

ON DIFFERENCES IN CHEMICAL COMPOSITION OCCURRING BETWEEN SURFACE AND NEAR BOTTOM WATER IN THE SZCZECIN LAGOON

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Abstract

The occurrence of differences in chemical composition between surface and near bottom water in the Great Szczecin Lagoon (Wielki Zalew) was studied between 1986-1994 under calm weather conditions, *i.e.* with the state of the Lagoon remaining <1°B for at least three days.

In the study 54 measurement series were obtained at 21 measurement stations and the measurements included: water temperature, dissolved oxygen concentration, pH and chlorinity taken at every 0.5-1.0 m on vertical profiles. At selected stations 7 series of day-round measurements were performed with sampling frequency of 2 hours. The selected water quality indicators (temperature, oxygen concentration, pH, Eh, chlorinity, alkalinity and nitrate concentration) were measured in the surface layer (0.5 m below the water surface) and 0.5 m above the bottom.

It was found out that under calm conditions water of the Szczecin Lagoon undergoes chemical transformations similar to those in enclosed water bodies.

Key words: aquatic chemistry, estuary, Szczecin Lagoon

INTRODUCTION

The Szczecin Lagoon and its Polish part, in particular, the Great Lagoon became in the eighties and nineties a natural fishing ground of considerable productivity, reaching up to 90 kg ha⁻¹ (Wolnomiejski 1994). This high productivity was attributed to the specific "habitat friendly" ecosystem of the Szczecin Lagoon, similar to other estuarine systems in the world (Guelorget and Perthuisot 1992), especially with regards of fresh water ichthyofauna (Garbacik-Wesołowska 1994).

The biotope of the Szczecin Lagoon forms an aqueous environment of specific salinity, changing seasonally from nearly fresh water in the spring to maximal salinity in autumn, though not higher than 5-6 ‰.

Simultaneously, such properties as: high trophic level and enhanced primary production, which amounting to 340-460 g C m^2 a⁻¹ (Chojnacki 1998), exceeded the primary production of the southern Baltic Sea 3-4 fold (Renk and Ochocki 1999), favourable mixing conditions of water and basin morphometry together with good oxygen situation both in surface and near bottom water (Majewski 1964, 1980; Jasińska 1991; Poleszczuk 1997a,b, 1998) facilitated the development of profuse feeding ground for ichthyofauna (Wolnomiejski and Grygiel 1989, 1992, 1994). The relatively moderate pollution level in the Lagoon (Protasowicki 1991, Protasowicki and Niedźwiecki 1991, Falkowski 1993, Protasowicki *et al*. 1993) was also of importance.

The representation of the Szczecin Lagoon as an ideal habitat of various hydrobionts is at times distorted by incidents causing severe changes in the biotope and endangering the biocoenosis like ecological catastrophes, *e.g*. oil spills (Wolnomiejski and Grygiel 1992) or floods, particularly the summer flood in 1997 (Poleszczuk and Sitek 2000), though these occur infrequently. Much more often, several times a year, appear sudden changes in water quality related to severe storms and inflows of salty marine water into the Lagoon. Unfavourable changes in water quality occur also due to eutrophication processes (Piesik 1992), *i.e*. temporal oversaturation (max. 250%, Poleszczuk 1997b) in surface water and oxygen deficits in the near bottom water appear quite frequently. As the oversaturation with oxygen is not dangerous to ichthyofauna, because fish escape the gas bubbles by diving deeper in the water (EIFAC 1971), *e.g*. in the waterway channel, and only fish farmed in live boxes are exposed to gas desease (Domagała *et al*. 1982), the deficit of oxygen, although occurring at rare occasions (Chlubek 1975), pose a real threat to fish in the water column and is leading to suboxic conditions at the interface water-bottom sediment dangerous to benthic organisms (Diaz *et al*. 1992).

The study on the occurrence, persistence and decline of differences in chemical composition of water in the Szczecin Lagoon was undertaken to put more light on the processes described above. The attention was focused on differences occurring between the surface and near bottom water. The temporal resolution of the analysed processes required continuous measurements of daily and several days duration (Osadczuk *et al*. 1996, Musielak *et al*. 1998).

MATERIAL AND METHODS

The occurrence of differences in chemical composition between surface and near bottom water in the Great Szczecin Lagoon was studied between 1986-1994 onboard of the vessels m/s SNB-ZB and SNB-US belonging to the Szczecin University and on m/s "Stynka" of the Sea Fisheries Institute in Gdynia.

The measurements were conducted solely on winless days, following 1-2 days of windless weather, *i.e*. when the state of the Szczecin Lagoon did not exceed 1ºB $(v_{wind} < 3 \text{ m s}^{-1}).$

Water samples were taken with Patalas or Ruttner samplers from the surface (0.5 m below the water surface) and at every 0.5 or 1m depth down to 0.5 m above the bottom. The measurements were conducted at 21 sampling stations (Fig. 1).

Fig. 1. Szczecin Lagoon - the Great lagoon, location of measurement stations (chemical composition of water in vertical profiles) and daily measurement cycles

During daily measurement cycles samples were taken every 2 hours; 7 series of daily measurements were conducted. Location of measurement stations in this part of the study is also shown in Fig. 1.

The following parameters were determined at the measurement station:

- water temperature with reversible thermometers,
- pH by potentiometric method (PN-74/C-04540.02) and the application of pH standard solutions (PN-81/C-06504),
- Eh by potentiometric method (Eaton *et al*. 1995) where the measuring kit was calibrated with ZoBell (1946) solution,
- alkalinity "f" and "m", acidimetrically (PN-74/C-04540.03).

Separate samples were drawn to analyse oxygen concentration by Winkler method (PN-72/C-04545.02). Samples preserved with sulphuric acid (VI) or chloroform (PN-88/C-04632.02) were transported to the land laboratory to determine nitrate concentrations (V) by scolorimetric method (PN-87/C-04576.07) and chlorinity by argentometric method using standard Copenhagen water as standard (Grasshoff 1976).

Meteorological parameters, particularly temperature, wind speed and direction, were measured onboard the research vessel and later compared with the respective data from the meteorological station in Świnoujście. Meteorological and mareograph data (H_{sea}) used in support of discussion were received from the Institute of Meteorology and Water Management in Gdynia. Monthly mean values of Odra flow (Q_s) in Gozdowice were supplied by the Poznań Branch of the Institute of Meteorology and Water Management.

During the study an attempt was undertaken to determine the direction of the surface flow by floating devices of the density slightly lesser than 1 g dm^3 .

The coefficients of mixing for inland and seawater were calculated after equations proposed by Macioszczyk (1987).

Statistical evaluation, and in particular the calculations of mean values (\bar{x}) , standard deviations (SD) and relative standard deviations (CV %) were done with the commercial software "STATGRAPHICS".

RESULTS

Variability of selected water quality parameters in vertical profiles

General characteristics of the obtained results

Temperature

Between April and October, the measuring period in the Szczecin Lagoon, the temperature of surface and near bottom water fell within the range from about 5.4 to 22.9° C. The general trends in water temperature were similar to those of inland waters - with the maximum from the mid-May to mid-September. The warmest water was usually found in Roztoka Odrzańska while the coolest - in the northern part of the Great Lagoon, cooler by 0.5-1.0ºC than in the Roztoka. Near bottom water was

usually cooler by 0.1-0.4ºC than the surface layer. During the period of the study warmer years can be distinguished (1986, 1988, 1989, 1992 and 1994) and cooler (1985, 1987, 1990 and 1993) when the temperature of water in the Lagoon did not exceed 20ºC.

Chlorinity

Chlorinity varied within the range 0.08 to 3.86‰. The highest chlorinity values were detected in the northern part of the Lagoon and the lowest, especially in respect of surface layer, in the Roztoka Odrzańska.

Chlorinity showed certain specific seasonal variability as well. In early spring low chlorinity values were measured at all measurement stations in the Lagoon later chlorinity increased to maximal level in late autumn.

Oxygen concentrations

Oxygen concentrations in water of the Szczecin Lagoon were found between 4.5 to 20.7 mg O_2 dm⁻³. The corresponding saturation values were 41-222%. The mean saturation was always around 100%. Surface water was usually slightly oversaturated with oxygen (105% on the average), while the near bottom water showed certain deficit of oxygen (mean saturation of about 96%). The extreme values of saturation were encountered incidentally. The relative standard deviations of oxygen concentrations and saturation reached 20% for all measuring stations indicating good and stable oxygen conditions in the Lagoon. However, this could not be understood that this good oxygen situation was found at any station and in any time. In this study the best oxygen conditions were found in north-eastern part of the Lagoon and the worst in the Roztoka Odrzańska.

Oxygen saturation showed the usual seasonal pattern of variability from maximal level in spring (May-June) and summer (August-September) to the autumnal minimum (October).

Water pH

pH of water in the Szczecin Lagoon varied from 7.15 to 9.60. The Roztoka Odrzańska water showed the lowest pH values (7.15-8.80) and the highest values were measured in the north-eastern part of the Lagoon (7.80-9.60). pH values also showed a seasonal rhythm attaining the maximum during the first peak of oxygen saturation.

Classification of results

The results of water quality indicators determined in vertical profiles were grouped, regardless the measurement date and station, according to the character of changes discerned. Four types of vertical profiles were established (Fig. 2):

1. practically constant salinity from the surface to bottom (maximal chlorinity $\langle 1\% \rangle$ and constant or nearly constant temperature, though season dependent, and oxygen concentration, season dependent, but practically equal from the surface to bottom. A clearly marked surface flow down the estuary was observed.

- 2. changeable salinity in the vertical profile, with rather low salinity in the surface and increasing with depth (from certain depth, different in different measurements) quite rapidly to relatively high level (maximal chlorinity $> 3\%$). According to salinity changes, oxygen concentrations, water pH and temperature altered. An increase of salinity was always accompanied by decline in oxygen concentration, pH and water temperature. A clearly marked surface flow down the estuary was observed.
- 3. practically constant salinity from the surface to bottom, often at higher level with very little movement of surface water down or up the estuary or under water stagnation. Other parameters showed also constant values, season dependent, from the surface to bottom.
- 4. salinity stable from the surface to bottom and ph and temperature relatively stable but distinct differences $(> 30\%)$ in saturation with oxygen between the surface and near bottom water. Similarly to the $3rd$ profile type - stagnation of water in the Lagoon was observed.

The results of measurements in the distinguished profile classes are shown in Table 1. The table contains also calculated coefficients of riverine and seawater mixing (n) , flow intensity values of the River Odra (0) , measured at Gozdowice bench mark and mean mareograph readings (H_{mar}) (on the measurement day and 2 predeceasing days) from Świnoujście.

It has to be mentioned that the stratification of chemical composition of water was observed more frequently in deeper parts of the Lagoon, in the vicinity of the waterway and regardless the season while in the shallow areas it appeared at random and in most cases in summer.

Daily variability of water quality indicators in the Szczecin Lagoon

All the results of measurements were collected during daily measurement cycles under calm weather conditions with cloudless sky and under very slow, non-turbulent flow of water down the estuary. Salinity was practically constant from the surface to the near bottom layer.

It is suggested that two types of chemical composition of water in the Szczecin Lagoon prevail under calm weather:

- 1. First (Fig. 3) was characterised by oxygen saturation stratification between the surface and near bottom water solely on extremely sunny days (6 series of measurements) and no differences as regards other water quality indicators. However a specific oxygen situation of near bottom water at night was observed - frequently they showed higher oxygen concentrations that the surface water. Surface and near bottom salinity did not differ and remained stable during the measurement cycle.
- 2. Second (Fig. 4) day round occurrence of stratification of chemical composition between the surface and near bottom water (1 measurement series). Especially characteristic were changes in oxygen content in surface and near bottom water, salinity was relatively stable.

Fig. 2. Szczecin Lagoon – the Great lagoon; four types of parameter variability: $(- \cdot - \square - \cdot)$ temperature, $(- \circ -)$ pH, $(\bullet \bullet \bullet \bullet)$ oxygen concentration, $(- \triangle - \cdot)$ chlorinity in vertical profiles under calm weather conditions $(< 1°B)$:

- a) no differences (*i.e*. the differences lesser than 10%) distinguished between the surface and near bottom water in all measured parameters and with clearly marked surface flow down the estuary,
- b) the difference in all measured parameters amounting to 10% between the surface and near bottom water with clearly marked surface flow down the estuary,
- c) no differences between the analysed parameters in the surface and near bottom water and relatively high chlorinity ($> 1\%$) under stagnation or weak mobility of surface water down or up the estuary,
- d) no differences (*i.e*. the differences lesser than 10%) in chlorinity between the surface and near bottom water and simultaneous distinct differences in oxygen saturation (> 30%) between both layers under stagnation or weak mobility of surface water down or up the estuary

Table 1

Chlorinity equal and stable in the surface and near bottom water: $(C1\%) = 0.83 \pm 0.01\%$, $Q_s = 207 \text{ m}^3 \text{ s}^{-1}$, $H_{\text{mar}} = 478 \text{ cm}$,

Sunset at 19.50 on 16.07.1992 and sunrise on 17.07.1992 at 3.35 summertime in Poland, sunshine on 16.07.1992 lasted 13 h 15 min

Fig. 4. Variability of temperature and selected water quality indicators in the surface (─○─), near bottom layer (─●─) of the Szczecin Lagoon and air (---▲---) during the diurnal measurement cycles 4/5.06.1992 at a station north-east to Warnołęka

Chlorinity equal and stable in the surface and near bottom water:

 $(C1\%) = 0.43 \pm 0.02\%$, $Q_s = 207 \text{ m}^3 \text{ s}^{-1}$, $H_{\text{mar}} = 484 \text{ cm}$,

Sunset at 19.51 on 04.06.1992 and sunrise on 05.06.1992 at 3.17 summertime in Poland, sunshine on 04.06.1992 lasted 10 h 30 min

During measurements carried out on 16 and 17 July 1992 during the day, when air temperature was definitely higher than the water temperature, oxygen concentration, alkalinity and pH were increasing at a uniform rate. Stratification was well developed. Nitrate concentrations and Eh clearly diminished, and both were considerably higher in the surface water than near the bottom. When air temperature decreased to the level of water temperature, this was accompanied by the appearance of the evening breeze coming from variable directions, and with the subsequent decrease of air temperature, dissolved oxygen, alkalinity and Eh relations in both water layers were disturbed and later reversed – at night higher values of these parameters and pH were measured in the near bottom water than in the surface. The reversed situation lasted until the sunrise.

During measurements carried out on 4 and 5 June 1992 when air temperature was higher from water temperature at all times, water column became thermically stratified and oxygen concentrations, pH and Eh showed quasi-sinusoidal variability and all parameters had higher values in surface water than near the bottom with the exception of nitrate which showed relatively constant concentrations and clearly lower in the surface.

DISCUSSION

The presented experimental data confirm the occurrence of differences in water quality between the surface and near bottom layer in the Szczecin Lagoon (Majewski 1964; Wypych 1970; Jasińska 1987, 1991; Jasińska and Robakiewicz 1987; Jasińska *et al*. 1989; Poleszczuk 1996a,b, 1997a,b, 1998). The ensuing situations can be classified into the following classed simultaneously indicating differences in water flow:

- Class 1 uniform flow towards the sea in the entire vertical profile,
- Class 2 water flowing in two directions: fresh water flowing down the estuary and saline water flowing up the estuary, or fresh water flowing over a stagnant saline water,
- Class 3 stagnation or insignificant movement, up the estuary or less frequently down, of water layers of relatively similar chemical composition, often with enhanced salinity,
- Class 4 stagnation or insignificant water movement, while the surface and near bottom layer show distinct differences in oxygen content but salinity and pH remain stable in the vertical profile.

The data in Table 1 point out that more saline waters were considerable poorer in oxygen content and had lower pH than the surface water in the estuary. The differences in temperature between the surface and near bottom layer were insignificant and did not exceed 0.5°C. It seems that the differences in salinity between both layers, and in consequence the differences in density, can reach the magnitude sufficient to resist even the density increase of the surface water at night (Dera 1983) related to the night's cooling which normally would cause effective mixing by convection. An additional impediment in convective mixing is probably posed by the fact that the apparent hydraulic density of the backwater is greater than the salinity indices, because it carries a greater load of suspended matter (Gurgul and Pawlak 1983). The disruption of haline stratification, which usually ends after a few to several days (Majewski 1964) or is earlier destroyed totally by wind action, is accomplished by entrainment of saline water by fresh water flowing down the estuary (Bowden 1975).

The occurrence of uniform, considerably fresh water in vertical profile (η_{surf} = 0.00-0.12 and $\eta_{\text{bott}} = 0.00$ -0.15 kg seawater/kg riverine water), *i.e.* the occurrence of stagnation or with water flowing down the estuary, under calm conditions depends solely on the intensity of the River Odra flow into the Lagoon. As pointed out by the data in Table 1, the uniform, considerably fresh water appeared when $Q_s = 251-1400$ m³ s⁻¹. This was usually accompanied by relatively low water level at the Świna outlet into the Pomeranian Bay ($H_{\text{mar}} = 468-510$ cm).

Distinct differences in salinity between the surface and near bottom water $(\eta_{surf} = 0.00 - 0.33$ and $\eta_{bot} = 0.03 - 2.53$ kg seawater/kg riverine water), appeared when $Q_s = 215-463 \text{ m}^3 \text{ s}^{-1}$ and $H_{\text{mar}} = 475-516 \text{ cm}$.

Stagnation or movement of the entire water column up the estuary took place when $Q_s = 167-370$ m³ s⁻¹ and H_{mar} = 499-545 cm. Water salinity and chemical composition strongly varied in such situations, as indicated by the values of mixing coefficients $\eta_{\text{surf}} = 0.03$ -22.06 and $\eta_{\text{bot}} = 0.05$ -27.00 kg seawater/kg riverine water.

The presented data point out that under calm weather conditions water level in the mouth of the River Świna into the Pomeranian Bay is an important factor controlling the flow of water in the Szczecin Lagoon in addition to the intensity of the River Odra flow. This water level is influenced mainly by air pressure (Majewski 1964, 1980; Jasińska 1991; Poleszczuk 1998; Robakiewicz 1993).

The differences occurring in oxygen saturation and pH between the surface and near bottom water have to related to biological processes undergoing in the estuary, phytoplankton blooms in the surface layer and biogeochemical degradation of organic matter in the near bottom layer.

Judging from Fig. 3, the variability in oxygen saturation in surface and near bottom water in the estuary is similar to inland enclosed ponds (Starmach *et al*. 1976). A well marked correlation between pH, Eh, nitrate concentrations and alkalinity and temperature alterations in both water layers is worth noticing; when air temperature drops below water temperature there is observed a "substitution" between the layers as if the surface layer became the bottom one. The ... substitution" was possible only due to mixing by convection. The scattering of results observed at dusk and in the evening, due to the evening breeze, is visible in Fig. 3.

In Fig. 3 and 4 specific inversion of nitrate concentrations is displayed where nitrate concentrations are higher in the surface layer only at night, while in Fig. 4 higher nitrate level appeared at night as well as during the day.

Alkalinity remained stable during the day and at night which can be explained by the fact that air temperature was higher than water temperature both at night and during the day. It means that surface water could not mix with the near bottom water by convection, but biological and biochemical processes altered the composition of water, especially oxygen content. Water pH and Eh remained stable as well. This can

be explained by significant buffer capacity and redox capacity of estuarine water. Relatively stable nutrient concentrations and other water quality indicators were observed during measurements performed in continuum of several days (Musielak *et al*. 1998, Osadczuk *et al*. 1996).

Similar results on water chemistry in the Szczecin Lagoon were presented by Chlubek (1975), who showed that oxygen saturation decreased at night to about 30% (ca. 2 mg O_2 dm⁻³) during simultaneous measurements at several stations in the Lagoon. An analysis of meteorological archives (24-25.08.1970) revealed that his measurements were done under very warm air masses over the Lagoon and air temperature > water temperature also at night restricting convective mixing.

CONCLUSIONS

- 1. In the deeper parts (depth > 5 m) of the Szczecin Lagoon and in the proximity of Szczecin–Świnoujście waterway, a phenomenon of significant differentiation in chemical composition between the surface and near bottom layer occurs under calm weather despite favourable conditions for convective mixing $(t_{\text{air}} < t_{\text{water}})$. These differences can be discerned because of the presence of water from the Pomeranian Bay, more saline and cooler and usually containing less oxygen (often to suboxic conditions) which backflows into the estuary.
- 2. In shallow (depth $\lt 5$ m) parts of the Szczecin Lagoon, where density stratification is not so frequent, the differences in water quality indicators between the surface and near bottom water are negligible. Under calm and sunny weather there can occur differences in oxygen saturation, less in pH, Eh and nutrient content which are related with assimilation and dissimilation processes and their different intensity in both water layers. The differentiation of chemical composition was found only during the day and vanished at nights due to strong convective mixing similarly to inland ponds.
- 3. In shallow (depth $\lt 5$ m) parts of the Szczecin Lagoon, when the density stratification was absent, the differences in water quality indicators between the surface and near bottom water are liable to occur though it was observed only seldom. The detected situations included oxygen concentration, pH, alkalinity, Eh and nutrient concentrations. The decrease in oxygen concentration was quite substantial reaching the suboxic level (≈ 2 mg O₂ dm⁻³). The maximal differences were detected at night when $t_{\text{air}} < t_{\text{water}}$, this being a characteristic feature of inland ponds as well.

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Polish standards:

- PN-72/C-04545.02. Woda i ścieki. Badania zawartości rozpuszczonego tlenu. Oznaczanie rozpuszczonego tlenu metodą Winklera [Water and waste water. Tests for dissolved oxygen. Determination of dissolved oxygen by Winkler method].
- PN-74/C-04540.02. Woda i ścieki. Badania wartości pH, kwasowości, zasadowości. Oznaczanie kwasowości i zasadowości mineralnej i ogólnej metodą miareczkowania potencjometrycznego [Water and waste water. Tests for pH, acidity and alkalinity. Determination of mineral and total acidity and alkalinity with titration potentiometric method].
- PN-74/C-04540.03. Woda i ścieki. Badania wartości pH, kwasowości, zasadowości. Oznaczanie kwasowości i zasadowości mineralnej i ogólnej metodą miareczkową wobec wskaźników [Water and waste water. Tests for pH, acidity and alkalinity. Determination of mineral and total acidity and alkalinity with titration indicator method].
- PN-81/C-06504. Woda i ścieki. Analiza chemiczna. Przygotowanie roztworów buforowych [Chemical analysis. Preparation of buffer solution].
- PN-87/C-04576.07. Woda i ścieki. Badania zawartości związków azotowych. Oznaczanie azotu azotanowego metodą kolorymetryczną po redukcji w kolumnie kadmowej [Water and waste water. Test for nitrogen. Determination of nitrate by colorimetric method after reduction in cadmium column].
- PN-88/C-04632.02. Woda i ścieki. Ogólne zasady pobierania próbek do badań fizycznych, chemicznych i biologicznych. Utrwalanie i przechowywanie próbek [Water and waste water. General principles of sampling for physical, chemical and biological examination. Preservation and storage.]
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O WYSTĘPOWANIU ZRÓŻNICOWANIA SKŁADU CHEMICZNEGO WÓD POWIERZCHNIOWYCH I PRZYDENNYCH W ZALEWIE SZCZECIŃSKIM

Streszczenie

W latach 1986-1994 badano zjawisko występowania zróżnicowania chemizmu wód powierzchniowych i naddennych Zalewu Szczecińskiego (Wielkiego Zalewu) w warunkach ciszy wiatrowej, tj. przy stanie Zalewu $\lt 1$ \degree B utrzymującym się przez co najmniej 1-3 dni.

Wykonano 54 serii badawczych w miejscu dla 21 punktów pomiarowych, oznaczając temperaturę, stężenie rozpuszczonego tlenu, pH i równowartość chlorkową w profilach pionowych, co 0,5-1,0 m od powierzchni, aż do dna. W wybranych stacjach pomiarowych, zrealizowano 7 całodobowych serii pomiarowych przy pobieraniu prób z częstotliwością co 2 godziny. Badano tam wybrane wskaźniki jakości wód powierzchniowych (0,5 m poniżej lustra wody) i naddennych (0,5 m powyżej dna). Podczas tych badań oznaczano: temperaturę, stężenie tlenu, pH, Eh, równowartość chlorkową, stężenie azotanów oraz alkaliczność. Wykazano, że w czasie ciszy wiatrowej w toni wodnej Zalewu Szczecińskiego zachodzą zmiany chemizmu wód analogiczne do zmian chemizmu zachodzących w wodach stojących zbiorników stawowych.