Oceanological and Hydrobiological Studies
International Journal of Oceanography and Hydrobiology
Vol. XXXV, No.3

Institute of Oceanography | (237-256) 2006 | University of Gdańsk

ISSN 1730-413X

Received: *June 14, 2006*
Accepted: *August 17, 2006*

Porewater nutrients (phosphate, ammonia and silicate) in the eastern part of the southern Baltic Sea

Bożena Graca[a1], Zbigniew Witek[b], Dorota Burska[a], Izabela Białkowska[a], Andrzej Pawelec[a], Jerzy Bolałek[a]

[a] *Department of Marine Chemistry and Environmental Protection*
Institute of Oceanography, University of Gdańsk
Poland
[b] *Sea Fisheries Institute in Gdynia*
Poland

Key words: nutrients, porewater, sediments, Gdańsk Basin, southern Baltic

Abstract

In the present work, results of studies concerning phosphate, ammonia and silicate in porewaters of the eastern part of the southern Baltic sediments are presented. A strong interaction was observed between the investigated compound concentrations and the sea bottom type, defined by means of the sediment water content (W) and loss on ignition (LOI) values. High concentrations and an exponential increase in concentration downwards in the sediment depth profile was observed in regions named here transport/accumulation bottom (LOI≥4%, W≥50%). Lower concentrations and irregular changes in concentration with depth occurred in regions

[1] Corresponding author: *graca@sat.ocean.univ.gda.pl*, *Fax: (+48) 58 660 16 78*

designated as erosion bottom type (LOI<4, W<50%). Only in areas under strong anthropogenic influence (Vistula river mouth, the vicinity of Gdynia harbour), in the erosion type bottom concentration periodically raised to the level observed in the transport/accumulation bottom areas. The mass of nutrients accumulated in porewaters in the 10 cm thick layer of surface sediments of the Gulf of Gdańsk in September 2000 was estimated to be 910 t P-PO_4^{3-}, 2780 t N-NH_4^+ and 5430 t DSi, while in March/April of 2001 estimated values equalled 908 t P-PO_4^{3-}, 1860 t N-NH_4^+ and 3080 t DSi.

In the erosion bottom areas, approximately 12 t, 210 t and 650 t of P-PO_4^{3-}, N-NH_4^+ and DSi, respectively, were flushed out of the sediments during the intensive autumn-winter mixing.

INTRODUCTION

Concentrations of nutrients in porewaters are a good indicator of processes occurring in the water column and the extent of eutrophication of the waterbody, as well as for mineralization pathways of organic matter in the sediments (Mikulski 1974, Samuelsson 1987). In areas with a high sedimentation rate, readily metabolizable compounds may become buried before they can be destroyed by aerobic organisms living in the overlying water. In this case, an increase in nutrient concentration in porewaters, even up to values several hundred times greater than in the near bottom water, occurs due to the effect of anoxic metabolism in the sediments (Suess 1976, Berner 1977). A portion of the degraded nutrients is subject to adsorption (or undergoes ion exchange) on the sediment solids, or is precipitated in the form of authigenic minerals (Hyacinthe and Van Cappellen 2004). Chemical composition of the porewaters is further modified by porewater dynamics, and the zoo- and phytobenthos. In most cases, influence of the above-mentioned factors leads to a nutrient concentration decrease and is also responsible for irregularities observed in the concentration depth profiles (Sørensen 1978, Svensson 1997, Sundbäck and Granéli 1988, Starmach et al. 1976, Tengberg et al. 2003, Tuominen et al. 1999). As a main source of ammonia in the porewaters remains organic matter, phosphate concentrations are additionally significantly dependent from its mineral forms, especially redox dependent phosphorus forms. In a reductive environment these forms are degraded and removed to porewaters (Gächter and Müller 2003, Koop et al. 1990, Sundby et al. 1992). Sources of silicate may include river waters and the dissolution of silicate from sand and flint gravel in addition to organic matter (primarily diatom-derived) (Casey and Neal 1986, Conley et al. 1997). In the Baltic, porewater nutrients have been studied by, amongst others, Balzer (1984), Carmam and Rahm (1997), Conley et al. (1997), Sundbäck et al. (1991), and Tuominen et al. (1999). Within the study area, this subject has been addressed by Bolałek et al. (1991), Bolałek (1992, 1993), Bolałek and Graca (1996), Maksymowska-Brosard and Piekarek-Jankowska (2001). However, the area covered by previous studies has been limited to date, and has concentrated primarily on phosphate and ammonia.

The aim of this study was to investigate the spatial (horizontal and vertical) distribution of the nutrients phosphate, ammonia and silicate in porewaters of the eastern part of the southern Baltic sediments. The study covered 24 sampling locations representing various environmental settings (type of sediment, water depth, distance from land, oxygen conditions).

STUDY AREA

The study area was the eastern part of the southern Baltic Sea, and most of the sampling stations were located in the Gdańsk Basin. The area of Gdańsk Basin equals 25 600 km^2 (Ehlin et al. 1974), and the basin consists of the Gdańsk Deep and the Gulf of Gdańsk. The southeastern part of the Gulf of Gdańsk is created by inner and outer Puck Bay (Fig. 1). These regions are separated from the open Baltic by the Hel Peninsula. The study area receives input from the Vistula, Pregola and Niemen rivers, as well as a number of smaller rivers. In the area of the Gulf of Gdańsk, the most important factor affecting hydrological conditions is the Vistula river inflow (Majewski 1994). The water of the Gdańsk Basin is heavily stratified, as is observed for waters throughout the Baltic. Surface waters (down to 40 m) are characterized by the seasonal occurrence of a thermocline (spring, summer): surface salinity and temperature varies seasonally (Cyberska 1990). In the open gulf, salinity varies within a narrow range (7.0 to 7.5), while in the shallow, nearshore areas, which are influenced by river inflows, salinity tends to drop to values lower than 6. At a depth of approximately 70 m, a permanent pycnocline occurs. Below the pycnocline, thermal, salinity and oxygen conditions all depend on the saline water inflows from the North Sea. Larger inflows improve oxygen conditions in deep waters and increase the salinity (up to 13-14). During stagnation, oxygen concentration decreases (even anoxia and hydrogen sulphide occur), and the salinity drops (10) (Majewski 1994). In the study area, a number of different sediments types occur, from muddy sands to silts. Dispersion of the sediments usually increases with increasing depth and distance from land (Emelyanov 2002). The study area is characterised by high primary productivity (190 g C m^{-2} y^{-1}, Renk 1997), and the productive season lasts from March-April to September-October (Latała 1993). In this period a decrease in nutrient concentration in the water column occurs. The study area, especially the Gulf of Gdańsk, is one of the most heavily impacted regions of the Baltic Sea with respect to external nutrient loads (Trzosińska 1994, Witek et al. 2003). The Vistula alone discharges 15% of the total nitrogen (TN) and 19% of total phosphorus (TP) from all land-based sources into the Baltic (HELCOM 1998).

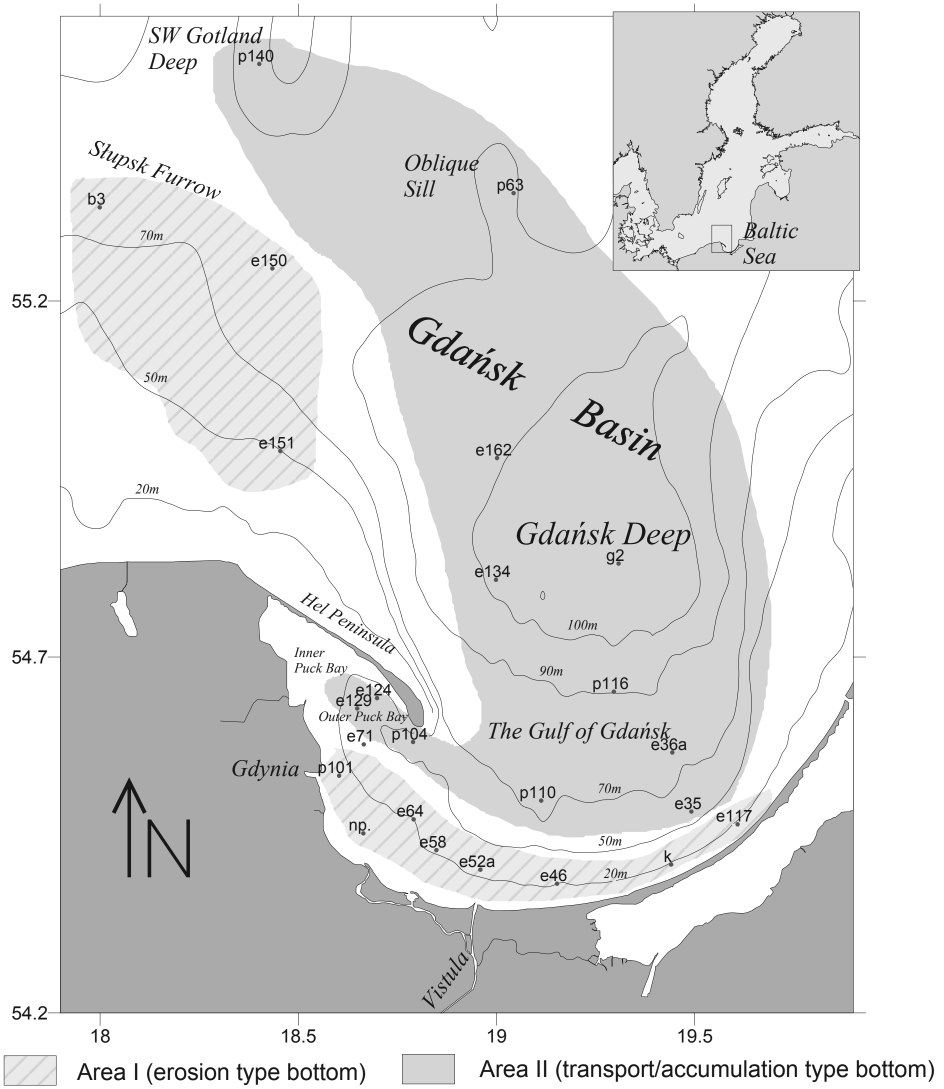

Fig. 1. Location of sampling sites and areas classified with regard to the two bottom types.

Material and Methods

Sediment cores were collected from aboard R/V Baltica at 24 sites in the eastern part of the southern Baltic (Fig. 1) in September 2000 (stations: e117, b3, zn2, p63, p140, e134, p116, p110, p104, p101, np, k, e129, g2, e64, e152a, e46, e36a, e35), March/April 2001 (stations: e117, e150, e151, e162, e52a, e58, e71, g2, k, p110, p104, zn2) and June 2002 (stations: e52a, e64, g2, p110, p63). Nemisto (for muddy) or Reineck (for sandy sediments) samplers were used in sample collection. The surface layer (0-5 cm) of each core was sliced into 1 cm or 2.5 cm thick layers; the 5-15 cm layer was sectioned at 2.5 – 5.0 cm-thick intervals. Porewater was extracted by centrifugation (3500 rpm for 20 min.) and phosphate, ammonia and silicate contents in porewater samples were determined immediately following extraction. Chemical assays were performed using appropriate marine chemistry methods (Grasshoff et al. 1983). Near-bottom water temperature and salinity (Practical Salinity Scale) were measured (CTD sonda) and Winkler titration was performed to determine dissolved O_2 concentration (Strickland and Parsons 1972).

The sediment water content (W% w.w.) was determined by drying sediment samples at 120°C until they reached a constant weight. The loss on ignition (LOI%) was determined after sediment sample combustion (500°C for 8 h). The sediment redox potential was measured with a redox electrode (Eijkelkamp).

Statistical methods

Sampling stations were divided into areas/groups based on cluster analysis (tree clustering, complete linkage). Significance of the differences between separated groups was tested by a U-Mann Whitney test, and differences with p-values lower than 0.05 were considered significant. Statistical analyses were completed using *Statistica 6.0* software.

RESULTS

Characteristics of sediments and porewaters

Two distinct areas were identified in the research region based on the sediment water content (W) and the organic matter content in sediments (LOI) (Fig. 1-2). The division was observed in cluster analysis results, which considered the LOI and the water content in the surface sediment layer (0-5 cm) (Fig. 2). Average W and LOI values for area I did not exceed 50% and 4%, respectively (Fig. 3). This region included the stations located both east and west of the Vistula river mouth down to the 30 m isobath, the slope of Hel Peninsula from the open sea side (station e151) and Słupsk Furrow (e150 and b3). The dominant sediment fractions in the area were sands (Kramarska 1995). In the near-bottom waters, oxygen concentration did not decrease below 3.36 $cm^3\ dm^{-3}$, and in the zone of water depths down to 30 m their temperature varied seasonally (from 17.1°C in September 2000 to 2.9°C in April 2001). The

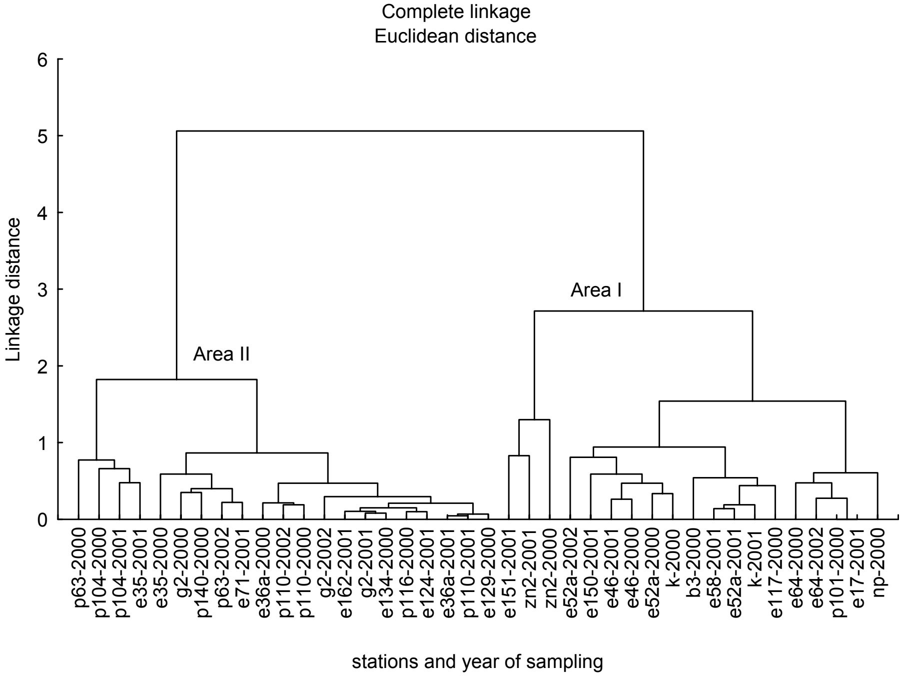

Fig. 2. Cluster dendogram of sampling stations, analyzed according to the sediment water content (W) and organic matter content (LOI).

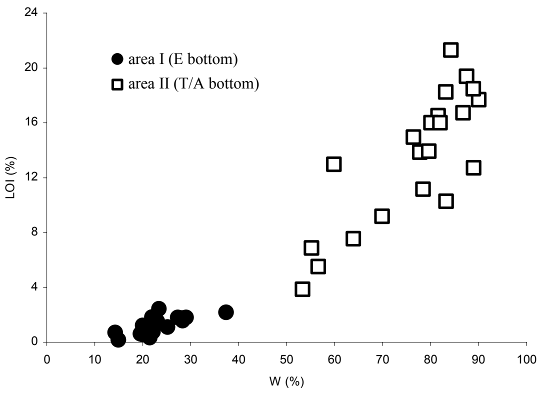

Fig. 3. The relation between sediment water content (W) and organic matter content (LOI).

salinity oscillated around 7, except within Słupsk Furrow, where it varied in range from 11 to 12. In the furrow, minimum oxygen conditions also were observed (3.36-3.47 cm^3 dm^{-3}) and the lowest Eh in the sediments (in the range –64 to 190 mV) was recorded. In the remaining areas, reductive conditions (Eh<100 mV; Boyd 1995) occurred sporadically in only the deeper layers of the sediments.

In area II (Fig. 1) fine

sediments dominated, such as silty-clays and clayey-silts (Kramarska 1995). Area II included Gdańsk Deep (g2, e134, p116, e162) together with its slope (e35, p110, e36a), the slope of Gotland Deep (p140), the Oblique Sill separating Gdańsk Deep from Gotland Deep (p63), and the areas of the outer Puck Bay with water depths greater than 30 m (p104, e124, e129, e71). Average W and LOI in the uppermost 5 cm sediment layer of area II did not decrease below 50% and 4%, respectively (Fig. 3). Relatively low values of these parameters (W<70%, LOI<10%) were observed at stations e71, p104, and periodically e35 (April 2001) as well as at p63 (September 2000). In Gdańsk Deep reducing conditions were encountered in the topmost 1 cm of sediment; on the slopes and in the gulf, reducing conditions were always found deeper than 5 cm below the sediment/water interface and in some cases closer to the sediment surface.

In the near-bottom water of the area in question (area II), temperature was relatively stable (4.4-7.0°C). In September 2000 and June 2001, Gdańsk Deep was anoxic. In April 2001 the Deep and its slope were reached by a saline water inflow from the North Sea. This inflow increased oxygen content in the area of the Deep (to a maximum of 3.34 cm^3 dm^{-3}), and decreased it on the slopes. Hypoxia (O_2<2 cm^3 dm^{-3}) and elevated salinity was recorded at the stations p110, e35 and e36a. At the remaining stations near-bottom waters were oxic.

Nutrients in porewaters

Area I. Concentrations of phosphate in area I (Fig. 1) did not exceed 27.9 μmol dm^{-3}, and 50% of the results were within the range of 1.9 μmol dm^{-3} to 6.9 μmol dm^{-3}. Ammonia and silicate concentrations varied across very broad ranges. They were found at concentrations ranging from 1.0 μmol dm^{-3} to 899.4 μmol dm^{-3} and from 10.0 μmol dm^{-3} to 1621.1 μmol dm^{-3} for ammonia and silicate, respectively. Additionally, 75% of ammonia concentration values did not exceed 129.9 μmol dm^{-3} (upper quartile), and silicate did not exceed 320.9 μmol dm^{-3} (upper quartile). Based on a cluster analysis applied separately for each nutrient, the sampling stations located in area I were divided into groups (Fig. 4-6). Each station was characterized by 2 concentration values – a maximum for the whole sediment core and the actual value in the first (0-1 cm) sediment layer. Differences between distinguished groups were statistically significant (U-Mann Whitney-p<0.05). Phosphate concentrations were low and relatively invariant in group 2, which was dominated by measurements from March/April 2001 (Fig. 4). Higher values and an increase in concentration with depth was recorded for samples in group 3, which included stations e117 (September), np (September) and e150 (April). Highest phosphate concentrations were observed in group 1, for stations located near the Vistula mouth (e52a and zn2) and station e64. High concentrations were characteristic

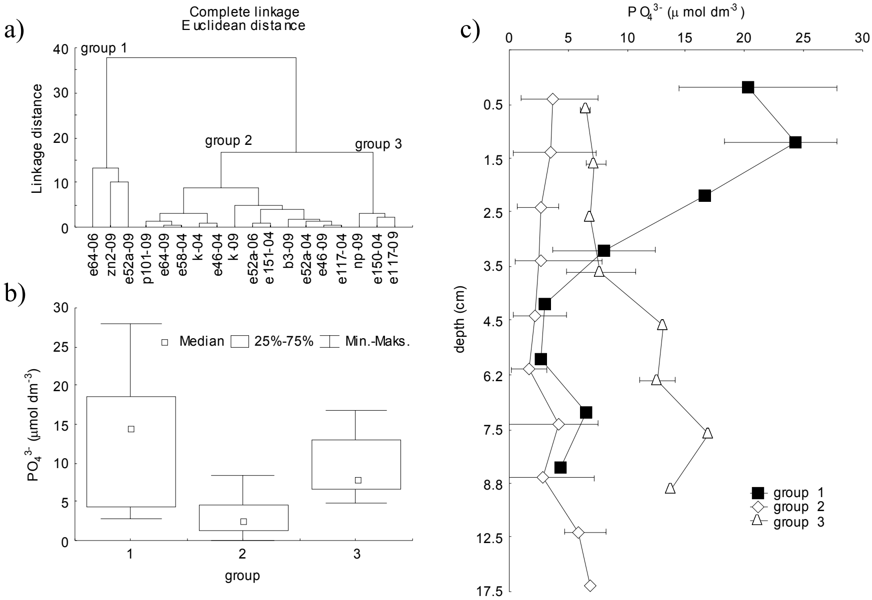

Fig. 4. Porewater phosphate characteristics in area I; a) Cluster dendogram of sampling stations, classification into groups, b) statistical characteristics of distinguished groups, c) concentration profiles in distinguished groups (means and ranges).

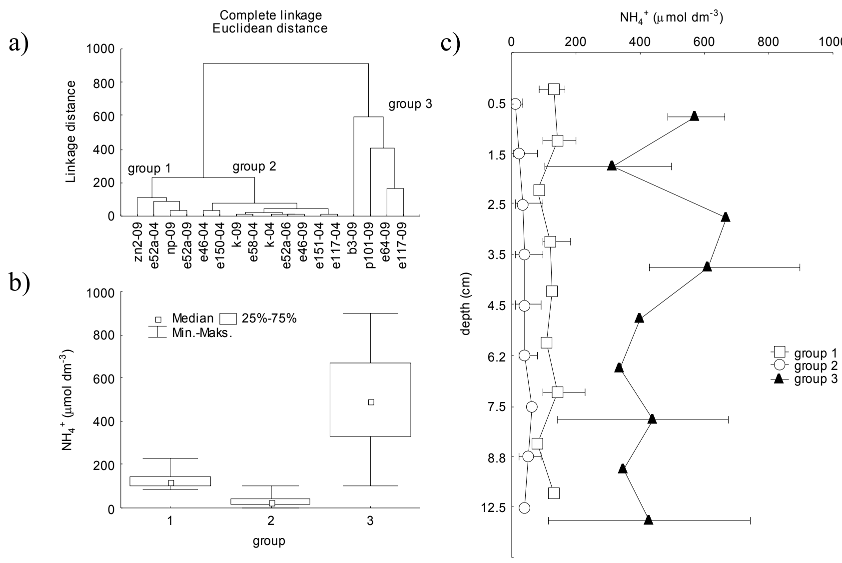

Fig. 5. Porewater ammonia characteristics in area I; a) Cluster dendogram of sampling stations, classification into groups, b) statistical characteristics of distinguished groups, c) concentration profiles in distinguished groups (means and ranges).