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Surface and near-bottom water saturation with $CaCO_3$ in the Pomeranian Bay in the vicinity of the Świna Channel mouth

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Abstract

Langmuir and Langelier calcite saturation indexes were calculated for water in the vicinity of the Świna Channel in the Pomeranian Bay. Measurements carried out in April-October of 1994 and 2004 indicated that $CaCO_3$ concentrations nearly reached the saturation level, though in spring and fall the water showed slight calcite unsaturation while in summer it was oversaturated with calcite. The observed saturation levels were related with the shifts in the equilibrium between assimilation and dissimilation processes in the Pomeranian Bay ecosystem.

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INTRODUCTION

The water in the Pomeranian Bay in area adjacent to the mouth of the Świna Channel (Fig. l) is a local biotope characterized by specific chemical properties related to the mixing of saline water (7.8-8.2 PSU) with water of a lower salinity (2.0-3.0 PSU) inflowing from the Szczecin Lagoon.

Water in this particular location is usually characterized by changeable oxygen saturation (80-120%), a pH lower than that in the open Pomeranian Bay, and enhanced concentrations of nutrients and organic matter in both the surface and near-bottom water layers (Wiktor and Wiktor 1961, Poleszczuk and Sitek 1995a, Poleszczuk et al. 2001). Additionally, during the flood crest discharge in 1997, the oxygen content in the near-bottom water fell to zero and hydrogen sulphide appeared (Trzosinska and Andrulewicz 1998).

The present study focused on the problem of the calcite ($CaCO_3$) saturation of the water close to the Świna Channel mouth in order to determine whether the conditions facilitated the crystallization and removal of $CaCO_3$ to the sediment or if, on the contrary, $CaCO_3$ suspensions transported with water from the Szczecin Lagoon underwent dissolution (Poleszczuk 1998). This issue is pertinent because calcium carbonate (solid $CaCO_3$ and $Ca(HCO_3)_2$ dissolved in interstitial water) present in sediments causes relatively durable binding of sparingly soluble compounds of mineral phosphorous obtained during the mineralization of organic matter deposited in the sediments after the adsorption of suspended $CaCO_3$ sediments to the deposits (Pitter 1989), or it precipitates as sparingly soluble iron compounds (Walter and Burton 1986).

MATERIALS AND METHODS

During the vegetation period from April to October in 1994 and 2004, surface (0.5 m depth) and near-bottom (10.5 m depth) water samples were collected at two sampling stations (Fig. l). The following indices were determined in the samples collected: water temperature; pH; total concentrations of Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-} and alkalinity f (with phenolphthaleine), total alkalinity and acidity f - to assess the ionic strength of water; residue after ignition to estimate water mineralization. The chemical analyses of seawater were conducted using methods described in Grasshoff et al. (1976), while estuarine water was analyzed with methods presented in Poleszczuk and Sitek (1995b). The measurement results obtained were used to calculate Langelier's Saturation Index (S_L) following the procedures and formulas described in Standard Methods (Eaton et al. 1991):

$$S_L = pH_{measured} - pH_{calcite\ saturation}$$

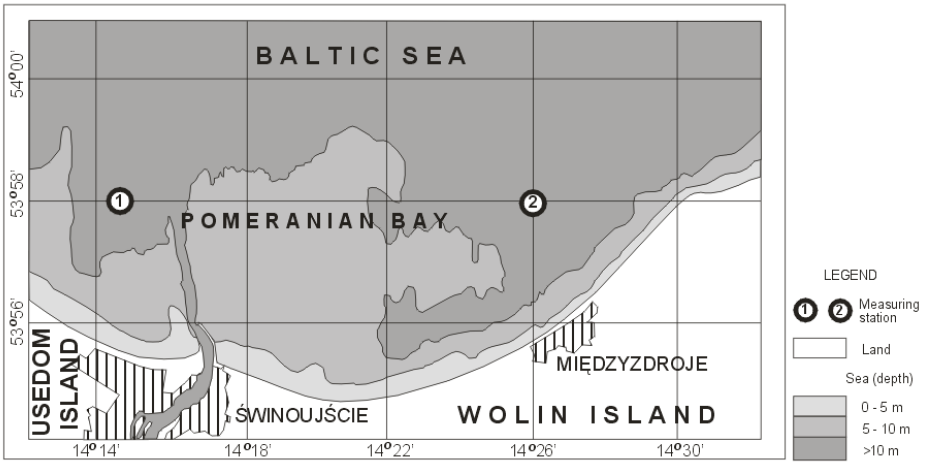

Fig. 1. Pomeranian Bay close to the Świna Channel mouth – location of sampling stations.

It is assumed that $S_L > 0$ is characteristic for water oversaturated with calcite, while $S_L < 0$ characterizes unsaturated water.
Additionally, the Langmuir Saturation Index (SI) was calculated with the following formula (Langmuir 1971):

$$SI_{Langmuir} = \lg \frac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{L_{CaCO_{3(calcite)}}}$$

The activity of calcium ions was measured using ion-selective electrodes (Cammann 1977), while that of CO_3^{2-} ions was calculated based on equilibrium in the carbonate system (Kelts and Hsu 1978) and the equilibrium constants in Plummer and Busenberg (1982). The ion activity coefficient of $I > 0.1$ mol dm^{-3} was determined by applying equations by Clegg and Whitefield (1991).

The Langmuir Saturation Index $SI > 0.1$ characterizes water that is oversaturated with calcite, while $SI > 0.1$ is specific for calcite unsaturated water.

RESULTS AND DISCUSSION

The values calculated for the Langelier Saturation Index (S_L) and the Langmuir Saturation Index (SI) are presented in Figs. 2 and 3, respectively. The

results indicate that the water in the Pomeranian Bay that is in close proximity to the Świna Channel mouth was nearly saturated with calcite during both study periods in 1994 and in 2004. In both periods slight undersaturation was observed in spring (April-June) and fall (October). In summer (July-September), the water was slightly oversaturated with $CaCO_3$. Generally, the surface water was slightly more saturated with calcite than was the near-bottom water. This observation was noted at both sampling stations, and it corresponds well with the hydrochemical phenomena active within the Oder River estuary.

The Oder supplies the estuary with water from its catchment area where soils contain large additions of marls, hence the water transports large amounts of suspended material with a considerable $CaCO_3$ content. Suspensions precipitate into the sediments mainly in the southern part of the estuary, and the bottom sediments in the Roztoka Odrzańska (the southern part of Szczecin Lagoon) contain up to 25% $CaCO_3$ (Majewski 1980). In the Szczecin Lagoon, where riverine water is mixed with saline marine water and the transformed water has a salinity of about 2.0 − 3.0, the solubility of all hardly dissolved substances increases (salt effect). Simultaneously, due to the intensive mineralization processes of autochthonic and allochthonic organic matter, the water in the Szczecin Lagoon becomes acidified by H_2CO_3, which is a product of mineralization, and this shifts the equilibrium within the carbonate system towards $CaCO_3$ dissolution. Hence, water in the Szczecin Lagoon becomes oversaturated with calcite only in summer (July-August) when it is more alkaline due to phytoplankton blooms, and the carbonate system equilibrium is shifted to higher concentrations of CO_3^{2-} (Poleszczuk 1998).

It appears that a similar situation occurred in the water of the Pomeranian Bay close to the mouth of the Świna Channel although the oscillations between undersaturation and oversaturation were of a much smaller amplitude. The changes observed in calcite saturation most probably resulted from shifts in equilibrium between assimilation processes, which dominate in summer, and dissimilation processes, which are responsible for the acidification of the aquatic environment and dominate in periods between phytoplankton blooms (Poleszczuk and Sitek 1995a). Water flowing into the Pomeranian Bay from the Szczecin Lagoon transports large amounts of seston throughout the year. This seston, together with autochthonic organic matter, sediments in the bay and becomes mineralized in the near bottom layer causing the acidification of this water. Wiktor and Wiktor (1961) described this process. Due to the sedimentation of suspended matter and its subsequent acidification, the surface water layer is less saturated with calcite than the near-bottom layer. In summer, more alkaline (pH between 9.0-9.5) and less saline water from the Szczecin Lagoon markedly influences water quality close to the mouth of the Świna Channel in the Pomeranian Bay.

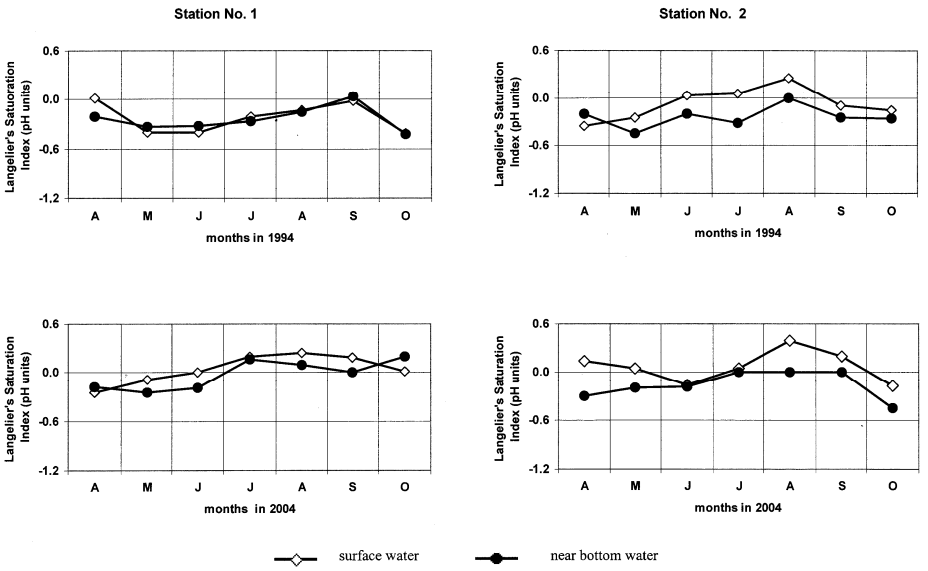

Fig. 2. Langelier's Saturation Index in surface and near-bottom water.

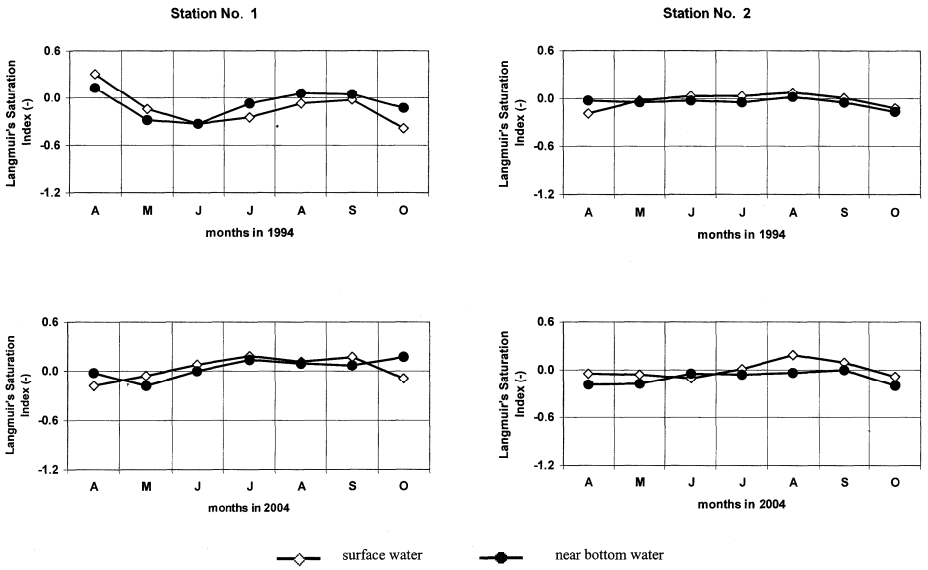

Fig. 3. Langmuir's Saturation Index in surface and near-bottom water.

Research results suggest that calcite deposition processes do not occur in the Pomeranian Bay. This is confirmed by the lack of data presenting $CaCO_3$ contents in bottom sediments near the mouth of the Świna Channel (Majewski 1974). Consequently, the possibilities of binding mineral forms of phosphorous as sparingly soluble calcium compounds are highly restricted. This is probably typical for the Baltic Sea, as is confirmed by the data of Carman and Jonsson (1990). Their surveys indicate that mineral compounds of phosphorous and calcium constitute from only several to a dozen or so percent of all the mineral phosphorous contained in surface layer of the Baltic Sea bottom deposits along the middle segment of the Swedish coast.

CONCLUSIONS

During the vegetation period (April-October) in 1994 and 2004, the surface and near-bottom Pomeranian Bay water in proximity to the mouth of the Świna Channel exhibited calcite concentrations close to the saturation level. A slight deviation from this saturation level occurred in spring and fall, while in summer slight oversaturation with $CaCO_3$ appeared. The surface water had slightly higher saturation values than the near-bottom water. The changes observed in calcite saturation level were attributed to summer phytoplankton blooms and discharges of more alkaline water from the Szczecin Lagoon. At the same time, water saturation with calcite outside of the summer period depended on acidification related to autochthonic and allochthonic organic matter mineralization within the Pomeranian Bay ecosystem.

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