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TOTAL CONCENTRATIONS OF MAGNESIUM AND CALCIUM IN SELECTED WATER BODIES OF THE ODRA RIVER ESTUARY (NW POLAND)

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Abstract

Basing on results of measurements of total concentrations of magnesium and calcium in surface and near bottom water of the river Odra estuary (at stations located in Roztoka Odrzańska, Great Lagoon and Wicko Lake) between 1991-1993 an attempt was undertaken to quantify the relation between the magnitude of the observed Mg^{2+}_{tot} and Ca^{2+}_{tot} concentrations, monthly mean river flow (Q_s – measured in Gozdowice) and sea level in the Pomeranian Bay (readings from the mareograph in the mouth of the river Świna to the Pomeranian Bay). It was found out that magnesium concentrations are most affected by the mean flow of the river Odra and the strongest relation (the magnitude of correlation coefficients and the highest statistical significance) was obtained between the total concentration of Mg^{2+}_{tot} and the mean Q_s in the month of measurements and the two preceding months. The variations in sea level in the Pomeranian Bay, which can be used as an indicator of saline seawater inflow into the estuary, influenced the studied concentrations only in the southern part of the Great Lagoon.

INTRODUCTION

The estuary of the river Odra comprises the following water bodies: Pomeranian Bay - characterised as the I-order estuary, Szczecin Lagoon together with the straits of the rivers Świna, Dziwna and Piana - the II-order estuary, and Roztoka Odrzańska, including Domiąża strait and the mouth sections of the western Odra and Dąbie Lake - the III-order estuary. The presented classification was based on the mixing degree of fresh and marine waters.

The mineralisation of water in the I-order estuary, i.e. in the Pomeranian Bay (salinity 7.5-8.0‰, chlorinity 4.0-4.5‰) is uniform with the salinity of the surface water in the southern Baltic Sea (Demel 1974) and it is stable. However, in the II- and III-order estuaries, transformed fresh/saline water is transported, with dominating rive-rine water component, hence the chemical composition of these waters changes, depending time and location. The Szczecin Lagoon and other mentioned water basins, straits as well as the river Odra bed are temporarily filled with saline water which enters the estuary via the Świna, Dziwna and Piana straits. Hence the resulting salinity in these basins depends on the current river Odra flow on one hand, and on the intensity of saline water inflow from the Pomeranian Bay, the latter being influenced by the storm surges driven by wind and variations in atmospheric pressure.

During the back flows of saline water from the Pomeranian Bay, water salinity in the Szczecin Lagoon increases up to 6-7‰. Hence, in practice, water in all the basins of the II- and III-order estuary of the river Odra is characterised by considerable variability of chemical composition (Mikulski 1960, 1970, Majewski 1964, 1972, 1980, Wypych 1970, Buchcholz 1990 a,b, Jasińska 1991, Mutko 1994, Poleszczuk 1996, 1997, 1998). Simultaneously, river Odra collects water from 122 712.1 km^2 of an industrialised and urbanised catchment area (Mikołajewski 1966) and transports large amounts of variable substances in the dissolved form or in suspensions (Dubrawski and Andrulewicz 1972). Particular importance in this respect has to be given to the municipal and industrial waste water input from the Szczecin agglomeration. The load of untreated waste water is discharged directly into the river Odra and is subsequently transported down the estuary (Mutko and Landsberg-Uczciwek 1993).

The evaluation of the magnitude of concentrations and the determination of the variability of chemical components in water is considered as one of the fundamental tasks in biotope characterisation (Perthuisot and Guelorget 1992). Among the numerous ionic macro-components - magnesium and calcium are the two bioelements playing an important role in biohydrogeochemical processes undergoing in natural waters (Macioszczyk 1987).

Literature concerning the mineral composition of water in the Szczecin Lagoon presents some results on measurements of the total concentrations of magnesium and calcium in Roztoka Odrzańska (Zaborowska-Młodzińska 1963, Poleszczuk 1996) and Great Lagoon (Młodzińska 1974, 1980 a,b, Poleszczuk 1997, 1998) which have been carried out between 1958-1994, however no attempt was ever undertaken to quantify the relation between the magnitude of the observed concentrations of these elements and parameters affecting the chemical composition of water in the estuary: monthly mean river flow (Q_s - measured in Gozdowice) - an indicator of the riverine flow and sea level in the Pomeranian Bay (readings from mareograph in the river Świna mouth to the Pomeranian Bay) - an indicator of the seawater back flow into the estuary.

This article presents results of the studies carried out in 1991-1993 on quantification of the relation of the total concentrations of magnesium and calcium in water of the selected basins within the river Odra estuary (Roztoka Odrzańska, selected basins of the Great Lagoon and Lake Wicko Wielkie) as a function of the river Odra flow and sea level in the Pomeranian Bay, as indicated by the mareograph in Świnoujście.

MATERIAL AND METHODS

Between 1991-1993 the studies were carried out during the vegetation season: from April to October. Water samples were collected at measurement stations No 1-7 (Fig. 1, Table 1), when the state of the Szczecin Lagoon was < 4°B.

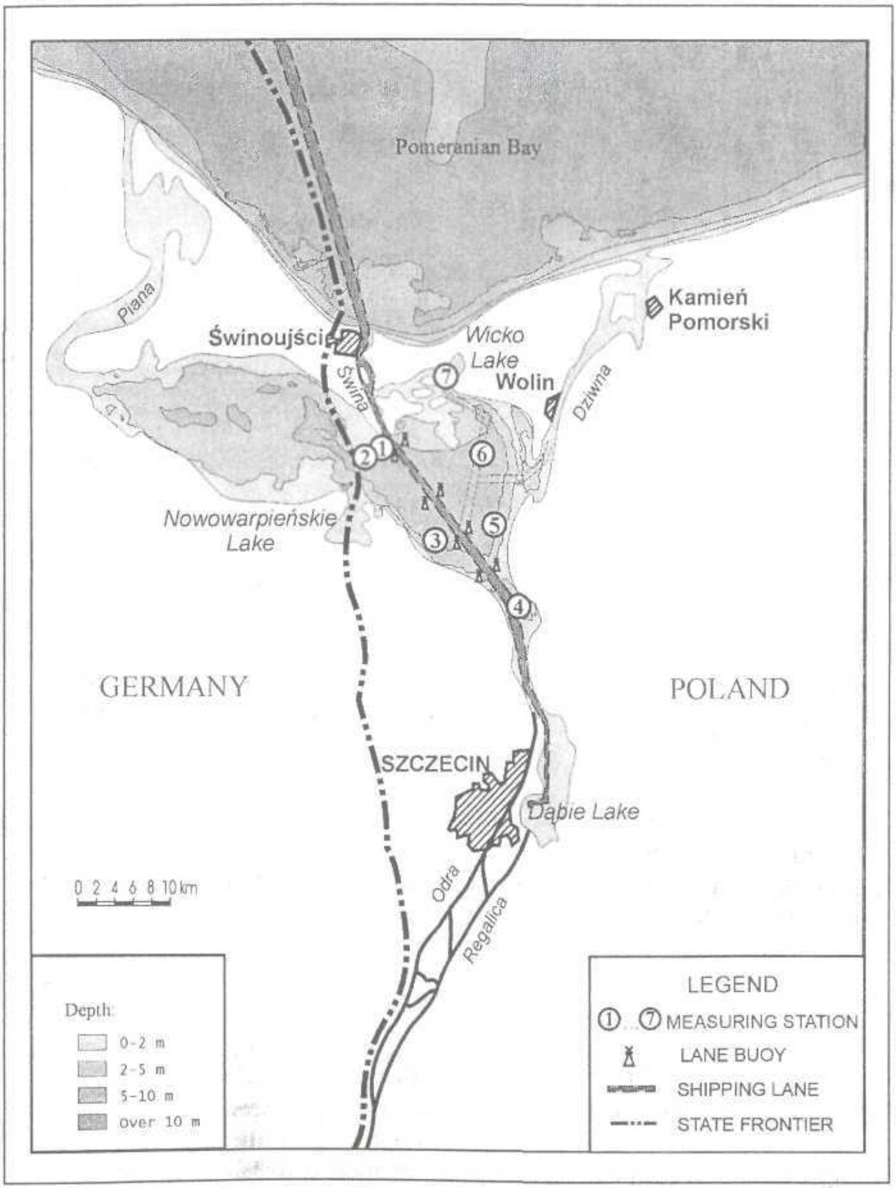

Fig. 1. Odra River estuary – location of measurement stations

Table 1

Location of sampling stations in the Roztoka Odrzańska, central zone of the Szczecin Lagoon (Great Lagoon) and Wicko Wielkie Lake

Station No.	Depth (m)	Station location	Short characteristics of the station location
1.	5.0	53°48'N 14°21'E	Great Lagoon - west to the Gate Way No. I
2.	6.0	53°46'N 14°19'E	Great Lagoon - near buoy MOS
3.	5.0	53°42'N 14°26'E	Great Lagoon –west to the Gate Way No. III
4.	3.5	53°38'N 14°34'E	Roztoka Odrzańska - east side of buoy no. 18
5.	5.0	53°44'N 14°31'E	Great Lagoon – east side of Gate Way No. III
6.	5.0	53°48'N 14°30'E	Great Lagoon – near buoy MI
7.	2.5	53°52'N 14°25'E	Wicko Wielkie Lake *vis a' vis* strait to Wicko Małe Lake

Water was sampled using the Patalas samplers from 0.5 m below the surface and 0.5 m above the bottom. The analyses were done on filtered samples (celulose acetate 0.45 μm) in the land laboratory up to 12 h after sampling (Polish Standard PN-86/C-04632.03., PN-86/C-04632.04.).

The general hardness and total concentration of calcium ions were determined complexometrically. The concentration of magnesium ions was evaluated as the difference between the total hardness and calcium determinations (Polish Standard PN-71/C-04554, PN-75/C-04562.01., PN-81/C-04551.01.) similarly to studies on the chemical composition of seawater in the Baltic Sea (Voipio 1957, Trzosińska 1976) and to studies of the mineral composition of water in the Szczecin Lagoon by Młodzińska (1974, 1980 a,b) and Poleszczuk (1996, 1997, 1998).

Calcium concentration determined by the described procedures comprises, in fact, the concentrations of calcium and strontium ions, which was already pointed out by Młodzińska (1980 b). And the total concentration of magnesium forms the sum of magnesium and other two- and tri-valent ions present in the dissolved form in the analysed water sample and titrated under the method conditions. In the case of seawater from the Baltic Sea the determination of the real concentration of calcium is simple formally, because the ratio between calcium and strontium in seawater is stable and well recognised (Bojanowski 1973). The corresponding molar relations between Ca and Sr in estuarine water of the river Odra estuary are not defined, hence such procedure could not be followed. The total concentrations of calcium and magnesium presented in this paper are therefore slightly elevated.

The concentration of chloride ions - chlorinity - was determined in water samples parallely to calcium and magnesium determinations (Poleszczuk and Piesik 2002).

Analytical precision of the procedures, determined as the relative standard deviation, was 3% in the case of calcium and magnesium analyses and 1% in the case of chlorinity.

The data on the monthly mean river flow of the river Odra, measured at the water gauge in Gozdowice, were supplied by the Poznań Branch of the Institute of Meteorology and Water Management, while the indications of the mareograph in Świnoujście were supplied by the Maritime Branch of IMGW (Gdynia). Statistical characteristics of the data set analysed in the article is presented in Table 2.

Table 2

Statistical evaluation of Q_{s1}, Q_{s2}, Q_{s3}, H_1 and H_2.
Data from April to October in 1991-1993

Statistical characteristics	Q_{s1}	Q_{s2}	Q_{s3}	$Q_{s4} = 0,5(Q_1 + Q_2)$	$Q_{s5} = 0,5(Q_2 + Q_3)$	$Q_{s6} = 0,33(Q_1 + Q_2 + Q_3)$	H_1	H_2
1	2	3	4	5	6	7	8	9
Min	167	167	167	167	167	170	464	479
$\bar{x}$	347	362	386	354	374	365	502	501
$\tilde{x}$	291	318	339	305	329	313	502	502
Max	982	982	982	799	799	710	540	523
SD	208	176	167	174	153	151	18	13
CV%	59,9	48,6	43,3	49,2	40,9	41,4	3,6	2,6

Notations:

Q_{s1}, Q_{s2}, Q_{s3} – monthly mean flows of the Odra Gozdowice ($m^3 \cdot s^{-1}$) in the month of measurement, one month before and two months before, respectively

H_i – sea level in the Świna Channel mouth to Pomeranian Bay (cm), respectively: H_1 - on the day of measurements, H_2 – average values by data for measuring day and one and two days before measurements

SD – standard deviation

CV% - coefficient of variation

The statistical characteristics of the obtained data included the calculation of the mean, median, standard deviations (SD) and coefficients of variation (CV). Seasonal variability of the determinands was analysed using the classical "box-whiskers" procedure (*Statistica* 1994), where the medians are presented in the form of "boxes" containing 50% of the results of an increasing series of these results, the results being equally divided below (25%) and above (25%) the median. The "whiskers" indicate the minimal and the maximal values among the remaining results. The measurement data differing 1.5-fold (minimal) or 3-fold (maximal) from the median are indicated in Fig. 2. as "o" and "+", respectively.

The Spearman rang correlation coefficients were determined between the i-pairs of determinands as well as multiple regression equations relating the water quality indicators (Mg^{2+}_{tot} and Ca^{2+}_{tot}) with the environmental factors (here: riverine flow Q_s and sea level H_i). The multicomponent regression equations were determined by the *á priori* step-rejection and addition (Forward) (*Statistica* 1994) using the algorythms from the "*Statgraphics*" software library, the rejection was done after verification by sequential Fisher-Snedecor test F = 4.

The following multiple regression equations were evaluated:

$$y_i = const + \sum_{i=1}^{b} A_i Q_{si} + \sum_{j=1}^{2} B_i H_i + SEE$$

The equations of simple linear regression:

$$y_i = const + A_i \cdot [Cl^-] + SEE$$

between the total concentrations of calcium and magnesium and the chlorinity were verified in the described manner.

All statistical analyses were carried out at the confidence level $\alpha = 0.05$ (Sokal and Rohlf 1995).

RESULTS AND DISCUSSION

The results of measurements and subsequent statistical analyses are presented in tables 3-5 and in Fig. 2. In tables 6-7 the equations are listed which paramerize the relation between the total concentrations of calcium and magnesium and chlorinity.

The study indicated that the total concentrations of calcium and magnesium in water at particular sampling stations vary to a considerable extent, the concentration of Mg^{2+}_{tot} was dependent on the time and location of the sampling and fell in the range 8-210 mg · dm^{-3}. This significant range of concentrations can be explained by the fact that, in general, the total concentrations of magnesium ions in riverine water from the river Odra were relatively low during the entire period of the study and seawater inflowing from the Pomeranian Bay, characterised by chlorinity of about 4‰, contained magnesium up to 270 mg · dm^{-3}. Hence the transformed fresh/saline water in the estuary revealed such high variability of Mg^{2+}_{tot} concentrations (Tab. 3; CV%=31-61). Contrary to that, calcium concentrations in estuarine water were relatively stable and fell within the range 85-90 mg Ca^{2+}_{tot} mg · dm^{-3}. This can be explained by the fact that both the concentrations of Ca^{2+}_{tot} in the riverine water from the river Odra and in seawater, inflowing temporarily from the Pomeranian Bay, were of similar magnitude. The concentrations of Ca^{2+}_{tot} in the Odra river were usually ca. 75 mg · dm^{-3} and in seawater – at chlorinity 4‰ - ca. 107 mg · dm^{-3}. Therefore, the resulting calcium concentrations in estuarine water did not show high variability (Tab. 3, CV% = 7-20) (Poleszczuk 1997, 1998).

Table 3

Statistical evaluation of the total concentrations of Mg^{2+} and Ca^{2+} ions in surface (s) and near bottom (b) waters in the Szczecin Lagoon. Data from April to October in 1991-1993

Statistical characteristics	All measurements		Station No 1		Station No 2		Station No 3		Station No 4		Station No 5		Station No 6		Station No 7	
	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)
Total concentrations of Mg^{2+}																
Min	8	12	29	28	20	26	12	15	10	12	8	13	20	28	25	38
$\bar{x}$	59	62	86	89	60	64	48	51	21	23	51	53	64	69	80	81
$\tilde{x}$	*51*	*53*	*70*	*77*	*53*	*56*	*49*	*49*	*19*	*21*	*50*	*50*	*60*	*68*	*83*	*82*
Max.	210	212	210	212	132	134	93	94	42	48	91	104	122	129	180	185
SD	36	37	52	53	27	30	21	21	7	9	21	23	24	25	38	38
CV%	61.2	59.6	61.0	59.6	44.8	46.3	44.2	41.6	34.3	38.6	40.7	42.7	37.1	35.4	46.9	46.3
Total concentrations of Ca^{2+}																
Min.	47	29	70	70	63	63	60	60	47	29	58	57	68	69	83	80
$\bar{x}$	80	80	87	87	81	80	76	74	74	72	76	76	79	79	90	89
$\tilde{x}$	79	79	81	84	75	77	72	73	76	72	73	75	78	78	88	87
Max.	119	126	114	126	119	105	96	92	102	95	96	98	98	91	103	109
SD	12	12	15	14	13	11	9	9	12	14	9	9	9	7	6	8
CV%	14.9	15.1	16.8	16.6	16.1	13.8	12.3	11.5	16.2	19.1	12.2	12.3	10.8	9.4	6.6	8.5

Notations:
(s) – surface waters
(b) – near bottom waters
SD – standard deviation
CV% - coefficient of variation (%)

The determined concentrations of both elements showed little differentiation between the surface and near bottom water, the total concentrations of magnesium being usually slightly higher in the near bottom water and calcium – in the opposite direction. This observation was particularly noticeable in water of Roztoka Odrzańska (station No 4) and in the south-western part of the Great Lagoon (station No 3). No differences between the surface and near bottom concentration of Ca^{2+}_{tot} was found at other stations in the Great Lagoon. A slight vertical stratification of calcium concentrations was noted in the lake Wicko Wielkie (station 7). Horizontal stratification of the total concentrations of magnesium and calcium in the studied parts of the river Odra estuary was also described in earlier papers, eg. Poleszczuk (1997, 1998). The stratification of magnesium concentrations is probably related to the inflows of saline water from the Pomeranian Bay in the near bottom layer along the estuary and its stagnation in the Great Lagoon's basin (Majewski 1980, Poleszczuk 1997). The specific situation of very weak differentiation in calcium concentrations between the surface and near bottom layer can be explained by coagulation and peptisation processes undergoing in colloidal sediments of organic matter. The colloids discharged into the estuary with riverine water from the river Odra precipitate after mixing with saline water as gel and absorb bi-positive ions (Ca^{2+}_{tot} and Mg^{2+}_{tot}) as well as bi-negative ones (SO_4^{2-} and CO_3^{2-}) which are incorporated into the micell structures of the gelatinating colloid.

Table 4

Statistically significant ($\alpha < 0.05$) values of Spearman R_i correlation coefficients r rank order for the variable pairs: total ion concentration - water flow intensity coefficients of Odra River[1)] or Baltic water level[2)] in Świna Channel mouth to Pomeranian Bay (bold font denotes the highest values of R_i coefficients)

i-pair of variables		Spearman R_i correlation coefficients values for i-tej pair of variables															
		All measurements		Station No. 1		Station No. 2		Station No. 3		Station No. 4		Station No. 5		Station No. 6		Station No. 7	
		(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)	(s)	(b)
Mg	Q_{S1}	-0,47	-0,48	-0,47	-0,48	-0,58	-0,63	-0,68	-0,73	-0,71	-0,73	**-0,81**	-0,78	-0,61	-0,64	-0,46	-0,40
	Q_{S2}	**-0,53**	-0,55	**-0,67**	**-0,70**	**-0,74**	**-0,75**	-0,75	-0,83	-0,72	-0,74	-0,76	**-0,81**	**-0,69**	-0,70	-0,56	-0,51
	Q_{S3}	-0,45	-0,47	-0,51	-0,52	-0,68	-0,67	-0,67	-0,72	-0,65	-0,66	-0,59	-0,65	-0,53	-0,62	-0,60	-0,58
	Q_{S4}	-0,52	-0,54	-0,61	-0,64	-0,69	-0,71	-0,76	-0,82	-0,75	-0,66	**-0,80**	**-0,82**	-0,66	-0,70	-0,55	-0,50
	Q_{S5}	-0,52	-0,54	-0,62	-0,64	**-0,75**	**-0,74**	-0,73	-0,81	-0,70	-0,72	-0,69	-0,76	-0,61	-0,69	**-0,64**	**-0,61**
	Q_{S6}	**-0,54**	**-0,57**	-0,63	-0,65	**-0,75**	**-0,75**	**-0,79**	**-0,85**	**-0,79**	**-0,79**	-0,78	**-0,82**	-0,65	**-0,74**	**-0,67**	**-0,62**
	H_1	**0,25**	**0,26**	*	*	*	*	**0,49**	**0,49**	**0,41**	*	**0,52**	**0,50**	*	*	*	*
	H_2	0,21	0,21	*	*	*	*	0,40	0,42	*	*	0,43	0,43	*	*	*	*
Ca	Q_{S1}	**-0,20**	**-0,21**	*	*	*	*	*	**-0,43**	*	*	**-0,54**	**-0,54**	*	-0,40	*	*
	Q_{S2}	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	Q_{S3}`	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	Q_{S4}	-0,17	-0,18	*	*	*	*	*	*	*	*	*	-0,46	*	**-0,42**	*	*
	Q_{S5}	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	Q_{S6}	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	H_1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
	H_2	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

Notations:

[1)] Q_{Si} - monthly average values of the Odra river flow ($m^3 \cdot s^{-1}$), respectively:
Q_{S1} - in the month of measuremens
Q_{S2} - one month before the month of measuremens
Q_{S3} - two months before the month of measuremens
Q_{S4} - $0,5 (Q_{S1} + Q_{S2})$
- $Q_{S5} - 0,5 (Q_{S2} + Q_{S3})$
- $Q_{S6} - 0,33 (Q_{S1} + Q_{S2} + Q_{S3})$

[2)] H_1 - Baltic water level in the Świna Channel mouth to the Pomeranian Bay (cm) on the day of measurements
H_2 - Baltic water level - average values on the day of measurements and one and two days before the measurements
* - N.S. – not significant
α - significant level
(s) - surface water
(b) - near bottom water

As a result of salinity decrease, caused by an enhancement in the riverine flow, the colloidal sediments peptised, whereupon the bi-positive and bi-negative ions were desorbed into the water of the estuary (Poleszczuk 1996). It is worth noticing that the amount of dissolved organic matter in the Szczecin Lagoon, becomes close to amount of dissolved mineral substances, i.e. attains considerable magnitude (Poleszczuk and Kosowska 2002). The variability in measured calcium concentrations was observed regarding both the location of sampling station and the time of sampling, corresponding to the variability of chloride ions in the Szczecin Lagoon (Poleszczuk 1997, 1998, Poleszczuk and Piesik 2002). The seasonal increase in calcium concentrations, observed at individual stations, differed quantitatively in various parts of the estuary – the maximal was found out in the northern part of the Lagoon and the minimal – in Roztoka Odrzańska.

Table 5

Statistically significant ($\alpha < 0.05$) values of „const” and coefficients in regression equation: [*total ion concentration in* $mg \cdot dm^{-3}$] = $const + \sum_{i=1}^{6} A_i Q_{si} + \sum_{i=1}^{2} B_i H_i + SEE$ for waters of selected parts of the Odra River estuary

Results for station	Surface (s) or near bottom (b) waters	Mg_{tot}			Ca_{tot}		
		Const, A and B_i coefficient	From regression analysis of the equation		Const, A and B_i coefficient	From regression analysis of the equation	
			SEE	R^2		SEE	R^2
All results (n = 182 number of data)	(s)	Const = 98.7±6.2 A_6=-0.110±0.016	31.8	0.21	Const = 80.2±0.9	11.9	0.00
	(b)	Const = 103.8±6.3 A_6=-0.115±0.016	32.5	0.22	Const = 79.6±0.9	12.0	0.00
No 1 (n = 26)	(s)	Const = 146.1±24.1 A_6=-0.165±0.061	46.9	0.23	Const = 86.8±2.9	14.6	0.00
	(b)	Const = 154.0±24.1 A_6=-0.177±0.061	46.8	0.26	Const = 86.8±2.8	14.4	0.00
No 2 (n = 26)	(s)	Const = 104.0±10.2 A_6=-0.121±0.026	19.8	0.48	Const = 80.5±2.5	12.9	0.00
	(b)	Const = 112.7±11.2 A_6=-0.134±0.028	21.8	0.48	Const = 78.0±5.4	10.4	0.00
No 3 (n = 26)	(s)	Const = 134.9±96.2* A_6=-0.109±0.014 B_1=1.141±0.355 B_2=-1.235±0.478	10.6	0.78	Const = 75.6±1.8	9.3	0.00
	(b)	Const = 92.3±6.6 A_6=-0.113±0.017	12.7	0.65	Const = 74.5±1.7	8.6	0.00
No 4 (n = 26)	(s)	Const = 33.0±2.7 A_6=-0.032±0.007	5.3	0.48	Const = 73.6±2.3	11.9	0.00
	(b)	Const = 37.7±3.5 A_6=-0.039±0.009	6.8	0.45	Const = 71.8±2.7	13.7	0.00
No 5 (n = 26)	(s)	Const = 83.4±5.6 A_4=-0.092±0.014	12.7	0.64	Const = 75.8±1.8	9.1	0.00
	(b)	Const = 93.9±8.0 A_6=-0.110±0.020	15.6	0.55	Const = 76.4±1.8	9.4	0.00
No 6 (n = 26)	(s)	Const = 96.1±8.0 A_4=-0.090±0.020	18.0	0.45	Const = 79.3±1.7	8.5	0.00
	(b)	Const = 102.9±8.1 A_4=-0.095±0.020	18.2	0.47	Const = 79.1±1.5	7.5	0.00
No 7 (n = 26)	(s)	Const = 129.0±16.5 A_6=-0.134±0.041	32.0	0.30	Const = 89.6±1.2	5.9	0.00
	(b)	Const = 127.3±17.0 A_6=-0.126±0.043	33.1	0.26	Const = 89.0±1.5	7.5	0.00

*α = 0.175

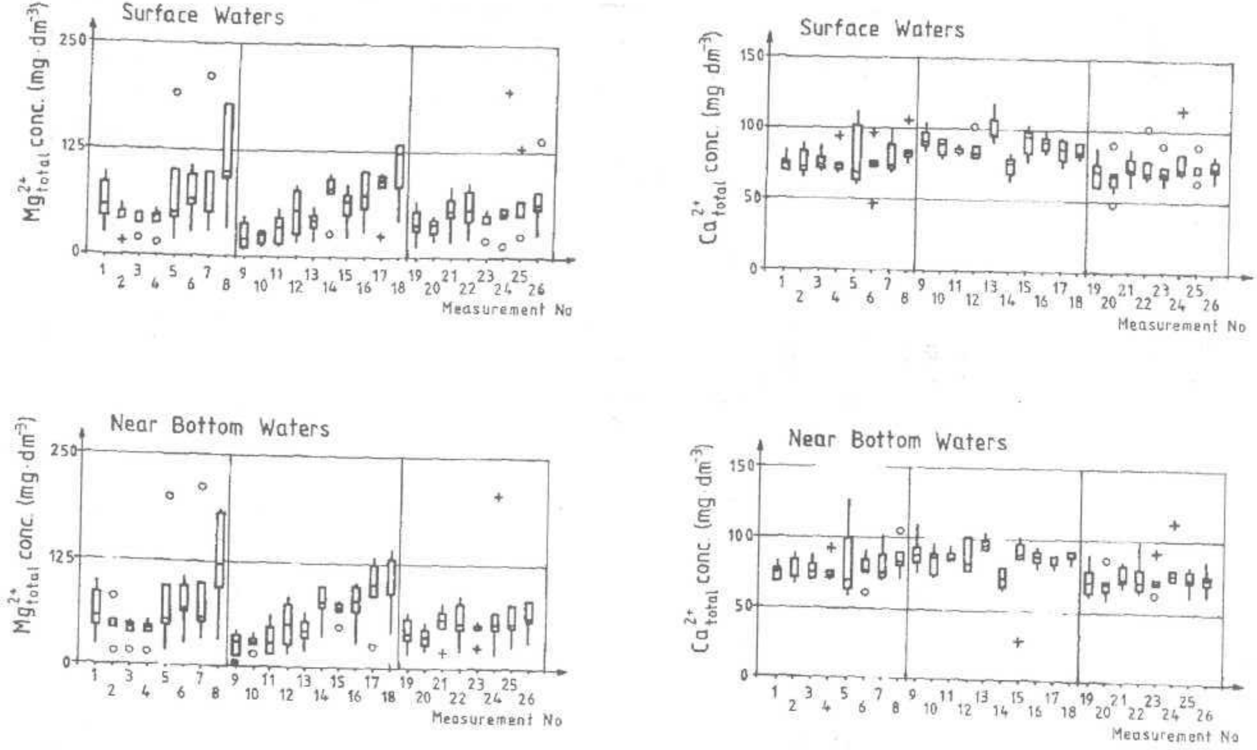

Fig. 2. Variability of the mean values of total magnesium and calcium concentrations (at 7 measurement stations)

1991: No. 1 - 25.04., No.2. - 29.05., No.3. - 30.06., No.4. - 21.07., No.5. - 02.09., No.6. - 18.09., No.7. - .10., No.8. - 23.10.,
1992: No. 9 - 19.04., No.10. - 30.04., No.11. - 21.05., No.12. - 25.06., No.13. - 09.07., No.14. - 23.07., No.15. - 10.08., No.16. - 24.08., No.17. - 18.09., No.18. - 29.10.,
1993: No. 19 - 12.05., No.20. - 24.05., No.21. - 28.06., No.22. - 15.07., No.23. - 17.08., No.24. - 02.09., No.25. - 03.10., No.26. - 27.10..

The obtained results do not allow definite determination of seasonality in the variability of total calcium concentrations. Particularly the data presented in Fig. 2 give evidence of exceptional uniformity of these concentrations at individual stations. This observation is in good agreement with the results of analyses on the relation between the total calcium and magnesium concentrations and water chlorinity (Tab. 6 and 7). The correlation between total concentrations of magnesium was statistically significant, while the total concentration of calcium did not show any dependence on chlorinity at all measurement stations, both in the surface an near bottom water with the exception of the near bottom water in Roztoka Odrzańska.

The results of Spearman rang correlation coeffcients (Tab. 4) calculations and linear regression equations between the total concentrations of $Mg^{2+}_{tot.}$ and $Ca^{2+}_{tot.}$ and the monthly mean Odra flows and sea level changes in Świnoujście, which characterise the inflows of marine water into the estuary (Tab. 5) revealed statistically significant correlation between the total magnesium concentrations at certain measurement stations (especially at stations No 3 and 5 and to a lesser extent at station 4) and both forcing agents.

The total concentration of magnesium in surface and near bottom water of Roztoka Odrzańska (station No 4) was inversely proportional to Q_{si} (Tab. 4), and the highest statistical significance was found in correlation between this concentration and Q_{s6} (Tab. 4 and 5), i.e. the mean flow of the river Odra in the month of measurements, the preceding month and two months before the month of measurements, with determination coefficients R^2 = 45-48 %. The magnitude of determination coefficients give evidence that the total concentration of magnesium in estuarine water was influenced not only by the effect of direct mixing, leading to dilution or concentration of $Mg^{2+}_{tot.}$ ions, but also by the mass exchange processes (sorption and coagulation). Similar conclusions were drawn from earlier studies by Młodzińska (1980b) and Poleszczuk (1996).

The influence of mareograph readings on the magnitude of $Mg^{2+}_{tot.}$ concentrations in estuarine water, determined from Spearman rang corelations (Tab. 4), pointed out to a direct proportionality between $Mg^{2+}_{tot.}$ and H_1. This observation carries conviction that the elevation of water level in the estuary from the mouth of the river Świna up to Roztoka Odrzańska is transferred very quickly, as if acting on the principle of liquid level equilibration in communicating vessels (Mielczarski 1987, Buchholz 1990b). This effect (Tab. 4) was particularly pronounced in the southern part of the Great Lagoon (stations No 3 and 5); station No 3 being a special example because the correlation between $Mg^{2+}_{tot.}$ concentration in surface water and Q_{si} and H_i was found here in an exceptional number of measurements (R^2 = 55-78%). Beside the presented correlations, inverse proportionality was detected at these stations between the magnesium concentrations and Q_{si} (Tab. 4 and 5), direct proportionality to H_1 (Tab. 4, stations No 3 and 5 and Tab.5, station No 3 – surface water) and inverse proportionality to H_2, that is to the mean readings from mareograph on the day of measurements, and two days preceding the measurements. The obtained results give evidence that in this part of the estuary, due to the effect of communicating vessels, saline water from the near bottom layer is very quickly "pushed" into the surface layer.

Table 6

Total magnesium (Mg^{2+}_{total}) concentrations (in g/1000g) versus chlorinity (Cl ‰) in selected water bodies of the Odra River estuary

Water body			Coefficient in equation: ion concentration = A (Cl ‰) + B		Correlation coefficient R	Chlorinity range	Period of investigations	Data source
			A	B				
1			2	3	4	5	6	7
Roztoka Odrzańska	Roztoka Odrzańska		0.0243	0.0099	0.373	0.06-0.39	October 1958 + December 1960	Zaborowska-Młodzińska 1963
	Roztoka Odrzańska1)		0.0491	0.0092	0.951	0.08-0.70	April-October in 1991-1993	Poleszczuk 1997
	Roztoka Odrzańska2)		0.0532	0.0082	0.962	0.08-0.70	March-November in 1991-1994	Poleszczuk 1996
	Roztoka Odrzańska1) (St. No. 4)	(s)	0.0392	0.0110	0.790	0,08 – 0,58	March-November in 1991-1994	this study
		(b)	0.0113	0.0192	0.390			
Szczecin Lagoon	Great Lagoon		0.0693	0.0056	0.980	0.10-2.50	1970	Młodzińska 1974
	all stations in Great Lagoon3)		0.0600	0.0080	0.933	0.08-2.89	March-November 1992	Poleszczuk 1998
	Great Lagoon – Central Zone3)		0.0668	0.0013	0.961	0.30-1.60	April-October 1991-1993	Poleszczuk 1997
	all stations in Great Lagoon3)		0.0588	0.0085	0.980	0.08-3.40	April-October 1991-1993	Poleszczuk 1997
	Great Lagoon3) (stations no. 1,2,3,5, 6)	(s)	0.0570	0.0103	0.965	0,08 – 3,40	March-November in 1991-1994	this study
		(b)	0.0486	0.0160	0.897			
	Wicko Wielkie Lake4) (St. no. 7)	(s)	0.0794	- 0.0030	0.907	0,33 – 2,05	March-November in 1991-1994	this study
		(b)	0.0575	0.0131	0.819			
Pomeranian Bay	Pomeranian Bay5)		0.0670	0.0020	-	4.00-4.50	1960-1966	Trzosińska 1970
	Central Zone		0.0670	0.0019	0.970	3.50-4.50	1960–1966	Trzosińska 1976
	Western Zone		0.0792	- 0.0510	0.970	4.00-4.50	1960–1966	Trzosińska 1976
	near Świnoujście - bottom waters6)		0.0619	0.0211	0.982	3.85-4.50	1991-1994	Poleszczuk et al. 2001
SB*	Western Zone7)		0.0664	0.0056	0.970	4.50-10.00	1960–1966	Trzosińska 1976
	Central Zone8)		0.0658	0.0100	0.970	4.50-9.50	1960–1966	Trzosińska 1976

Explanations to Table 6:

*SB – Southern Baltic

1) surface and near bottom waters (depth ≤ 7 m)

2) surface waters (depth only ≤ 0,5 m)

3) surface and near bottom waters (depth ≤ 6 m)

4) surface and near bottom waters (depth ≤ 3,5 m)

5) in Trzosińska (1970); equation which determined relation for the southern Baltic, but the chlorinity range probably from the Pomeranian Bay water;

6) near bottom waters (depth ≤ 10 m)

7) surface and near bottom waters (depth ≤ 20 m)

8) surface and sampling from different depths (depth ≤ 70 m)

(s) - surface waters (depth ≈ 0,5 m)

(b) – near bottom waters (depth difference in stations – vide Tab. 1)

Table 7

Total calcium (Ca^{2+}_{total}) concentrations (in g/1000g) versus chlorinity (Cl ‰) in selected water bodies of the Odra River estuary

Water body			Coefficient in equation: ion concentration = A (Cl ‰) + B		Correlation coefficient r	Chlorinity range	Period of investigations	Data source
			A	B				
1			2	3	4	5	6	7
Roztoka Odrzańska	Roztoka Odrzanska		0,0796	0,0621	0,618	0,06-0,39	October 1958 – December 1960	Zaborowska-Młodzinska 1963
	Roztoka Odrzańska[1)]		0,0128	0,0714	0,154	0,08-0,70	April-October in 1991-1993	Poleszczuk 1997
	Roztoka Odrzańska[2)]		0,0162	0,0662	0,243	0,08-0,70	March-November in 1991-1994	Poleszczuk 1996
	Roztoka Odrzańska[1)] (St. no. 4)	(s)	0,0164	0,0694	0,201	0,08 – 0,58	March-November in 1991-1994	this study
		(b)	- 0,0017	0,0724	- 0,039			
Szczecin Lagoon	Great Lagoon		0,0161	0,0646	0,780	0,10-2,50	1970	Młodzinska 1974
	all stations in Great Lagoon[3)]		0,0100	0,0860	0,053	0,08-2,89	March-November 1992	Poleszczuk 1998
	Great Lagoon – Central Zone[3)]		0,0018	0,0777	0,073	0,30-1,60	April-October 1991-1993	Poleszczuk 1997
	all stations in Great Lagoon[3)]		0,0093	0,0722	0,438	0,08-3,40	April-October 1991-1993	Poleszczuk 1997
	Great Lagoon[3)] (St. no. 1,2,3,5, 6)	(s)	0,0088	0,0717	0,425	0,08 – 3,40	March-November in 1991-1994	this study
		(b)	0,0077	0,0714	0,444			
	Wicko Wielkie Lake[4)] (St. no. 7)	(s)	- 0,0020	0,0916	- 0,143	0,33 – 2,05	March-November in 1991-1994	this study
		(b)	- 0,0042	0,0941	- 0,302			
Pomeranian Bay	Pomeranian Bay[5)]		0,0180	0,0350	-	4,00-4,50	1960-1966	Trzosinska 1970
	Central Zone		0,0228	0,0127	0,920	3,50-4,50	1960–1966	Trzosinska 1976
	Western Zone		0,0143	0,0503	0,800	4,00-4,50	1960–1966	Trzosinska 1976
	near Świnoujście - bottom waters[6)]		0,0120	0,0598	0,805	3,85-4,50	1991-1994	Poleszczuk et al 2001
SB*	Western Zone[7)]		0,0210	0,0189	0,920	4,50-10,00	1960–1966	Trzosinska 1976
	Central Zone[8)]		0,0204	0,0239	0,920	4,50-9,50	1960–1966	Trzosinska 1976

Explanations to Table 7:

*SB – Southern Baltic

1) surface and near bottom waters (depth ≤ 7 m)

2) surface waters (depth only ≤ 0,5 m)

3) surface and near bottom waters (depth ≤ 6 m)

4) *surface and near bottom waters (depth ≤ 3,5 m)*

5) in Trzosinska (1970): equation which determined relation for the southern Baltic, but the chlorinity range probably from the Pomeranian Bay water;

6) near bottom waters (depth ≤ 10 m)

7) surface and near bottom waters (depth ≤ 20 m)

8) surface and sampling from different depths (depth ≤ 70 m)

(s) - surface waters (depth ≈ 0,5 m)

(b) – near bottom waters (depth difference in stations – vide Tab. 1)

High sea level in the mouth section of the river Świna, persisting for a prolonged time (3 days) obscures (blocks) the surficial outflow of riverine water, which is retained in the upper part of the estuary where the surface water layer becomes more fresh but stagnating.

Total concentration of magnesium in surface and near bottom water at stations in the middle part of the Great Lagoon (stations No 2 and 6) depend mainly on the intensity of riverine flow; at station No 2 on $Q_{s6} = 0.33\ (Q_{s1} + Q_{s2} + Q_{s3})$ and at station No 6 on $Q_{s4} = 0.5\ (Q_{s1} + Q_{s2})$ (Tab. 5). This result indicates that the chemical composition of water at station No 6 was strongly dependent on fresh, inland water and this water was currently influencing Mg^{2+}_{tot} concentration by dilution. This observation forms an argument for the role played by the Coriolis force (Druet 1995) which facilitates the surficial flow of water in the Szczecin Lagoon to north and north-eastern direction under wind-less conditions. Hence, the surface riverine current flowing down the estuary is shifted towards the station No 5 and then 6. The data presented in Tab. 3-5 strongly support the occurrence of such effect. Similarly, marine water inflowing into the Szczecin Lagoon in the near bottom layer, via the Piastowski Channel, spills out of the water-way furrow and flows into south and south-west directions, this having been detected as an increase in salinity and Mg^{2+}_{tot} concentrations in the near bottom water of this part of the estuary. The data from station No 1 (Tab. 3) strongly support the above conclusions. The bathymetry and the shape of the bottom in the Szczecin Lagoon in the vicinity of the water-way, illustrated in Fig. 3, are the additional arguments for the described preferencies in water movement in the Lagoon, though occurring temporarily.

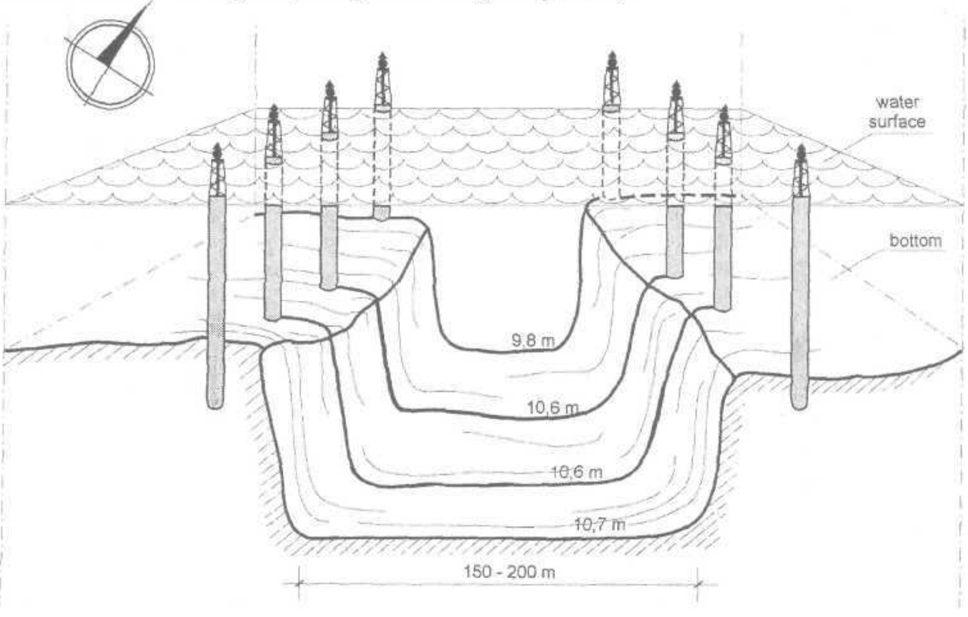

Fig. 3. Topographic features of the Szczecin - Świnoujście water way from the Piastowski Channel (Gate Way No. I), to Roztoka Odrzańska (Gate Way No. IV) according to Staszewski (1990)

The possibility of saline water spilling out of the water-way furrow into south or west was also mentioned by Jasińska (1991).

Mg^{2+}_{tot} concentrations in water of the lake Wicko Wielkie (station No 7) depended mainly on Q_{s6} (the mean Q_s from 3 months), meaning that the chemical composition of water in the lake was strongly related with the surficial flow of fresh inland water along the "old"* water-way leading from the Gate III up to the lake Wicko Wielkie. The conclusion from this observation is that the major part of inland water is flowing into the Pomeranian Bay in the surface layer via this very route. This conclusion is also convinced by the occurrence of deep areas (6-8 m deep) in the river-bed of the Old Świna, the formation of which in the area of the retrograde delta of the river Świna was possible under strong, one-way currents. Saline water, as pointed out by Poleszczuk et al. (1992) and Jasińska (1991), could flow by this route only under extremely strong surges of marine water from the mouth of the river Świna.

The data presented in Tab. 4 and 5 indicate that the total concentration of calcium in water of the studied basins was extremely stable, with the exception of stations No 3 and 5, and to a lesser degree at station No 6 (Tab. 4). In the latter area an inverse proportionality between the calcium concentrations and Q_{s1} (station No 3; both: surface and near bottom layer) and Q_{s4} (stations No 5 and 6: near bottom water) was observed, described already in this paper and in the paper by Poleszczuk and Piesik (2002). The riverine water flowing from the river Odra and containing lower concentrations of calcium is diluting water at these stations. Sorption of calcium ions on the freshly formed and sedimenting gels can not be excluded either.

The horizontal stratification of Mg^{2+}_{tot} was very similar to chloride ions stratification in the Szczecin Lagoon presented in the paper by Poleszczuk and Piesik (2002), giving the indication of dilution and concentration effects of Mg^{2+}_{tot} ions during the mixing process of riverine and marine waters. Much lower amplitudes of Mg^{2+}_{tot} concentrations in comparison to chloride amplitude and stabilisation of Ca^{2+}_{tot} concentrations are undoubtedly the result of physico-chemical processes ongoing in the Lagoon ecosystem on a large scale. Already the data obtained by Zaborowska-Młodzińska (1963) suggested the occurrence of stabilisation processes in total cocenntrations of Mg^{2+}_{tot} and Ca^{2+}_{tot} in the river Odra estuary. In the subsequent studies Młodzińska (1974, 1980b) definitely confirmed the presence of stabilisation effect and undertook an attempt to explain its mechanism by suggestion that it is related to processes of equilibrium formation in ion exchange between calcium and magnesium on aluminosilicates suspended in the water and deposited in the surface sediments. Such processes are certain to occur in the estuary, but the "vanishing" of magnesium ions is not accompanied by an increase in calcium concentrations as the ion exchange equation is proposing. Poleszczuk (1996) suggested that the stability of magnesium and calcium concentrations in the Szczecin Lagoon is governed by processes shifting the equilibrium between coagulation ↔ peptisation, which rhythmically alternate in accordance with water salinity, what seems a more probable explanation in this case. In the cited paper the author stated that the decline of salinity

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* the former water-way functioning between Szczecin and Świnoujście until the Piastowski Channel was cut through in 1880, at present it is a water-way for smaller vessels

below 0.19 ‰ Cl^-, gives the start to the process of organic matter colloids peptisation and during this process the ions: Ca^{2+}, Mg^{2+}, SO_4^{2-} and CO_3^{2-}, incorporated earlier to the gel structure, are released into water. The process duration is regulated by the amount of colloidal suspensions in water and deposited on the surface of the bottom sediments. When water salinity increase above 0.19‰ Cl^-, during an inflow of saline seawater, an opposite effect is observed - the "vanishing" of bi-positive ions from water into the suspensions and sediments.

The absence of strongly marked declines in calcium concentrations, the calcium ions should be bound into the gels in great amounts in the case of strong saline water inflow, can be explained by ion exchange processes ongoing between calcium and magnesium, as described by Młodzińska (1974, 1980b) and on the other hand by the process of calcite dolomitisation as suggested by Poleszczuk (1996, 1998) as well as by so-called salt-effect, that is solubility increase of hardly soluble calcium derivatives (calcite, dolimitised calcite, hydroxyapatite, etc.) due to salinity increase. A decline of water salinity leads to an opposite effect.

CONCLUSIONS

1. Water in the basins of the river Odra estuary, examined between 1991-1993 (measurement seasons: April – October), was characterised by significant variability of total magnesium concentrations depending on the basin and time of the year. Simultaneously, slight differences in $Mg^{2+}_{tot.}$ concentrations were observed between the surface and near bottom water layer at all measurement stations, with the higher magnesium concentration in the near bottom water.
2. $Mg^{2+}_{tot.}$ concentrations in individual parts of the Szczecin Lagoon were related by statistically significant correlations (inverse proportionality) with the river Odra flow intensity; the strongest relation was found between the ion concentrations and the mean flow in the month of measurements and two month preceding the month of measurements in sequence. Statistically significant equations between $Mg^{2+}_{tot.}$ and mareograph readings were found only at station No 5 in the southern part of the Great Lagoon.
3. The results obtained in this study indicate that the total concentration of calcium in water of the examined basins varied locally, but it showed considerable stability in time and did not show any dependence on the riverine flow intensity, neither on the mareograph readings in Świnoujście.
4. The southern part of the Great Lagoon (stations No 3 and 5) was the basin showing exceptional variability of calcium and magnesium ions. The variations in the chemical composition of water in this basin were caused by the changes in sea level in the mouth of the river Świna.
5. The specific decline of magnesium concentrations in time as compared to the amplitude of chloride concentrations confirmed that ion concentrations in water of the estuary are regulated by various processes ongoing in the ecosystem of the Szczecin Lagoon, from the concentration averaging after saline and riverine water mixing, through organic matter gel coagulation and peptisation, to processes of ion exchange on aluminosilicates and dolomitised calcite and salt-effect, re-

sponsible for the release of hardly-soluble calcium compounds with salinity increase.

6. The analysis of Mg^{2+}_{tot} and Ca^{2+}_{tot} in relation to fresh water inflow from the land and mineral composition of water on both sides of the water-way pointed out that under condition of riverine flow down the Szczecin Lagoon, undisturbed by *wind, the effect of Coriolis force is noticeable, which diverts the surface water* flow to north and north-east, while the water outflowing in the near bottom layer from the Piastowski Channel was flowing towards south and south-east direction. The same direction as water entering the Szczecin Lagoon from the Pomeranian Bay.

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PN-81/C-04551.01. Water and waste water. Tests for calcium. Determination of calcium (calcium hardness) by EDTA method.

PN-75/C-04562.01. Water and waste water. Tests for magnesium. Determination of magnesium by EDTA method.

PN-86/C-04632.03. Water and wastewater. General recommendations for sampling for physical, chemical and biological investigations. Sampling technique.

PN-86/C-04632.04. Water and wastewater. General recommendations for sampling for physical, chemical and biological investigations. Sample stabilisation and storage.

STĘŻENIA OGÓLNE MAGNEZU I WAPNIA W WODACH WYBRANYCH AKWENÓW ESTUARIUM ODRY (NW POLSKA)

Streszczenie

Podjęto próbę określenia ilościowej zależności pomiędzy stężeniami ogólnymi magnezu i wapnia a wielkościami charakteryzującymi napływ wód rzecznych (Q_S rzeki Odry mierzony w Gozdowicach) i napływ wód morskich (wskazania mareografu w ujściu Świny do Zatoki Pomorskiej) na bazie danych pomiarowych zebranych w pomiarach w miejscu siedmiu stacji pomiarowych w Roztoce Odrzańskiej, na Wielkim Zalewie i na jeziorze Wicko Wielkie podczas badań prowadzonych w sezonach kwiecień - październik w latach 1991-1993. Przeprowadzone badania stężeń ogólnych magnezu i wapnia wykazały znaczne zróżnicowanie stężeń ogólnych magnezu w miejscach poszczególnych stacji pomiarowych zarówno od akwenu jak i pory roku, wykazując pewne zróżnicowanie koncentracji pomiędzy wodami powierzchniowymi i naddennymi, przy czym stężenie $Mg^{2+}{}_{og}$ było zawsze wyższe w wodach naddennych.

Stężenie ogólne magnezu wykazywało zmienność sezonową podobną do zmienności równowartości chlorkowej w wodach Zalewu, tzn. wzrastało od wartości niskich wiosną do maksymalnych zmierzonych jesienią. Stężenie $Mg^{2+}{}_{og}$ w części północnej Zalewu było zawsze wyższe niż w wodach na stacjach pomiarowych w części południowej. Stężenia ogólne wapnia w wodach w miejscu kolejnych stacji pomiarowych przechodząc od stacji w południowej części Zalewu do stacji w północnej części Zalewu były coraz to wyższe i równocześnie były wyraźnie ustabilizowane w czasie. Z badań współczynników korelacji rang Spearmana oraz z obliczonych równań korelacyjnych wynika, że wartości stężeń ogólnych magnezu były statystycznie istotnie zależne od wartości natężenia spływu wód rzeki Odry, a szczególnie z wartościami średniej dla wartości Q_S w miesiącu pomiaru i dwóch miesiącach poprzedzających miesiąc pomiarowy. Z analizy wartości współczynników Spearmana wynika, że akweny w południowej części Wielkiego Zalewu (stacja nr 3 i 5) wyróżniały się specyficzną zmiennością stężeń ogólnych magnezu, której wartości zależały od Q_S i wahań poziomu morza. Specyficzne zmniejszenie amplitudy zmian $Mg^{2+}{}_{og}$ w porównaniu z amplitudą zmian stężeń Cl^- oraz wyjątkowa stabilizacja stężeń $Ca^{2+}{}_{og}$ w miejscach i w czasie, przemawiają za tym, że w estuarium zachodziły w dużej skali procesy fizykochemiczne, które były odpowiedzialne za stabilizowanie warto-

ści stężeń obu tych biopierwiastków. Wydaje się, że najważniejszymi były, opisane już w literaturze, procesy kształtowania się równowagi koagulacji ↔ peptyzacji koloidów materii organicznej, których zachodzenie łączyło się z procesami depozycji do osadów (koagulacja) lub „uwalnianie" do toni wodnej (peptyzacja) znacznych ilości m.in. jonów magnezu i wapnia.