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**“Lets hurry up to love people –  
They go away so quickly...”**  
– *priest Jan Twardowski*  
(quote from “Signs of trust”)

We offer that paper  
in remembrance of  
**Professor Zbigniew Piesik**

### ON GREAT LAGOON (SZCZECIN LAGOON) WATER SALINITY – ONCE AGAIN

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#### Abstract

Between May and October of 2003, mineral composition of surface (0.5 m deep) and bottom (5.0 meters) waters, at measurement stations in north-western and south-eastern parts of Great Lagoon (Szczecin Lagoon), have been studied. Total concentrations of ionic macrocomponents: Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> have been determined. Differentiation of ionic composition and changing level of concentrations of ionic macrocomponents in waters, depending on location of measurement station, depth of water sample collection and time of examination, have been proved. Bottom waters in south-eastern part of Great Lagoon had highest salinity level, whereas surface waters in the same location had lowest degree of salinity. Taking into consideration relatively small number of measurements, authors of present paper regard outlined investigations as diagnostic and obtained conclusions as preliminary ones. Towards substantial variability in ionic composition and magnitudes of concentrations, it is practically impossible to forecast and define values of concentrations of individual ionic components and general salinity degrees, basing on chlorides concentrations, what was often pursued, until now.

**Key words:** freshwater, salination, ionic components, Szczecin Lagoon, Great Lagoon

## INTRODUCTION

Researches on water salinity of the Great Lagoon which is the greatest water region of Szczecin Lagoon (Fig. 1) have a long history, since the first surveys on Szczecin Lagoon salinity level had been published on the turn of the 19<sup>th</sup> century in papers of Brandt (1896, 1906). Systematical investigations in the subject were carried in the fifties of the last century.

Among papers referring to the issue, papers of Mikulski (1960, 1970), Majewski (1964, 1972, 1980), Zaborowska-Młodzińska (1963), Wypych (1970), Młodzińska (1974, 1980a, b), Chlubek (1975), Buchholz (1990a, b), Jasińska (1991), Robakiewicz (1993), Mutko (1994) and Poleszczuk (1996a-c, 1997a, b, 1998, 2003) seem to be of the greatest value. In most of quoted publications salinity was determined in terms of chlorinity by the Knudsen method (Oxner 1952). Chlorinity was re-counted basing on Knudsen oceanographic tables (1901), applied for determining salinity of marine and oceanic waters.

Procedure described above had been used for examining waters of Szczecin Lagoon in the fifties of the last century by Wypych (1970) and later was generally applied by other scientists, except Młodzińska (1974, 1980b), and Poleszczuk (1997a, 1998). Mentioned scientist admitted that it is more proper and adequate to determine concentrations of chlorides using methods provided for studies on inland fresh waters, considering low mineralization level of Szczecin Lagoon which is mixed marine-freshwater reservoir with waters of low degree of salinity. Only papers of Młodzińska (1974, 1980b) and Poleszczuk (1998) present results of complex examinations of all ionic macrocomponents of waters as well as detailed analysis of changes in mineral composition of Szczecin Lagoon waters within its annual cycle.

All quoted papers prove that waters of all regions of Szczecin Lagoon are characterized by changing salinity level, within passage of time and depending on place, alike. It is obvious since waters of Rostoka Odrzańska are less filled with salt than waters within Szczecin-Świnoujście shipping channel close to I. channel gate in the northern part of Great Lagoon, where backflow of marine waters flowing from Pomeranian Bay is strongly marked. Simultaneously, what was proved by Poleszczuk (2003), mineral composition of waters in south and especially in south-eastern part of Great Lagoon should be different from waters in north-western part of Lagoon, where inflow of sodium-chloride waters from the north is distinct, due to surface inflow of inland river waters (effect of Coriolis Force), rich in calcium and hydrocarbonates.

It is important to emphasize that during evaluation of water composition of mixed marine-inland waters, rule of additivity should not be applied for determining mineralization degree (Młodzińska 1974, 1980b), because during merging river waters into marine, series of processes leading to concentrations changes of particular components occur. Among them essential are processes of sorption exchange (Młodzińska 1980a, Poleszczuk 1998), deposition and dissolution of substances, when exchange of mass between water depths and deposits takes place and other processes until equilibrium between peptization and coagulation of colloids is settled (Poleszczuk 1996b).

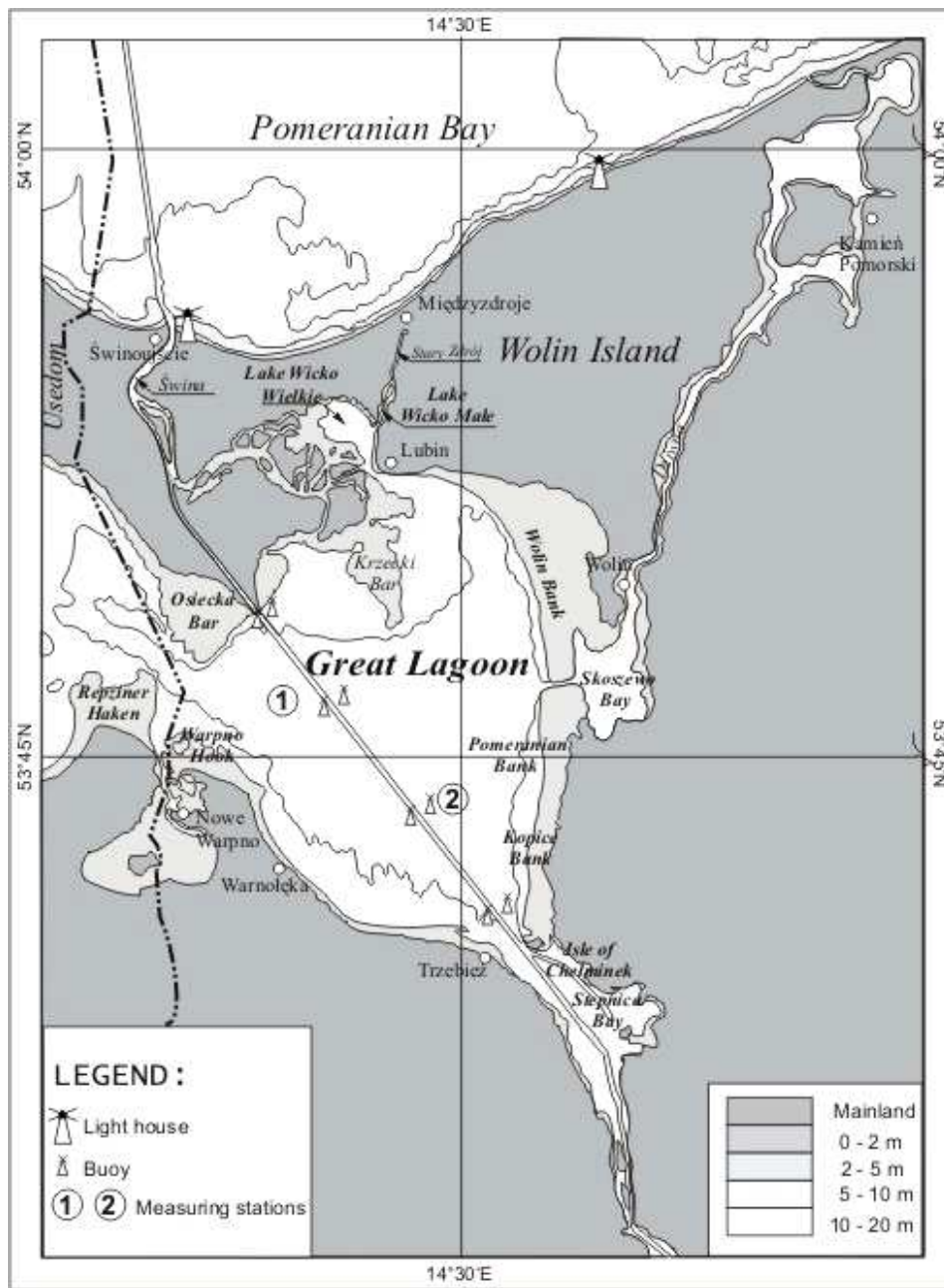


Fig. 1. Great Lagoon – measuring stations location

Therefore while we examine the degree of salinity (S‰) basing on formula established by Młodzińska (1974, 1980b) which presents general, average for the Szczecin Lagoon relation between S‰, precisely between  $\sum m_{ion}^1$  and Cl‰, and applying other formulae which enclose relation between (Cl‰) and water concentration of particular ionic macrocomponents, we may expect that calculated values of concentrations of individual ionic macrocomponents from various water regions may be incorrect. As well as results of evaluation of total mineralization are also faulty.

It's important to stress, that formulae of Młodzińska (1974, 1980b) were fixed on the strength of outcomes carried in 1970, while results of analogical researches which also gave foundation for establishing of similar formulae – presented by Poleszczuk (1998) had been collected in 1992.

Determining the mineralization size and mineral composition of waters, belongs to essential tasks when characteristics of water biotopes has to be elaborated (Directive 2000). In present work an attempt was made to define the real relation between concentrations of individual ionic macrocomponents of waters as well as between sum of mentioned macrocomponents concentrations ( $\sum m_{ion}$ ) and concentration of chlorides in subsurface layer and bottom waters of Great Szczecin Lagoon, alike. Researches were carried between May and October of 2003. Examined waters derived from measurement stations in north-western and south-eastern parts of Great Lagoon.

## MATERIALS AND METHODS

Investigations were carried between May and October of 2003. Samples of water were collected once a month at station No. 1 and No. 2, in north-western and south-eastern parts of the Great Szczecin Lagoon, respectively (Fig. 1, Tab. 1). Water has

Table 1  
Measuring stations in Great Lagoon (Szczecin Lagoon) – location

Station No.	Geographic location data	Depth (m)	Type of bottom deposits	Location characteristics
1	53°49'86N 14°22'56E	5.9	black silt	Great Lagoon – near buoy “TW-1” (on North-West from II. Gate Way)
2	53°44'36N 14°26'73E	5.3	black silt	Great Lagoon – on East from buoy “6” at fairway Świnoujście-Szczecin (on East from III. Gate Way)

<sup>1</sup> indicator – used by Trzosińska (1970), as a measure of total salinity of waters of South Baltic, and also found in papers of Młodzińska (1974, 1980b) where was applied to define mineralization degree of Szczecin Lagoon waters – and was described as a sum of ionic macrocomponents concentrations in waters ( $g \cdot dm^{-3}$ ).

been taken with Patalas scooper from the depth of 0.5 m above Lagoon bed. After filtrating (filter with micro pores 0.45  $\mu\text{m}$  in diameter) – samples were analyzed in laboratory within 12 hours after collecting. Following parameters were measured: chlorides (argentometrically), sulphates (gravimetrically), concentrations of calcium and magnesium (complexometrically), concentration of bicarbonates as total alkalinity – were determined acidimetrically and concentrations of ions:  $\text{Na}^+$  and  $\text{K}^+$  – using the method of atomic absorption spectrophotometry (AAS) (Polish Standards).

Obtained data were subjected to statistic evaluation. Average, lower, upper quartiles, standard deviations (SD) and variation coefficients (CV%) has been reckoned. Medians of set of separate measured ionic macrocomponents had also been taken into account. Equations of linear regression  $m_{ion}(\text{g}\cdot\text{dm}^{-3})=A+B\cdot(\text{Cl}\%) + \text{SEE}$  containing relations between concentrations of particular ionic macrocomponents of waters and chlorides concentrations have been estimated. Equations describing sum of concentrations of all the waters ionic macrocomponents ( $\sum m_{ions}$ ) ( $\text{g}\cdot\text{dm}^{-3}$ ) from chlorides concentrations (Cl‰) have also been considered.

All of the calculations were made in statistics applications contained within computer library Statgraphics (Statistica for Windows 1994) with significance level 0.05 (Sokal and Rolf 1995).

## RESULTS AND DISCUSSION

Outcomes of measurement and determination of particular ionic macrocomponents of water from the Great Szczecin Lagoon between May and October of 2003, has been presented in Table 2 in the form of adequate sets of results. In Table 3 equations of linear regression displaying relations between values of concentration of individual ionic macrocomponents and sums of mass of particular ions contained in 1  $\text{dm}^3$  of water  $\sum m_{ions}$  in the function of Cl<sup>-</sup> concentrations.

In relation to comparatively small number of data obtained from measured indices, our studies should be regarded as pioneer and diagnostic whereas results of statistic calculations and initial outcomes and conclusions as preliminary ones.

Simultaneously we have to point out, that in waters examined in 2003, Cl<sup>-</sup> concentrations and concentrations of other ions of “marine derivation” were relatively low (max. chlorinity = 1.72  $\text{g Cl}\cdot\text{dm}^{-3}$  when  $\bar{x}_{\text{Cl}} = 0.99 \text{ g Cl}\cdot\text{dm}^{-3}$ ), whereas set of results was clearly asymmetric in relation to median, which indicates the predomination of processes of water desalination over processes of salination caused by backflow of Pomeranian Bay waters.

Presented data show that surface waters (to 0.5 m under water surface) at both measurement stations were less saline than bottom waters (at the depth of 5.0 m) evaluating it in accordance with concentrations of Cl<sup>-</sup>,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  when  $\text{HCO}_3^-$  concentrations in both layers of water were balanced and concentrations of  $\text{Ca}^{2+}$  in surface waters were slightly higher. Similar situation was ascertained in earlier studies (for instance: Poleszczuk 1996a, b, 1997a, b, 1998, 2003).

Table 2  
 Statistical evaluation of the total ions concentrations ( $g \cdot dm^{-3}$ ) in surface and near bottom waters for stations No. 1 and No. 2  
 in the Great Lagoon. Data from May to October 2003

Ion	Statistical characteristics	All results for stations No.1 and No. 2 (n=24)		All results for station No.1 (n=12)		All results for station No.2 (n=12)		Surfaces waters for stations No. 1 and No. 2 (n=12)		Near bottom waters for stations No. 1 and No. 2 (n=12)		Surfaces waters		Near bottom waters	
		3	4	5	6	7	8	9	10	11	Station No. 1 (n=6)	Station No. 2 (n=6)	Station No. 1 (n=6)	Station No. 2 (n=6)	
Cl <sup>-</sup>	2														
	Min.	0.369	0.520	0.369	0.369	0.422	0.520	0.369	0.520	0.520	0.369	0.520	0.369	0.520	0.422
	$\bar{x} / \tilde{x}$	0.991 / 1.030	1.009 / 0.940	0.972 / 1.030	0.940 / 0.975	1.041 / 1.075	0.977 / 0.903	0.903 / 0.975	0.903 / 0.975	0.977 / 0.903	0.903 / 0.975	0.903 / 0.975	0.903 / 0.975	0.903 / 0.975	1.042 / 1.075
	Max.	1.720	1.720	1.630	1.640	1.720	1.640	1.640	1.640	1.640	1.640	1.640	1.149	1.720	1.630
	Upper / Lower quartile	1.200 / 0.743	1.220 / 0.713	1.139 / 0.870	1.114 / 0.713	1.220 / 0.780	1.200 / 0.700	1.060 / 0.890	1.200 / 0.700	1.200 / 0.700	1.200 / 0.700	1.060 / 0.890	1.220 / 0.760	1.220 / 0.760	1.200 / 0.850
Na <sup>+</sup>	SD / CV(%)	0.364 / 36.751	0.404 / 40.035	0.337 / 34.615	0.338 / 35.916	0.397 / 38.129	0.412 / 42.150	0.279 / 30.889	0.412 / 42.150	0.412 / 42.150	0.279 / 30.889	0.432 / 41.549	0.432 / 41.549	0.399 / 38.375	
	Min.	0.225	0.291	0.225	0.225	0.228	0.298	0.225	0.298	0.298	0.225	0.291	0.225	0.228	
	$\bar{x} / \tilde{x}$	0.565 / 0.592	0.571 / 0.520	0.558 / 0.592	0.544 / 0.576	0.586 / 0.619	0.555 / 0.520	0.532 / 0.576	0.555 / 0.520	0.555 / 0.520	0.532 / 0.576	0.588 / 0.555	0.588 / 0.555	0.584 / 0.619	
	Max.	0.976	0.976	0.913	0.915	0.976	0.915	0.915	0.915	0.915	0.688	0.976	0.976	0.914	
	Upper / Lower quartile	0.679 / 0.434	0.704 / 0.409	0.657 / 0.487	0.652 / 0.415	0.696 / 0.434	0.687 / 0.390	0.617 / 0.511	0.687 / 0.390	0.687 / 0.390	0.617 / 0.511	0.721 / 0.428	0.721 / 0.428	0.661 / 0.462	
SD / CV(%)	0.205	0.228	0.191	0.188	0.228	0.226	0.162	0.226	0.226	0.162	0.249	0.249	0.228		
CV(%)	36.382	39.829	34.174	34.568	38.922	40.735	30.444	42.428	42.428	30.444	39.120	39.120	39.120		

1	2	3	4	5	6	7	8	9	10	11	
K <sup>+</sup>	Min.	0.011	0.013	0.011	0.011	0.012	0.013	0.011	0.014	0.012	
	$\bar{x} / \bar{x}$	0.021 / 0.021	0.021 / 0.020	0.020 / 0.021	0.020 / 0.019	0.022 / 0.022	0.021 / 0.020	0.018 / 0.019	0.022 / 0.021	0.021 / 0.022	
	Max.	0.035	0.035	0.032	0.033	0.035	0.033	0.026	0.035	0.032	
	Upper / Lower quartile	0.026 / 0.014	0.026 / 0.014	0.024 / 0.013	0.025 / 0.013	0.026 / 0.014	0.025 / 0.013	0.023 / 0.013	0.023 / 0.013	0.026 / 0.015	0.026 / 0.014
	SD / CV(%)	0.007 / 34.570	0.008 / 36.860	0.007 / 33.051	0.007 / 33.051	0.008 / 35.340	0.008 / 38.880	0.008 / 30.668	0.006 / 0.072	0.008 / 38.174	0.008 / 35.769
Ca <sup>2+</sup>	Min.	0.062	0.062	0.070	0.072	0.062	0.076	0.072	0.062	0.070	
	$\bar{x} / \bar{x}$	0.082 / 0.081	0.082 / 0.083	0.081 / 0.080	0.083 / 0.081	0.081 / 0.082	0.082 / 0.081	0.083 / 0.080	0.082 / 0.080	0.082 / 0.087	0.079 / 0.080
	Max.	0.110	0.096	0.110	0.110	0.096	0.090	0.110	0.096	0.086	
	Upper / Lower quartile	0.087 / 0.076	0.090 / 0.076	0.084 / 0.075	0.086 / 0.076	0.088 / 0.073	0.088 / 0.076	0.084 / 0.074	0.084 / 0.074	0.084 / 0.060	0.084 / 0.076
	SD / CV(%)	0.010 / 12.735	0.011 / 13.325	0.010 / 12.698	0.010 / 12.322	0.011 / 13.573	0.006 / 7.237	0.014 / 16.628	0.014 / 18.421	0.015 / 18.421	0.006 / 7.247
Mg <sup>2+</sup>	Min.	0.010	0.010	0.035	0.035	0.035	0.036	0.035	0.035	0.035	
	$\bar{x} / \bar{x}$	0.063 / 0.064	0.060 / 0.061	0.066 / 0.067	0.061 / 0.055	0.073 / 0.072	0.064 / 0.063	0.058 / 0.055	0.071 / 0.070	0.071 / 0.070	0.074 / 0.075
	Max.	0.117	0.102	0.117	0.102	0.117	0.102	0.084	0.102	0.102	
	Upper / Lower quartile	0.081 / 0.043	0.080 / 0.037	0.081 / 0.051	0.080 / 0.043	0.087 / 0.056	0.081 / 0.038	0.070 / 0.049	0.070 / 0.056	0.092 / 0.056	0.081 / 0.063
	SD / CV(%)	0.025 / 39.369	0.027 / 45.426	0.023 / 34.633	0.022 / 35.553	0.024 / 33.582	0.027 / 42.095	0.017 / 29.313	0.017 / 29.313	0.024 / 34.394	0.027 / 35.733
SO <sub>4</sub> <sup>2-</sup>	Min.	0.106	0.106	0.112	0.106	0.112	0.106	0.141	0.113	0.112	
	$\bar{x} / \bar{x}$	0.186 / 0.180	0.186 / 0.196	0.185 / 0.174	0.181 / 0.172	0.191 / 0.185	0.190 / 0.196	0.172 / 0.161	0.172 / 0.184	0.182 / 0.184	0.199 / 0.185
	Max.	0.287	0.284	0.287	0.284	0.287	0.284	0.223	0.268	0.287	
	Upper / Lower quartile	0.121 / 0.141	0.234 / 0.128	0.208 / 0.146	0.218 / 0.146	0.244 / 0.133	0.228 / 0.130	0.192 / 0.151	0.192 / 0.151	0.219 / 0.126	0.285 / 0.141
	SD / CV(%)	0.057 / 30.582	0.061 / 32.617	0.055 / 29.844	0.050 / 27.616	0.065 / 33.981	0.066 / 34.641	0.031 / 17.933	0.031 / 17.933	0.061 / 33.566	0.073 / 36.66

1	2	3	4	5	6	7	8	9	10	11
	Min.	0.152	0.152	0.152	0.159	0.152	0.159	0.159	0.152	0.152
	$\bar{x} / \tilde{x}$	0.165 / 0.162	0.163 / 0.162	0.167 / 0.165	0.166 / 0.162	0.164 / 0.164	0.165 / 0.162	0.168 / 0.168	0.162 / 0.161	0.165 / 0.165
	Max.	0.180	0.177	0.180	0.180	0.180	0.177	0.180	0.177	0.180
HCO <sub>3</sub> <sup>-</sup>	Upper / Lower quartile	0.172 / 0.159	0.169 / 0.159	0.170 / 0.159	0.175 / 0.159	0.169 / 0.155	0.171 / 0.159	0.177 / 0.159	0.168 / 0.152	0.171 / 0.159
	SD / CV(%)	0.009 / 5.324	0.008 / 5.059	0.0093 / 5.388	0.008 / 5.090	0.009 / 5.637	0.007 / 4.536	0.010 / 5.780	0.009 / 5.853	0.009 / 5.769
	Min.	0.935	1.154	0.974	0.977	1.023	1.208	1.012	1.187	1.031
	$\bar{x} / \tilde{x}$	2.073 / 2.130	2.122 / 1.982	2.049 / 2.129	1.995 / 2.040	2.158 / 2.219	2.054 / 1.945	1.934 / 2.034	2.147 / 2.088	2.164 / 2.221
	Max.	3.425	3.390	3.269	3.264	3.411	3.241	2.460	3.374	3.246
$\Sigma m_{ion}$	Upper / Lower quartile	2.366 / 1.610	2.523 / 1.536	2.363 / 1.801	2.350 / 1.565	2.530 / 1.645	2.480 / 1.506	2.223 / 1.847	2.540 / 1.597	2.508 / 1.765
	SD / CV(%)	0.677 / 95.713	0.747 / 213.151	0.632 / 184.603	0.623 / 185.467	0.742 / 199.164	0.752 / 210.274	0.519 / 161.655	0.798 / 214.385	0.750 / 42.429

Notations:

$\bar{x}$  – average

$\tilde{x}$  – median

SD – standard deviation

CV(%) – coefficient of variation (%)

$\Sigma m_{ion}$  – amount of the all ionic macrocomponents concentrations in (g · dm<sup>-3</sup>) with chlorinity (Cl‰) increased



Table 3  
Ionic macrocomponents totals concentrations and salinity (as  $\sum m_{ion}^1$ ) in ( $g \cdot dm^{-3}$ ) of Great Lagoon waters versus its chlorinity (Cl‰)

Results for station No. 1 or 2 and surfaces or near bottom waters (simple size)	Ion body	Coefficients in equation of the linear regression $y_i = A + B \cdot (Cl\text{‰})$		By analysis of variance			Chlorinity (Cl‰) range (‰)
		A	B	SEE	$\alpha$ for equation	R <sup>2</sup> (%)	
1	2	3	4	5	6	7	8
all results for stations No. 1 and No. 2 (n=24)	Na <sup>+</sup>	(0.008±0.012)	(0.562±0.011)***	0.018	0.0000	99.10	0.369-1.720
	K <sup>+</sup>	(0.002±0.001)	(0.019±0.001)***	0.001	0.0000	90.99	
	Ca <sup>+</sup>	(0.082±0.002)***	-	0.009	0.9099	0.00	
	Mg <sup>+</sup>	(0.025±0.013)	(0.038±0.012)**	0.020	0.0044	28.32	
	SO <sub>4</sub> <sup>2-</sup>	(0.091±0.028)**	(0.095±0.026)**	0.055	0.0016	34.32	
	HCO <sub>3</sub> <sup>-</sup>	(0.179±0.004)***	(-0.014±0.004)**	0.007	0.0061	29.13	
	$\sum m_{ion}$	(0.387±0.060)***	(1.700±0.054)***	0.109	0.0000	94.82	
station No. 1 – surfaces and near bottom waters (n=12)	Na <sup>+</sup>	(0.004±0.013)	(0.562±0.012)***	0.012	0.0000	99.47	0.520-1.720
	K <sup>+</sup>	(0.002±0.001)	(0.019±0.001)***	0.000	0.0000	96.31	
	Ca <sup>+</sup>	(0.082±0.003)***	-	0.013	0.9631	0.00	
	Mg <sup>+</sup>	(0.060±0.008)***	-	0.025	0.3055	0.00	
	SO <sub>4</sub> <sup>2-</sup>	(0.079±0.036)	(0.106±0.034)*	0.049	0.0102	44.93	
	HCO <sub>3</sub> <sup>-</sup>	(0.163±0.002)***	-	0.011	0.4493	0.00	
	$\sum m_{ion}$	(0.390±0.063)***	(1.687±0.047)***	0.110	0.0000	94.96	

1	2	3	4	5	6	7	8
station No. 2 – surfaces and near bottom waters (n = 12)	Na <sup>+</sup>	(0.011±0.021)	(0.563±0.021)***	0.021	0.0000	98.53	0.369-1.630
	K <sup>+</sup>	(0.002±0.002)	(0.018±0.002)***	0.001	0.0001	83.04	
	Ca <sup>+</sup>	(0.081±0.003)***	-	0.009	0.8304	0.00	
	Mg <sup>+</sup>	(0.005±0.008)	(0.063±0.008)***	0.004	0.0000	84.85	
	SO <sub>4</sub> <sup>2-</sup>	(0.185±0.016)***	-	0.043	0.8485	0.00	
	HCO <sub>3</sub> <sup>-</sup>	(0.185±0.006)***	(-0.019±0.006)*	0.010	0.1454	41.18	
	∑ m <sub>ion</sub>	(0.469±0.056)***	(1.625±0.037)***	0.088	0.0000	94.33	
	Na <sup>+</sup>	(0.023±0.019)	(0.553±0.019)***	0.021	0.0000	98.76	
	K <sup>+</sup>	(0.002±0.002)	(0.019±0.002)***	0.000	0.0000	87.38	
	Ca <sup>+</sup>	(0.083±0.003)***	-	0.013	0.8771	0.00	
surfaces waters for stations No. 1 and No. 2 (n = 12)	Mg <sup>+</sup>	(0.004±0.007)	(0.060±0.007)***	0.001	0.0000	86.45	0.369-1.640
	SO <sub>4</sub> <sup>2-</sup>	(0.085±0.034)*	(0.102±0.034)*	0.039	0.0127	42.64	
	HCO <sub>3</sub> <sup>-</sup>	(0.166±0.002)***	-	0.014	0.4644	0.00	
	∑ m <sub>ion</sub>	(0.360±0.067)***	(1.734±0.062)***	0.088	0.0000	94.37	
	Na <sup>+</sup>	(-0.011±0.013)	(0.573±0.012)***	0.017	0.0000	99.53	
	K <sup>+</sup>	(0.002±0.002)	(0.019±0.001)***	0.004	0.0000	92.62	
	Ca <sup>+</sup>	(0.081±0.001)***	-	0.007	0.9262	0.00	
	Mg <sup>+</sup>	(0.012±0.007)	(0.058±0.006)***	0.010	0.0000	88.79	
	SO <sub>4</sub> <sup>2-</sup>	(0.097±0.048)	(0.090±0.043)	0.062	0.0568	23.31	
	HCO <sub>3</sub> <sup>-</sup>	(0.180±0.006)***	(-0.016±0.005)*	0.013	0.0150	40.84	
∑ m <sub>ion</sub>	(0.362±0.077)***	(1.724±0.067)***	0.113	0.0000	93.40	0.422-1.720	
near bottom waters for stations No. 1 and No. 2 (n = 12)							

1	2	3	4	5	6	7	8
station No. 1 – surfaces waters (n=6)	Na <sup>+</sup>	(0.020±0.017)	(0.548±0.017)***	0.010	0.0000	99.53	0.520-1.640
	K <sup>+</sup>	(0.002±0.001)	(0.019±0.001)***	0.001	0.0000	97.61	
	Ca <sup>+</sup>	(0.082±0.002)***	-	0.005	0.6558	0.00	
	Mg <sup>+</sup>	(0.002±0.008)	(0.063±0.008)**	0.000	0.0015	92.25	
	SO <sub>4</sub> <sup>2-</sup>	(0.056±0.043)	(0.137±0.041)*	0.023	0.0278	67.59	
	HCO <sub>3</sub> <sup>-</sup>	(0.165±0.003)***	-	0.016	0.3747	0.00	
	∑ m <sub>ion</sub>	(0.327±0.074)***	(1.767±0.067)***	0.055	0.0001	98.90	
	Na <sup>+</sup>	(0.012±0.035)	(0.576±0.038)***	0.019	0.0000	97.91	
station No. 2 – surfaces waters (n=6)	K <sup>+</sup>	(0.003±0.005)	(0.017±0.005)*	0.006	0.0297	62.94	0.369-1.149
	Ca <sup>+</sup>	(0.083±0.006)***	-	0.007	0.8516	0.00	
	Mg <sup>+</sup>	(0.011±0.015)	(0.052±0.015)*	0.001	0.0279	67.54	
	SO <sub>4</sub> <sup>2-</sup>	(0.172±0.013)***	-	0.028	0.7519	0.00	
	HCO <sub>3</sub> <sup>-</sup>	(0.168±0.004)***	-	0.011	0.7463	0.00	
	∑ m <sub>ion</sub>	(0.449±0.078)**	(1.645±0.058)**	0.072	0.0026	89.70	
	Na <sup>+</sup>	(-0.011±0.022)	(0.576±0.012)***	0.019	0.0000	99.42	
	K <sup>+</sup>	(0.002±0.002)	(0.019±0.002)***	0.011	0.0008	94.12	
station No. 1 – near bottom waters (n=6)	Ca <sup>+</sup>	(0.082±0.006)***	-	0.008	0.9412	0.00	0.520-1.720
	Mg <sup>+</sup>	(0.016±0.011)	(0.053±0.010)**	0.010	0.0060	84.53	
	SO <sub>4</sub> <sup>2-</sup>	(0.182±0.025)***	-	0.062	0.8453	0.00	
	HCO <sub>3</sub> <sup>-</sup>	(0.162±0.004)***	-	0.010	0.3441	0.00	
	∑ m <sub>ion</sub>	(0.433±0.070)*	(1.648±0.024)**	0.120	0.0020	91.07	

1	2	3	4	5	6	7	8
station No. 2 – near bottom waters (n=6)	Na <sup>+</sup>	(-0.010±0.018)	(0.570±0.017)***	0.020	0.0000	99.58	0.422-1.630
	K <sup>+</sup>	(0.002±0.003)	(0.018±0.003)**	0.005	0.0029	89.25	
	Ca <sup>+</sup>	(0.079±0.002)***	-	0.001	0.8925	0.00	
	Mg <sup>+</sup>	(0.007±0.009)	(0.065±0.008)**	0.007	0.0012	92.84	
	SO <sub>4</sub> <sup>2-</sup>	(0.199±0.030)**	-	0.070	0.9284	0.00	
	HCO <sub>3</sub> <sup>-</sup>	(0.188±0.005)***	(-0.022±0.004)**	0.001	0.0072	83.05	
	∑ m <sub>ion</sub>	(0.465±0.067)*	(1.631±0.032)***	0.104	0.0006	95.24	

Notations:

$\sum_{i=1}^n m_{ion}$  - amount of the all ionic macrocomponents concentrations in (g·dm<sup>-3</sup>) with chlorinity (Cl‰) increased

Confidence level for constant A and coefficient B:

\* 0.010 ≤ α ≤ 0.050

\*\* 0.001 ≤ α ≤ 0.010

\*\*\* α ≤ 0.001

Significant is fact that bottom waters taken at station No. 2 reveal that ion concentrations in waters of “marine derivation” were largely higher than those measured at the station No. 1, whereas concentrations of ions from inland freshwaters<sup>2</sup> in bottom waters at station No. 2 were lower than those determined in waters collected at station No. 1, what is the evidence of occurrence of highly saline waters in bottom layers of Great Lagoon in its southern parts. Described phenomenon had been observed earlier (Poleszczuk 1997a, b) and had been profoundly and fully explained. Great Lagoon constitutes a part of estuary where flow occurs in both directions, but only when intensity of river waters inflow contains within range:  $395 < Q < 790 \text{ m}^3 \text{ s}^{-1}$ .

In surface layer, inland waters are flowing down the estuary, raising and carrying salt waters laying in bed layers what leads to gradual growth of salinity in surface waters, when bottom waters are constantly supplied in “fresh” saline sea waters which are ceaselessly inflowing by the shipping channel Szczecin-Świnoujście. It usually happens in accordance with following principle: the lesser down flow of river waters – the greater inflow of sea waters.

Therefore, mineralization degrees of bottom and surface waters at both measurement stations was so differentiated. Mineralization levels at both stations were not substantially different from each other whereas mineralization of surface waters was considerably varied at both stations.

Specific relations between concentrations of particular macroionic components of waters and  $\text{Cl}^-$  concentrations are drawing attention. At stations No. 1 in surface waters,  $\text{Cl}^-$  concentrations were linearly correlated with concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and in lesser degree (because of  $R^2$ ) with  $\text{SO}_4^{2-}$ , whereas at station No. 2,  $\text{Cl}^-$  concentrations were correlated with  $\text{Na}^+$ , to a lesser extent with  $\text{K}^+$  and  $\text{Mg}^{2+}$ , what gives evidence of changes, probably physico-chemical, caused by relations between ionic macrocomponents in waters of Great Szczecin Lagoon. For bottom waters at station No. 1, changes in  $\text{Cl}^-$  concentration were positively correlated with  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , when correlation with  $\text{SO}_4^{2-}$  was not proved. At station No. 2 – with  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , and – with concentrations of  $\text{HCO}_3^-$  (coefficient of proportionality – minus value), while correlation with  $\text{SO}_4^{2-}$  was not found.

Specific lack of correlation with  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  (apart from bottom waters at station No. 2) – is obvious because  $\text{Cl}^-$  ions, present in waters of Great Lagoon (Szczecin Lagoon) are derived from sea water, while  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  have “inland” origin. The lack of correlation between  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in bottom waters at both stations and in surface waters at station No. 2, seems to witness stabilized  $\text{SO}_4^{2-}$  concentration, what convinces of occurrence of ecosystem processes, which cause “binding” of  $\text{SO}_4^{2-}$ , when  $\text{SO}_4^{2-}$  level is rising (as a result of marine waters inflow) and contrary – when  $\text{SO}_4^{2-}$  concentration in waters is decreasing (as a result freshwater down flow) ions  $\text{SO}_4^{2-}$  are “released into water depths”.

<sup>2</sup> nominally – because Odra river are calcium-bicarbonates waters, although simultaneously average concentrations of  $\text{Ca}^{2+}$  in waters of Pomeranian Bay are higher (ca.  $107 \text{ mg Ca} \cdot \text{dm}^{-3}$ ) than concentrations in Odra (ca.  $75 \text{ mg Ca} \cdot \text{dm}^{-3}$ ). Only concentrations of  $\text{HCO}_3^-$  in Odra waters reach  $150 \text{ mg HCO}_3 \cdot \text{dm}^{-3}$  in comparison to  $92 \text{ mg HCO}_3 \cdot \text{dm}^{-3}$  in Pomeranian Bay waters (where chlorosity constitutes 4‰) by Poleszczuk (1997a).

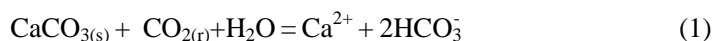
Table 4

Mass of ionic macrocomponents ( $\sum m_{ion}$ ) for Great Lagoon (Szczecin Lagoon) waters as in chlorinity function and comparison in the function index versus chlorinity range for Baltic Sea, Seas and Ocean waters

Reservoir of water	All waters (surfaces and near bottom)	Coefficients in equation of the linear regression $y_i = A + B \cdot (Cl\text{‰})$		Correlation coefficient R	Chlorinity range	Period of research	Source data
		A	B				
Great Lagoon (Szczecin Lagoon)	All waters	0.272	1.768	0.990	0.10-2.50	year 1970	Młodzińska 1974
	as highly	0.262	1.778	0.998	0.08-2.89	March-November 1992	Poleszczuk 1998
	as highly	0.387	1.700	0.948	0.37-1.72		
	Surfaces waters of the N-W part of Great Lagoon (station No. 1)	0.327	1.767	0.989	0.52-1.64		
	Surfaces waters of the S-E part of Great Lagoon (station No. 2)	0.449	1.645	0.897	0.37-1.15	May-October 2003	this work
Southern Baltic (Pomeranian Bay?)	Near bottom waters of the N-W part of Great Lagoon (station No. 1)	0.433	1.648	0.912	0.52-1.72		
	Near bottom waters of the S-E part of Great Lagoon (station No. 2)	0.465	1.631	0.952	0.42-1.63		
Southern Baltic	Equation $\sum m_{ion} = f(Cl\text{‰})$ for Southern Baltic water (Trzosińska 1970) at practical chlorinity range (<4.50 ‰) – most probably answered Pomeranian Bay water (Majewski 1974) for waters: 0-20m depth	0.098	1.811	-	4.50	1960-1965	Trzosińska 1970
Baltic Sea after Knudsen	Salinity (S‰) as function of chlorinity (Cl‰) – for waters 0-20m depth	0.074	1.809	0.999	4.00-5.00	-	Trzosińska 1967
Seas and oceans	Salinity (S‰) as function of chlorinity (Cl‰) – all waters	0.115	1.805	-	-	-	after Jasińska (1991)
Ocean	as highly	0.030	1.805	-	S‰ = 0-40	near 1900	Knudsen 1901
Ocean	as highly	0.069	1.811	-	-	-	Lyman 1959
Ocean	as highly	0	1.806	-	S‰ = 30-40	-	Momin 1979

It seems, that processes responsible for such a changes are processes of coagulation  $\leftrightarrow$  peptization of colloids of organic matter, which are accompanied by incorporation of bivalent anions and bivalent cations into structures of gel micelles during coagulation (occurring under influence of salinity increase) and disintegration of micelles during peptization (caused by freshwater down flow). Described effect should also be accompanied by changes (decrease and increase) of bivalent cations:  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Such an effect has been confirmed, because correlations between  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  concentrations and  $\text{Cl}^-$  are respectively poor or statistically insignificant. Outlined processes evidently occur, also in surface waters at station No. 2.

Statistically significant correlation between concentrations of  $\text{Cl}^-$  and  $\text{HCO}_3^-$  in bottom waters at station No. 2 (with minus mark of coefficient of proportionality) can be explained by saline activity of chlorides on  $\text{CO}_{2(\text{r})}$ , causing shifting the reaction equilibrium towards the left:



to such an extend, that it makes up the effect of growth of  $\text{CaCO}_3$  solubility, due to rising of water ionic strength (salt effect) and shifting the reaction equilibrium towards the right:



Bottom deposits of Róztoka Odrzańska and of southern part of Great Lagoon are exceptionally rich in  $\text{CaCO}_3$  (Majewski 1980), whereas pH of waters in that part of estuary used to be relatively low with comparison to pH values of waters from other regions of Szczecin Lagoon (Poleszczuk 1997a).

Equations which depict dependence of total mineralization values ( $\sum m_{\text{ion}}$ ) upon the concentration of  $\text{Cl}^-$ , which had been presented in Tab. 3, were put in the Tab. 4, together with analogical dependences for waters of Szczecin Lagoon, Pomeranian Bay and World Ocean. Collected data show that bottom waters at stations No. 1 and No. 2 in Great Lagoon (Szczecin Lagoon) in 2003 were more mineralized in comparison to surface waters. Mineralization in bottom waters at station No. 1 was exceptionally strongly dependant (highest values of number coefficient at the concentration of chlorides) on concentration of chlorides, in other words: dependant on backflow of sea waters. Salinity of surface waters at station No. 1 was distinctively strongly dependant on marine waters backflow. Surface waters at station No. 2 had lower mineralization level and had characteristic composition – more dependent on concentration of chlorides.

## CONCLUSIONS

On the ground of collected data, (which were assumed as poor and not sufficient), we can admit that researches on mineralization of waters of Szczecin Lagoon carried in 2003, should be regarded as preliminary, whereas results of statistic calculations as initial. Summarizing we can come to following conclusions:

1. Mineral composition of waters from north-western and south-eastern parts of Szczecin Lagoon in 2003 was in the high degree differentiated for surface (0.5 m deep) and bottom (5.0 m deep) waters, as far as quality (ion composition) and degree of total mineralization, were concerned. Bottom waters were always more mineralized than surface waters, showing considerable resemblance of composition and concentration at both stations. Surface waters at both stations were less mineralized, and salinity of surface waters in north-western part was substantially higher than salinity of south-eastern waters of Great Szczecin Lagoon.
2. Specific differences in ionic composition and in level of total salinity of Great Szczecin Lagoon waters, dependent on location of measurement station and depth, prove that in ecosystem of Szczecin Lagoon important transformations take place. Outlined transformations cause changes of contents of some ionic macrocomponents which flow down the estuary waters and – as the consequence – calculation on concentrations of individual ionic macrocomponents (when there is necessity to obtain precise data about mineral composition) in waters of Great Lagoon basing on equations available in literature is potentially erroneous. Accessible equations showing relations between average concentrations of particular ionic macrocomponents, average total salinity of Szczecin Lagoon and concentration of chlorides can be faulty and improper. That is why, most appropriate way of obtaining reliable data are researches on mineral composition of waters taken at adequate locations within Great Szczecin Lagoon, carried for every water depth.

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- PN-81/C-04551. 01. Woda i ścieki. Oznaczanie wapnia (twardości wapniowej) metodą wersenianową (Water and waste water. Tests for calcium. Determination of calcium (calcium hardness) by EDTA method), (in Polish).
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## O ZASOLENIU WODY W WIELKIM ZALEWIE SZCZECIŃSKIM RAZ JESZCZE

### Streszczenie

W roku 2003 w okresie od maja do października oznaczano stężenia ogólne makroskładników jonowych ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ) i na podstawie tych oznaczeń obliczono przybliżone wartości zasolenia wód Wielkiego Zalewu (Zalew Szczeciński). Próby wody do badań pobierano w miejscach stacji pomiarowych zlokalizowanych w północno-zachodniej (stacja nr 1) i w południowo-wschodniej (stacja nr 2) częściach Zalewu. Wodę czerpano z warstwy powierzchniowej (z głębokości ok. 0,5 m) i naddennej (z głębokości ok. 5,0 m). Próby wody do badań pobierano z częstotliwością raz w miesiącu. Ze względu na niedużą liczbę pomiarów, badania te traktowano jako rozpoznawcze, zaś ich wyniki – jako ustalenia wstępne. Badania potwierdziły znany wcześniej fakt znacznego zróżnicowania składu jonowego i stężenia substancji mineralnych w wodach Wielkiego Zalewu w zależności od miejsca poboru prób i głębokości, z jakiej próby pobierano. Wody naddenne były wyraźnie bardziej zasolone od wód powierzchniowych i to na obu ww. stacjach, przy czym –

co było dość zaskakujące – bardziej zasolone były wody naddenne w południowo-wschodniej części Zalewu. Jeżeli chodzi o wody powierzchniowe, to – jak było też wiadome z wcześniejszych badań – bardziej zasolone były wody w północnej części Zalewu. Z równań regresji liniowej, ujmujących zależności pomiędzy wartościami stężeń poszczególnych składników mineralnych a stężeniami jonów chlorkowych, a także z równań ujmujących zależności pomiędzy łącznymi masami makroskładników jonowych zawartych w 1 dm<sup>3</sup> wód (oznaczanymi w tekście pracy jako  $\sum m_{ion}$ ) – także ze stężenia jonów chlorkowych, w wodach na obu stacjach i w obu badanych warstwach wynika, że istotne statystycznie korelacje uzyskano jedynie dla stężeń Na<sup>+</sup> i K<sup>+</sup> oraz Emion – przy czym wartości stałej i współczynnika w równaniu regresji liniowej – dla każdej z 4 kategorii wód (2 stacje × 2 warstwy wody) – były wyraźnie różne. Związane to było z zachodzeniem w ekosystemie Zalewu (wzdłuż drogi spływu wód w dół estuarium) przemian prowadzących do zmiany składu chemicznego wód. Ustalenia te wskazują, że wyniki obliczeń składu jonowego wód i zasolenia wykonywane na podstawie ogólnych (uśrednionych) dla całego Wielkiego Zalewu równań korelacyjnych ujmujących zależność pomiędzy stężeniami wybranych składników makrojonowych wód oraz ich ogólnego zasolenia od stężenia chlorków mogą prowadzić do otrzymania wyników znacznie różniących się od wartości rzeczywistych. W tej sytuacji jedynym i najpewniejszym sposobem na ustalenie składu jonowego i wartości stężeń wybranych makroskładników jonowych oraz zasolenia ogólnego wód jest wykonanie odpowiednich oznaczeń stężeń wszystkich składników makrojonowych wód Wielkiego Zalewu.