to total variance (PC2 – 14.28%, PC3 – 11.34%, PC4-10.17%, PC5 – 7.28%). In PC2 the high correlation between Cu and pesticides were observed, while in PC4 between PAHs (anthracene, fluoranthene, pyrene) and hydrocarbons (dekane, ethylobenzene). In the case of Orłowo and Sopot C_2Cl_4, pentane, heptachlor epoxide, fenitrothion, o, p'-DDE and o, p'-DDE were removed, respectively, from chemometrical analysis. In both sampling points the scheme of major factors is similar. The PC1's have very high factor loadings for variables from the PAH group

Table 6. Factor loading and explained variance for five different sampling sites.

Hel					
	Rotated Factor 1	Rotated Factor 2	Rotated Factor 3	Rotated Factor 4	Rotated Factor 5
Zn		-0.81			
Cu			0.92		
Naphtalene		-0.87			
Acenaphtalene		-0.86			
Acenaphtene		-0.83			
Fluorene	0.74				
Anthracene	0.81				
Fluoaranthene	0.92				
Pyrene	1.00				
Benzo(a)an[1]	0.99				
Chryzene	0.99				
Benzo(b)flu[2]	1.00				
Benzo(k)fl[3]	1.00				
Benzo(a)[4]	0.99				
Indeno[5]	0.99				
Dibenzo[6]	0.98				
Benzo(ghi)[7]	0.95				
$CHCl_3$				-0.73	
C_2Cl_4			0.83		
CCl_4			0.83		
Pentan					-0.73
Toluen				0.75	
Ksylen				0.55	
Dekan	1.00				
Etylobenzen	1.00				
Simazine					-0.83
Lindan					-0.83
Eigenvalue	13.40	4.91	4.11	3.28	2.71
Variance %	34.38	12.60	10.55	8.41	6.95
Cum. variance %	34.38	46.98	57.54	65.95	72.90

Władysławowo					
	Rotated Factor 1	Rotated Factor 2	Rotated Factor 3	Rotated Factor 4	Rotated Factor 5
Pb		-0.79			
Cu		-0.95			
Naphtalene					-0.78
Fluorene			-0.87		
Fluoaranthene	-0.95				
Pyrene	-0.88				
Chryzene	-0.72				
Benzo(b)flu[2]				-0.79	
Benzo(k)fl[3]				-0.76	
Indeno[5]	-0.82				
Dibenzo[6]				-0.87	
Benzo(ghi)[7]	-0.82				
$CHBr_2Cl$		-0.80			
$CHBr_3$		-0.95			
CCl_4		-0.95			
Heptan		-0.80			
Ksylen				-0.77	
Etylobenzen	-0.85				
Fenitrothion			-0.81		
Chlorfenvinphos			-0.80		
Tertbuthyloazine			-0.91		
o.p'-DDE		-0.95			
Eigenvalue	9.56	6.12	5.02	4.39	3.14
Variance %	22.77	14.57	11.96	10.46	7.48
Cum. variance %	22.71	37.35	49.31	59.77	67.25

Benzo (a) an[1] – Benzo (a) anthracene
Benzo (b) flu[2] – Benzo (b) fluoranhene
Benzo (k) fl[3] – Benzo (k) fluoranthene
Benzo (a) [4] – Benzo (a) pirene

Indeno[5] – Indeno (1,2,3-cd) pirene
Dibenzo[6] – Dibenzo (ah) anthracene
Benzo (ghi) [7] – Benzo (ghi) perylene
Epoksyd[8] – EpoksydHeptachlor
$CHBrCl_2$+[9] – $CHBrCl_2+C_2HCl_3$

continued Table 6.

Puck					
	Rotated Factor 1	Rotated Factor 2	Rotated Factor 3	Rotated Factor 4	Rotated Factor 5
Zn			-0.77		
Cd				-0.73	
Cu		-0.84			
Naphtalene					-0.82
Acenaphtalene					-0.79
Anthracen				-0.79	
Fluoranthene				-0.80	
Pyrene				-0.72	
Benzo(a)an[1]	-0.91				
Chryzene	-0.95				
Benzo(b)flu[2]	-0.80				
Benzo(a)[4]		-0.72			
Benzo(ghi)[7]	-0.81				
Dekan				-0.74	
Etylobenzen				-0.74	
Atrazine		-0.98			
p.p'-DDT			-0.80		
Epoksyd[8]		-0.98			
o.p'-DDE		-0.98			
Eigenvalue	8.49	6.14	4.87	4.37	3.13
Variance %	19.74	14.28	11.34	10.17	7.28
Cum. variance %	19.74	34.03	45.37	55.55	62.83

Orłowo					
	Rotated Factor 1	Rotated Factor 2	Rotated Factor 3	Rotated Factor 4	Rotated Factor 5
Zn				-0.78	
Pb		-0.81			
Fluorene					-0.90
Phenantrene					-0.94
Anthracene					-0.93
Fluoranthene	0.96				
Pyrene	0.93				
Benzo(a)an[1]	0.99				
Chryzene	1.00				
Benzo(b)flu[2]	0.89				
Benzo(a)[4]	0.93				
Indeno[5]	0.96				
Dibenzo[6]	0.99				
Benzo(ghi)[7]	1.00				
$CHBrCl_2$+[9]			-0.89		
$CHBr_2Cl$			-0.80		
$CHBr_3$		-0.97			
CCl_4			-0.88		
Heptan		-0.97			
Benzen			-0.81		
Dekan	0.99				
Etylobenzen	0.99				
Simazine					
Atrazine		-0.97			
Malathion		-0.97			
Eigenvalue	11.71	6.30	4.50	3.48	2.99
Variance %	26.62	14.32	10.24	7.93	6.79
Cum. variance %	26.62	40.94	51.18	59.11	65.91

Benzo (a) an[1] – Benzo (a) anthracene
Benzo (b) flu[2] – Benzo (b) fluoranhene
Benzo (k) fl[3] – Benzo (k) fluoranthene
Benzo (a) [4] – Benzo (a) pirene
Indeno[5] – Indeno (1,2,3-cd) pirene

Dibenzo[6] – Dibenzo (ah) anthracene
Benzo (ghi) [7] – Benzo (ghi) perylene
Epoksyd[8] – EpoksydHeptachlor
$CHBrCl_2$+[9] – $CHBrCl_2$+C_2HCl_3

continued Table 6.

Sopot					
	Rotated Factor 1	Rotated Factor 2	Rotated Factor 3	Rotated Factor 4	Rotated Factor 5
Zn				-0.90	
Cd	-0.79				
Pb		-0.80			
Cu			-0.90		
Acenaphtene					-0.88
Fluorene					-0.89
Phenantrene					-0.90
Fluoranthene	-0.95				
Pyrene	-0.95				
Benzo(a)an[1]	-0.86				
Chryzene	-0.96				
Benzo(k)fl[3]	-0.99				
Benzo(a)pirene	-0.99				
Indeno[5]	-0.99				
Benzo(ghi)[7]	-0.99				
Benzo(a)[4]		-0.94			
$CHBrCl_2$+[9]		-0.92			
$CHBr_2Cl$			-0.95		
$CHBr_3$			-0.97		
C_2Cl_4				-0.89	
CCl_4		-0.93			
Pentan			-0.74		
Heptan			-0.98		
Benzen		-0.85			
Toluen	-0.72				
Dekan	-0.99				
Etylobenzen	-0.99				
Atrazine			-0.97		
Propazine				-0.96	
Malathion				-0.79	
Chlorfenvinphos				-0.96	
p.p'-DDT				-0.90	
Metoxychlor		-0.88			
Eigenvalue	11.04	6.27	6.00	5.10	3.65
Variance %	24.00	13.64	13.05	11.09	7.94
Cum. variance %	24.00	37.65	50.70	61.79	69.74

with strong influence of dekane and ethylobenzene, and have the greatest contribution of the total variance of the data set (26.62% and 24.00% respectively for Orłowo and Sopot). In both cases (Orłowo and Sopot) PC2's are similar to PC2 for Władysławowo and are highly correlated with volatile organohalogen compounds and Pb. As mentioned before, this may be attributed to decomposition of tetraethyl lead. For Orłowo and Sopot fluorene, phenantrene and anthracene create a major factor, but separately they do not show any strong correlation (factor loadings) with other variables.

Analysis of Time Series and Analysis of Variance

The next step of chemometrical data processing was an attempt to evaluate the time variation of analyzed compound concentration sums, and also of their variability in each sampling point. For this purpose time series analysis (TS) and analysis of variance (ANOVA) have been applied.

TS is a sequence of intercorrelations between variables (observations) describing specified effect in successive points on the time axes.

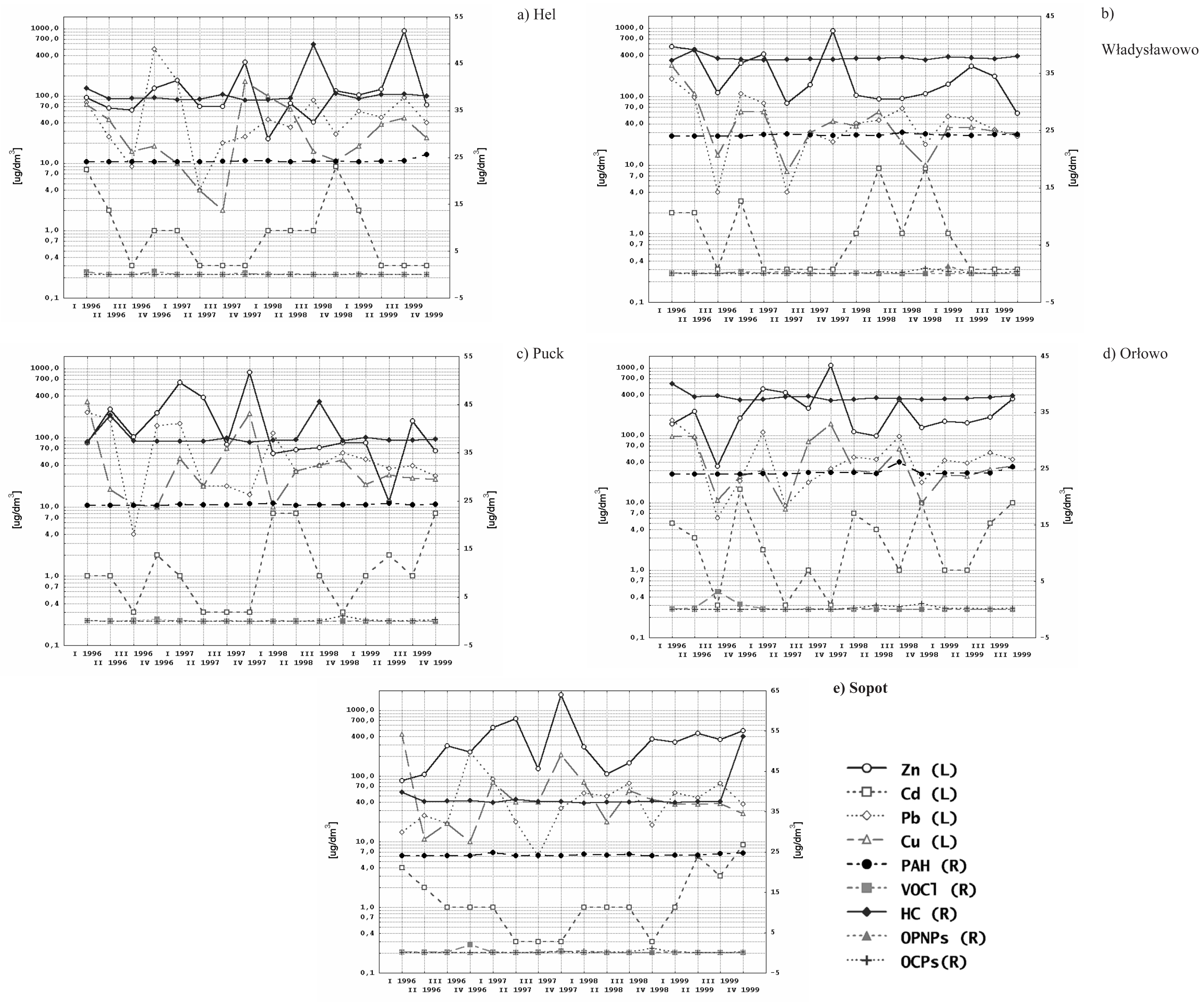
Aims of time series analysis are:

- statistical analysis of correlations between consecutive observations;
- prediction (forecasting) of future values of time series;
- indication of mechanisms ruling observed effect variations with time, i.e. defining the phenomenon represented by the sequence of observations.

Analysis of variance is a powerful and very general method which separates contributions to the overall variation in a set of experimental data and test their significance. The sources of variation (one of which is invariably the random measurement error) are each characterized by a sum of squares (SS), i. e. the sum of a number of squared terms representing the variation in question, a number of degrees of freedom (DF), and a mean square, which is the former divided by the latter and can be used to the significance of the variation contribution by means of the F-test. The mean square and the number of degrees of freedom for the over-all variation are, respectively, the sums of the mean squares and degrees of freedom of the several contributing sources of variation: this additive property greatly simplifies the calculations which are now widely available on personal computer software [43].

Analysis of Time Series

Time series analysis was performed for sum values of specified analyte concentrations, with consideration to group partition and sectioning into 5 sampling locations. This research was focused on exploring periodical correlations between variables. Fig. 2 (a-e) shows the sequence of concentration changes for selected groups of compounds in each sampling point, as quarterly periods starting from 1996 up to 1999.



a) Hel

b) Władysławowo

c) Puck

d) Orłowo

e) Sopot

Fig. 2. The sequence of concentration changes for selected groups of compounds in each sampling point, as a quarterly periods starting from 1996 up to 1999.

As a result of time series analyses carried through with consideration to sampling points, there were no statistically important differences discovered in trends of changes from 1996 up to 1999 for any of examined groups of compounds. Characteristic is lack of important fluctuations in sum of PAHs, concentrations and also for organophosphoric and organonitrogenous pesticides in all sampling points.

A similar conclusion can be drawn on the basis of organochlorine pesticides and volatile organochlorine compound concentration sums in seawater. However, in the fourth quarter of 1998 an increase in organochlorine pesticide concentrations in four (Sopot, Orłowo, Puck, Władysławowo) of five sampling locations were observed, and in the third quarter of 1996 the increase of volatile organochlorine compound concentrations in Gdynia and Orłowo were noted. Lindane caused the total increase of volatile organochlorine compound concentrations. The concentration of Lindane was as follows: Władysławowo – 0.85 µg/dm^3, Puck 1.05 µg/dm^3, Orłowo – 1.01 µg/dm^3, Sopot 1.01 µg/dm^3. The increase was evident. The concentration value observed in the fourth quarter of 1998 was about 17 times higher comparing with the average concentration value for 11 of the remaining quarters of the period from 1996-1999 for Sopot (0.058 µg/dm^3). In the case of organochlorine, the compounds recorded a difference in the third quarter of 1996 in $CHBr_2Cl$ concentration in seawater (1.87 µg/dm^3) in Gdynia Orłowo excided almost 450 times the average concentration for all sampling points in the period from 1996 to1999 (0.004 µg/dm^3). Performed analysis proves that for volatile organochlorine compounds and organochlorine pesticides the sum of concentrations in seawater in the area of Gdańsk Bay is constant and on a very low concentration level. It shows that the Baltic Sea coastal zone loading of the chemical compounds' groups mentioned above is negligible. The observed unitary decrease of concentrations is of random type. In Baltic sea coastal zone water the concentration of compounds belonging to petroleum hydrocarbons' group is relatively constant. From 1996 to 1999 the average concentration value was about 37.0 μg/dm^3 for 5 sampling points. However, there were 3 quarters in a four-year period when the sum of petroleum hydrocarbons' group concentration increased up to 45.56 μg/dm^3 (Puck – 3rd quarter of 1998), 49.09 μg/dm^3 (Hel – 3rd quarter of 1998) and 53.59 μg/dm^3 (Sopot – 4th quarter of 1999). In all cases the increasing tendency did not remain stable and the next quarter the concentration level was coming back to the value close to the average. An assumption can be made that these events were related to not harmful, in global scale, fuel spills from small ships.

TS of metal concentration level changes in seawater samples showed the presence of many short-term extremes in comparison with the average concentration for particular metals. In seawater collected in Hel the average concentration of Zn was 154 μg/dm^3. However, in 1st and 4th quarter of 1997 and in 3rd quarter of 1999 the concentration increased by turns to: 170 μg/dm^3, 320 μg/dm^3 and 921 μg/dm^3. In seawater samples collected in the four remaining stations a drastic increase of Zn concentration level was observed in analogical time periods. The comparison of averages and maximal concentrations of Zn in see water samples for four remaining sampling points is given below:

- Władysławowo – average – 256 μg/dm^3 (I quarter of 1997 – 420 μg/dm^3; IV quarter of 1997 – 920 μg/dm^3);
- Puck – average – 204 μg/dm^3 (I quarter of 1997 – 630 μg/dm^3; IV quarter of 1997 – 880 μg/dm^3);
- Orłowo – average – 274 μg/dm^3 (I quarter of 1997 – 490 μg/dm^3; IV quarter of 1997 – 1090 μg/dm^3);
- Sopot – average – 399 μg/dm^3 (I quarter of 1997 – 550 μg/dm^3; IV quarter of 1997 – 1720 μg/dm^3).

The highest average Zn concentration values in seawater samples were found for Orłowo and Sopot, where the possibility of water exchange with the open see is limited (bay). The Helski Peninsula is a natural barrier for water flow in parallel of latitude directions. It is highly probable that the limited possibility of water mass exchange in this region caused a shift of local maximum Zn concentration in samples collected in Sopot in 2nd quarter of 1997– 750 μg/dm^3.

Correlation analysis previously performed showed well the accordance with time series analysis for the same metal pairs. High correlation coefficient between Pb and Cd (0.88) in seawater collected in Władysławowo is also seen in a very similar time series function of concentration level changes structure. It can be seen that maximum values for both analytes were observed in 1st quarter of 1996: Pb (182 μg/dm^3) and Cu (285 μg/dm^3), and did not appear again. Similarly, the high correlation coefficient observed for Cu and Zn (0.61) in seawater collected in Orłowo reflects a very similar time series function of concentration level changes structure.

Analysis of Variance

The technique of one-dimentional variance analysis was applied to show statistically significant variances in sums of analyte concentrations with time and the variability of their occurrence in seawater originating from each sampling location (Hel, Władysławowo, Puck, Orłowo, Sopot). Fig. 3 (a-d) presents the comparison of concentration changes obtained for different

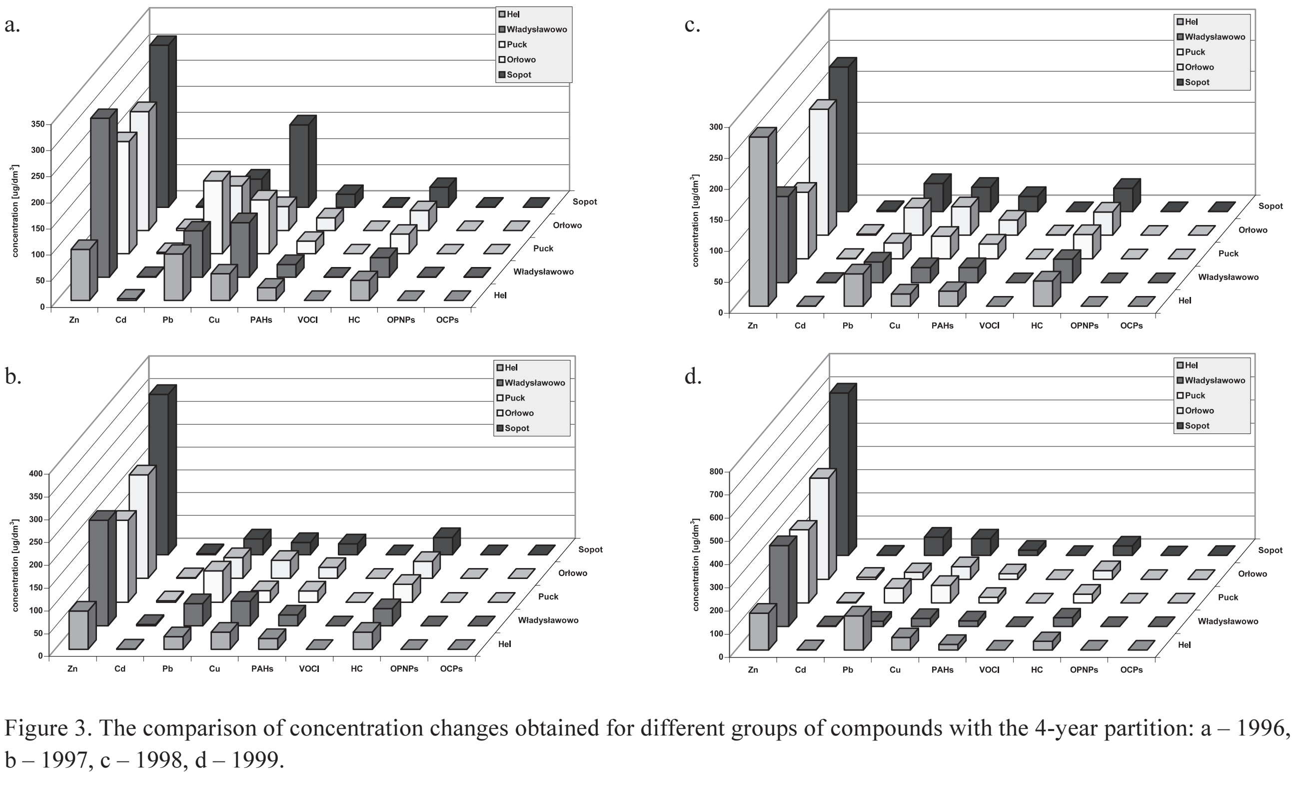


Figure 3. The comparison of concentration changes obtained for different groups of compounds with the 4-year partition: a – 1996, b – 1997, c – 1998, d – 1999.

groups of compounds with the 4-year partition (1996 to 1999).

Data have been transformed because of their strongly asymmetric distribution. The skewness factor > 2 indicates the necessity of the logarithmic transformation application in the form of x'=log(x) [44, 45].

ANOVA application showed that for the level of significance $\alpha=0.05$ there are statistically important differences in logarithms of concentration values in successive years for: Zn, Cd, PAH and VOCl. The course of time appeared to be non-significant for logarithms of Pb, Cu, HC, OPNPs and OCPs concentration changes. It means that the range of analytes' concentrations (Pb, Cu, HC, OPNPs and OCPs) in examined samples is similar in following years, and any occurring variation fits within the error range and is statistically unimportant. Table 7 presents results of ANOVA for logarithms of Zn, Cd, PAH and VOCl concentrations in sea water, and Figures 4a and 4b show the logarithms of analysed groups' average concentration distribution.

Comparison of calculated F values amounting for consecutive analytes correspondingly to: 6.241; 8.281; 5.000; 24.789, with the critical value of 2.728, evidently indicates the necessity of the zero hypothesis (stating about equal averages in groups) rejection (with the confidence level $\alpha<0.05$).

On the basis of the obtained data set analysis it was shown that for PAHs and VOCls statistically significant differences in the period of 1996-1999 occurred. Taking into account two-year periods, such differences were not observed. However, for the total period, there was a slightly seen, but significant trend of changes. The sum of volatile organochlorine compound concentrations was systematically decreasing (from the value of 0.482 μg/dm^3 in 1996 to 0.019 μg/dm^3 in 1999), whereas the sum of polycyclic aromatic hydrocarbon concentrations was slightly, but systematically increasing (from 24.0 μg/dm^3 in 1996 to 24.3 μg/dm^3 in 1999). The reason is connected with the PAH sources. A very heterogeneous group of PAHs originates primarily from combustion of organic material, especially fossil fuels and their products [46]. This increase is presumably caused by the sea transport growing and oil spillages appearing, especially in the case of the semi-enclosed area of Gdańsk Bay.

In the case of Zn and Cd content analysis in seawater, one can say that in spite of the statistically significant differences present in following years, the determined values oscillate close to average values (Zn – 257 μg/dm^3, Cd – 2.41 μg/dm^3). Therefore, the content of these metals in sea water can be treated in general as constant. It is presumed that the coastal zone of the Baltic Sea at the Gdańsk Bay territory is not significantly polluted with

Table 7. Results of ANOVA with singular classification for logarithms of Zn, Cd, PAH and VOCl concentrations in seawater.

log (Zn) [μg/dm^3]				
Variance type	Sum of squares	Number of degrees of freedom	Medium square deviation	F (F_{crit})
Between groups	13.247	3	4.416	6.241 (2.728)
Inside groups	53.768	76	0.707	
Total	67.015	79	0.848	
log (Cd) [μg/dm^3]				
Variance type	Sum of squares	Number of degrees of freedom	Medium square deviation	F (F_{crit})
Between groups	28.611	3	9.537	8.281 (2.728)
Inside groups	87.520	76	1.151	
Total	116.131	79	1.470	
log (PAH) [μg/dm^3]				
Variance type	Sum of squares	Number of degrees of freedom	Medium square deviation	F (F_{crit})
Between groups	0.0024	3	0.0008	5.000 (2.728)
Inside groups	0.0128	76	0.0002	
Total	0.0152	79	0.00019	
log(VOCl) [μg/dm^3]				
Variance type	Sum of squares	Number of degrees of freedom	Medium square deviation	F (F_{crit})
Between groups	62.663	3	20.887	24.789 (2.728)
Inside groups	64.039	76	0.8426	
Total	126.702	79	1.604	

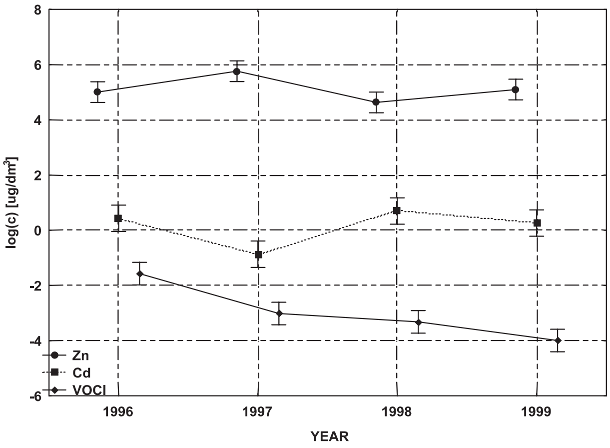


Fig. 4a. Logarithms of Zn, Cd and VCls average concentration distribution.

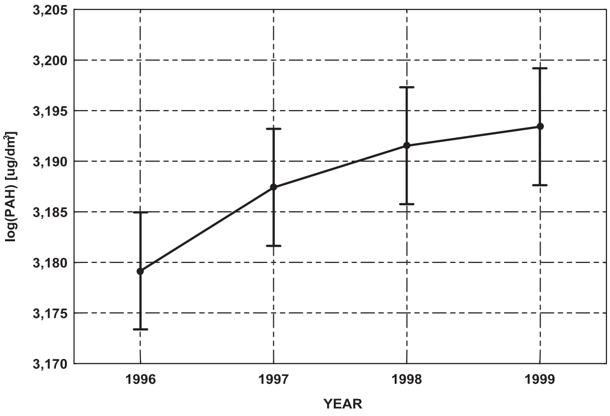


Fig. 4b. Logarithms of PAHs average concentration distribution.

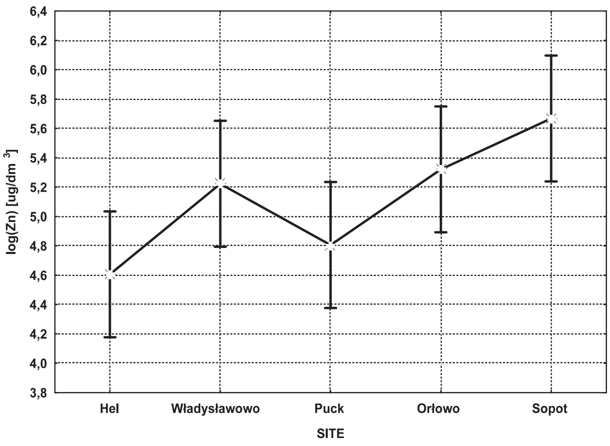


Fig. 5. The distribution of Zn concentration average logarithms with sampling point partitions.

compounds containing Zn and Cd, and the limited possibility of water mass exchange with the oceans, in this case plays a role of a barrier protecting the ecosystem equilibrium. The specific feature of Cd and Zn concentration changes in sea water is the inversely proportional characteristics. Cd concentration level was increasing in seawater samples, while Zn concentration was decreasing:

	(1996)	→	(1997)	→	(1998)	→	(1999)
Zn [$\mu g/dm^3$]:	189	↑	479	↓	127	↑	236
Cd [$\mu g/dm^3$]:	2.76	↓	0.525	↑	3.73	↓	2.64

As described before, in 1998 several events of high Cd wet deposition occurred, which were not reproduced by their model and were not always correlated with other metals [47]. These events probably caused a significant contamination of the Gdańsk Bay area. However, authors did not suggest any reason of these events, but only showed compatibility with numerical models. Occurrence of these events was confirmed before and suggested that a strong Cd source must have existed in northern Poland, and had a pronounce impact on the deposition at sampling points in the neighbourhood [7].

Moreover, using ANOVA technique in data set investigation, with the partition of this set into categories covering sampling points, resulted in lack of statistically significant differences for most analytes. The only exception was Zn, for which it has been shown (on the confidence level α=0.05) that its concentration in water from Sopot differed significantly and was higher from concentrations determined in samples collected in Hel and Puck. Determined correlations are given in Fig. 5.

The performed two-dimensional ANOVA technique for Zn concentrations, with two categories specification (sampling year and location), showed no interaction between grouping factors. This means that the occurrence of statistically significant differences in Zn concentration levels in seawater in the following years is not correlated with sampling location. It was observed that in two cases (station Puck – 1999, station Władysławowo – 1996), determined Zn contents in seawater samples differed from those collected elsewhere. The average value for Zn in water samples collected in Władysławowo in 1996 was equal to 361 $\mu g/dm^3$, whereas for other locations the total concentration average in this year amounted to 146 $\mu g/dm^3$. Another correlation was observed in the case of samples originating from Puck. The average Zn concentration value in seawater collected in Puck in 1999 was equal to 84.3 $\mu g/dm^3$, whereas for other locations the total concentration average in this year amounted to 273 $\mu g/dm^3$. Figure 6 presents the distribution of log (Zn) values with two categories specification (sampling year and location).

Another result of ANOVA technique application, with the data partition into categories covering seawater sampling points, was lack of statistically important differences for compounds related to PAHs. From works of other authors presented before [31, 46] it can be concluded that benzo(a)pyren can be treated as an environmental pollution indicator. This is the reason why the ratio of benzo(a)pyren average concentration to the sum of PAH average concentrations in sea water was calculated in all sampling points for all years of collection. Results obtained are given in Table 8.

It is evident that in points located in the Baltic Sea

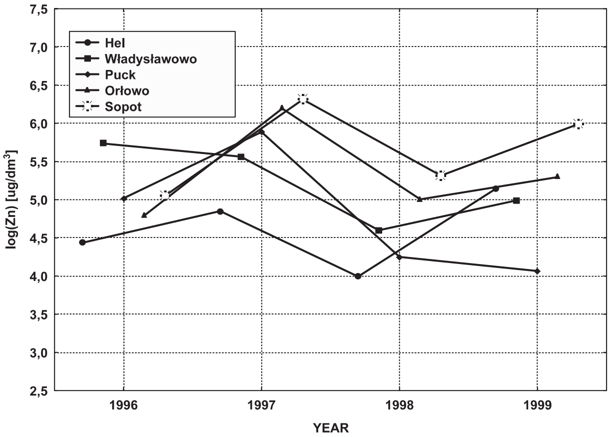


Fig. 6. The distribution of Zn concentration averages logarithms with two categories specification (sampling year and location).

Table 8. Benzo(a)pyren average concentration values and sums of PAH average concentrations in seawater samples collected in 5 sampling locations.

Sampling point	Benzo(a)pyren [µg/dm^3]	PAH [µg/dm^3]	Benzo(a)pyren/ PAH
Hel	0.0045	0.2042	~0.02 (0.022)
Puck	0.0032	0.1948	~0.02 (0.016)
Władysławowo	0.0015	0.2060	~0.01 (0.007)
Orłowo	0.0071	0.3524	0.02
Sopot	0.0046	0.2557	~0.02 (0.018)

coastal zone, at Gdańsk Bay, the value of benzo(a)pyren/PAH calculated ratio is oscillating close to 0.02, whereas in seawater samples collected at the open sea region (Władysławowo) it amounts to 0.01. This fact suggests that in spite of lack of statistically significant differences in PAHs' concentrations compared to remaining sampling locations, water from Władysławowo contains 50% of benzo(a)pyrene less than water from other points. This could result from lack of barriers limiting the possibility of water mass circulation between central and southern parts of the Baltic Sea.

Conclusions

3840 results were analyzed with use of chemometrics (organic and inorganic pollutants' concentration levels in seawater samples). This data set has been obtained as a result of broad research performed in the framework of EUROCAT project [31, 48]. The following groups of compounds were found in the examined area: petroleum hydrocarbons, volatile organochlorine compounds, policyclic aromatic hydrocarbons, pesticides (organochlorine, organonitrogenous and organophosphorus), polichlorinated biphenyles and selected heavy metals. Analyte concentration levels were relatively low, which can indicate the moderate pollution level of Baltic Sea water in the Polish coastal zone. For most of variables no statistically significant differences were found considering concentration levels for sampling points located within the Tricity area (Gdańsk Bay) and other points, located in the vicinity of this region, but at the open sea area. The observed differences were occurring just for Zn ions (check Fig. 6) and were significant, both in time and with geographical location change. The value of benzo(a)pyren average concentration to the sum of PAH average concentrations calculated ratio for seawater samples collected from 5 sampling stations suggests that water in Władysławowo contains 50% less benzo(a)pyrene than water from other points.

The results of TS performed for selected variables showed differences in pollutant concentration levels in the period from 1996 to 1999. Particularly evident trends of changes were observed for heavy metal ions (Zn, Cd – see Fig. 4a), policyclic aromatic hydrocarbons (see Fig. 4b) and volatile organochlorine compounds (see Fig. 4b). It can prove the occurrence of alternating types of pollution sources in the area under investigation. This variability can result from the fact that the 1990s where a period of dynamic industrial alteration, and also of changes in the environmental approach to the problem of pollution (e. g. new laws and regulations, introduction of ISO standards).

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