

**Seasonal variability
of benthic ammonium
release in the surface
sediments of the
Gulf of Gdańsk
(southern Baltic Sea)***

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Abstract

This paper describes the seasonal and spatial variations of diffusive sediment-water ammonium fluxes in the western part of the Gulf of Gdańsk (southern Baltic). It assesses the potential environmental controls of these fluxes, such as the inflow of organic matter to bottom sediments and its quality, temperature-induced degradation of organic matter, and the redox potential of sediments. Ammonium fluxes, calculated using Fick's first law, were always in the direction from the sediment into the water column and differed significantly with respect to sediment type. Fluxes were most intensive in sediments with the highest silt-clay fraction located in the deepest parts of the study area. The mean annual diffusive fluxes of ammonium from sediments to near-bottom water were estimated at 5.24 tonnes

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$\text{km}^{-2} \text{ year}^{-1}$ for silty-clays, $1.85 \text{ tonnes km}^{-2} \text{ year}^{-1}$ for silty-sands and $1.03 \text{ tonnes km}^{-2} \text{ year}^{-1}$ for sandy sediments. There was a high seasonal variation, with the greatest ammonium release in summer and early autumn, when the temperature of near-bottom water was the highest. On the basis of the calculated diffusive ammonium fluxes, we estimated that approximately 2700 tonnes of N-NH_4^+ are released annually from the surface sediments of the western part of the Gulf of Gdańsk, providing a minimum of 10% of the mineral nitrogen essential for primary production in surface waters. Our results are undoubtedly underestimated, as we disregarded advective ammonium fluxes, which in some areas of the Gulf of Gdańsk could well be comparable to diffusive fluxes.

1. Introduction

Nitrogen cycling in estuarine and coastal marine sediments is of the utmost importance since it influences water-column productivity and eutrophication. In most coastal environments, much of the nitrogen recycled in the sediments is in the form of NH_4^+ (Kemp et al. 1990). Ammonium nitrogen dissolved in interstitial waters usually originates from two important biological processes: deamination of organic matter and excretion by benthic organisms. In aerobic conditions this NH_4^+ can be oxidised to NO_3^- during nitrification, assimilated by microphytobenthos and/or bacteria, and involved in exchange reactions between the adsorbed and pore-water NH_4^+ pool (van der Loeff et al. 1981, Kemp et al. 1990). Concentrations of ammonium nitrogen in the interstitial waters of surface sediments are usually higher than in near-bottom waters. Therefore, available pore-water N-NH_4^+ penetrates from the surface sediments to near-bottom waters, mainly through molecular diffusion. The exchange of dissolved substances across the sediment–water interface is an important process affecting the chemical composition of estuarine and coastal marine environments, where nutrients regenerated in benthic sediments can supply a significant part of the requirements of primary producers in the overlying waters (Nixon et al. 1976, Billen 1978).

In this study we have addressed the question of how sediment–water diffusive fluxes of ammonium vary seasonally and spatially in the western part of the Gulf of Gdańsk, and we have tried to assess the potential environmental controls of these fluxes. We have estimated the annual release of N-NH_4^+ from the sediment due to molecular diffusion and assessed its potential influence on primary production in the Gulf. To the best of our knowledge, this is the first study covering seasonal investigations of ammonium release from the sediments of the Gulf of Gdańsk.

2. Study area

Located in the eastern part of the southern Baltic Sea (Fig. 1), the Gulf of Gdańsk covers an area of 4940 km² and forms the highly eutrophic estuary of Poland's greatest river, the Wisła (Vistula) (Jędrasik et al. 1994). The mean annual flow rate of the Wisła is 1081 m³ s⁻¹ (Niemirycz & Borkowski 1996); during the study period in 1996, it ranged from around 500 m³ s⁻¹ in summer and winter to as much as 3000 m³ s⁻¹ during the spring thaws (Heybowicz & Borkowski 1997). The direction, range and depth of expansion of these riverine water masses are highly variable and depend on the amount of discharged waters and the wind direction (Cyberska 1990). The waters of the Wisła most frequently expand eastwards and north-eastwards.

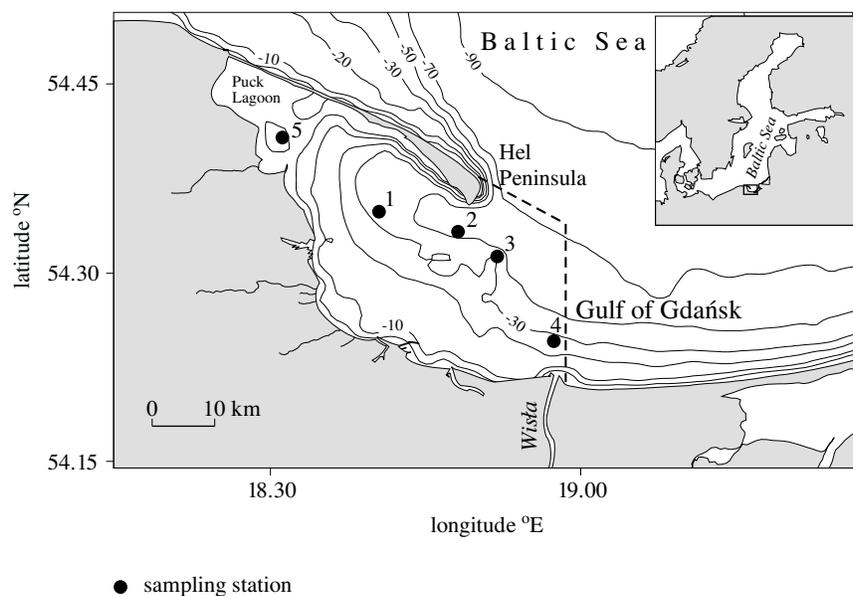


Fig. 1. The Gulf of Gdańsk – location of sampling stations. (The dashed line delimits the area where the annual N-NH₄⁺ release from the sediment was estimated)

The mean depth of the Gulf of Gdańsk is 59 m, reaching a maximum of 118 m in the Gdańsk Deep (Majewski 1994). The westernmost part of the Gulf, the shallow Puck Lagoon, is enclosed by the Hel Peninsula and is isolated from the rest of the Gulf by a sandbank (Fig. 1). The mean depth of Puck Lagoon is 3.1 m, the maximum 5.5 m (Nowacki 1993).

The waters of the Gulf of Gdańsk are characterised by complex temperature and salinity structures. In the surface water layers (down to 40–60 m) the salinity varies seasonally (Cyberska 1990). In the open Gulf, the salinity

remains within the narrow range from 7.0 to 7.5, but in the shallow coastal part of the Gulf, which is influenced by the freshwater discharge of the Wisła, the salinity in spring is often below 6.0.

There are various types of sediments in the Gulf of Gdańsk, from coarse sand to clay. Sediment dispersion usually increases with greater depth and distance from the shore. Sandy sediments predominate near the mouth of the Wisła, down to a depth of 30 m, and in Puck Lagoon. Silty and silty-clay sediments predominate in the deeper parts of the Gulf (Kepińska & Wypych 1990, Jankowska 1993).

3. Material and methods

3.1. Sampling procedures

The study was conducted in 1996 at five sampling stations situated in the western part of the Gulf of Gdańsk (Fig. 1). The choice of sampling stations was subject to the following criteria: distance from the land and the principal sources of terrigenous influence, water depth, types of sediment, and concentrations of organic matter in the sediments. The characteristics of the sampling stations – water depth, sediment type, and concentrations of organic matter (C and N) in the sediments – are presented in Table 1.

Surface sediments and seawater samples were taken monthly, except in June and July, for which, owing to technical difficulties, no complete data are available. During winter, ice cover or bad weather precluded sampling in Puck Lagoon.

Sediments were collected with a Nemistö sediment corer – 10 cm \emptyset cores of silty sediments and 2 cm \emptyset cores of sandy sediments. The five-centimetre-thick surface sediment layer was sliced into 1 cm segments and kept frozen until analysis. The near-bottom water samples were taken approximately 50 cm above the sediment surface using Niskin bottles. Water samples for ammonium concentrations were analysed immediately after sampling. Seawater samples for other measurements were kept frozen until analysis. Water temperature was measured during sampling.

3.2. Analytical procedures

Concentrations of nitrates and nitrites were analysed by the Bend-schneider and Robinson method modified by Grasshoff (1976), ammonium by the indophenol method developed by Koroleff, with the addition of trisodium citrate (*New Baltic Manual* 1972), and dissolved oxygen by Winkler's method (UNEP/IOC/IAEA 1988).

Table 1. Characteristics of sampling stations (values measured in the 0–1 cm layer of sediments; data are presented as mean annual values with standard deviation and number of samples)

Sampling station	Depth of the station [m]	Sediment type	C [mg g ⁻¹]	N [mg g ⁻¹]	C/N _{at}	Eh [mV]
1	37	silt-clay	33.7 ± 2.1 (10)	3.96 ± 0.7 (10)	10.1 ± 1.2 (10)	-43.8 ± 77.9 (10)
2	52	silt-clay	40.7 ± 2.9 (10)	4.82 ± 0.5 (10)	9.4 ± 0.4 (10)	-50.1 ± 105.6 (10)
3	34	fine sand	4.5 ± 1.2 (10)	0.38 ± 0.1 (10)	10.1 ± 1.0 (10)	35.7 ± 64.0 (10)
4	30	fine sand	3.4 ± 1.0 (10)	0.40 ± 0.1 (10)	10.1 ± 0.9 (10)	51.7 ± 91.7 (9)
5	5.5	silty-sand	5.5 ± 2.8 (5)	0.96 ± 0.3 (5)	9.5 ± 0.7 (5)	13.4 ± 8.1 (5)

Interstitial waters were extracted by sediment centrifugation (2000 r.p.m. for 10 min) immediately after sampling. Ammonium concentrations were determined directly after extraction of interstitial water, by the same method as was used for near-bottom waters.

The redox potential (Eh) in bottom sediments was measured immediately after sampling using an automatic Eijkelkamp 18.37 pH/mV/T analyser equipped with a Pt-Ag/AgCl electrode.

Prior to analysis sediments were freeze-dried to avoid losses of organic matter and were decarbonated using 2N HCl. Samples for organic carbon and total nitrogen analysis were then prepared in accordance with the method given by Hedges & Stern (1984). Homogenised sediment samples were subsequently analysed for particulate organic carbon and particulate nitrogen with a Carlo Erba EA CHNS autoanalyser in order to calculate their C/N atomic ratio C/N_{at} . 100 sediment samples were analysed in triplicate so as to estimate the analytical error of the method. Standard error (SE) for both organic carbon and total nitrogen was $\pm 3\%$.

3.3. Flux calculation

The diffusive fluxes of ammonium nitrogen at the sediment–water interface were calculated using Fick’s first law from concentration gradients in the interstitial waters and near-bottom waters (e.g. Billen 1978, Simon 1988, Bolałek & Graca 1996, Feuillet-Girard et al. 1997)

$$J_x = -D_s^{\text{sed}} \Phi_0 (C_{x'} - C_0) x'^{-1}, \quad (1)$$

where

J_x – ammonium flux at depth x [$\mu\text{mol cm}^{-2} \text{s}^{-1}$],

D_s^{sed} – total sediment diffusion coefficient for ammonium [$\text{cm}^2 \text{s}^{-1}$],

Φ_0 – sediment porosity,

$C_{x'}$ – ammonium concentration [$\mu\text{mol dm}^{-3}$] for $x = x'$,

C_0 – ammonium concentration [$\mu\text{mol dm}^{-3}$] for $x = 0$,

x – sediment depth (0.5 cm) (the negative sense towards the sediment).

Values of the total sediment diffusion coefficient for ammonium were calculated using the equation (Krom & Berner 1980)

$$D_s^{\text{sed}} = \frac{D_s^0}{\Phi_0 F'}, \quad (2)$$

where

D_s^0 – water diffusion coefficient at infinite dilution for ammonium [$\text{cm}^2 \text{s}^{-1}$] (Li & Gregory 1974),

Φ_0 – sediment porosity,

F' – the modified Krom & Berner (1980) formation factor, corrected for viscosity and deviation from the Archie relation $F = \Phi^{-2}$ (Manheim 1970),

$$F' = 1.28 \Phi^{-m} \quad (3)$$

$m = 2$ if $\Phi < 0.7$, $m = 3$ if $\Phi > 0.7$.

The temperature of the near-bottom water during the sampling period ranged from 0.5 to 20.5°C. Values of D_s^0 for each sampling month and sampling station were calculated by correcting the diffusivities of NH_4^+ for changes in temperature by using the Stokes–Einstein relation (Li & Gregory 1974).

Sediment porosity was determined with Berner's equation (1971)

$$\Phi = \frac{W \rho_s}{W \rho_s + (1 - W) \rho_w}, \quad (4)$$

where

W – moisture content of sediment,

ρ_s – sediment density,

ρ_w – water density (1.0057 g cm⁻³).

Sediment moisture W was measured as the weight loss following freeze-drying of the sediment to constant weight.

The total sediment diffusion coefficients D_s^{sed} varied from 3.44×10^{-6} cm² s⁻¹ to 9.17×10^{-6} cm² s⁻¹. Mean coefficients were $7.28 \times 10^{-6} \pm 1.14 \times 10^{-6}$ cm² s⁻¹ for silty-clays, $6.16 \times 10^{-6} \pm 1.32 \times 10^{-6}$ cm² s⁻¹ for silty-sands and $4.70 \times 10^{-6} \pm 0.92 \times 10^{-6}$ cm² s⁻¹ for sands. The considerable variability in these coefficients were due to seasonal variations in the temperature of near-bottom waters and to differences in sediment porosity. Coefficients were highest in silty-clay sediments (stations 1 and 2) in summer and early autumn. Such elevated values were due to the high temperature of the near-bottom waters and the substantial porosity of these sediments. Coefficients were lowest for sandy sediments (of poor porosity) in winter, when the near-bottom-water temperatures were the lowest. The total sediment diffusion coefficients used in this study were similar to those used by other authors. For example, Berner (1974) used a diffusion coefficient of 3.5×10^{-6} cm² s⁻¹, while Krom & Berner (1980) used a value of 9.3×10^{-6} cm² s⁻¹ (for sediments of porosity between 0.64 and 0.79 at a water temperature of 20°C).

3.4. Statistical analysis

Since all measurements were performed on randomly selected independent cores, analysis of variance was used to test the homogeneity of ammonium fluxes and of the depth profiles of NH_4^+ concentrations, Eh and the C/N_{at} ratio between the sampling date and station. Variance and correlation analyses at the 95% confidence level were determined using the STATISTICA program (StatSoft Inc. 1993).

4. Results and discussion

4.1. Surface sediment – characteristics of organic matter and redox conditions

The C/N ratio is often used to characterise organic particles, both with regard to organic matter origin and quality (e.g. Bordovskiy 1965, Koop et al. 1990). The C/N_{at} value of fresh planktonic organic matter is close to 6–7, whereas that of terrigenous or highly degraded particulate organic matter (POM) is usually higher than 10 (e.g. Bordovskiy 1965, Roman 1980). In this work, the values of C/N_{at} for organic matter deposited in surface sediments serve as an indicator of the inflow of fresh organic matter to the sediment.

The mean annual values of C/N_{at} in the 1-cm surface sediment layer were similar in all sediment types and in all the areas of the Gulf of Gdańsk studied (Table 1). However, significant monthly variations in these parameters were found ($p < 0.05$). The C/N_{at} ratio varied significantly from 7.9 to 14.4 and its mean value was 10.2. The lowest values, indicative of the inflow of fresh organic material, were recorded in spring and autumn 1996 in the top 1-cm sediment layer (Fig. 2).

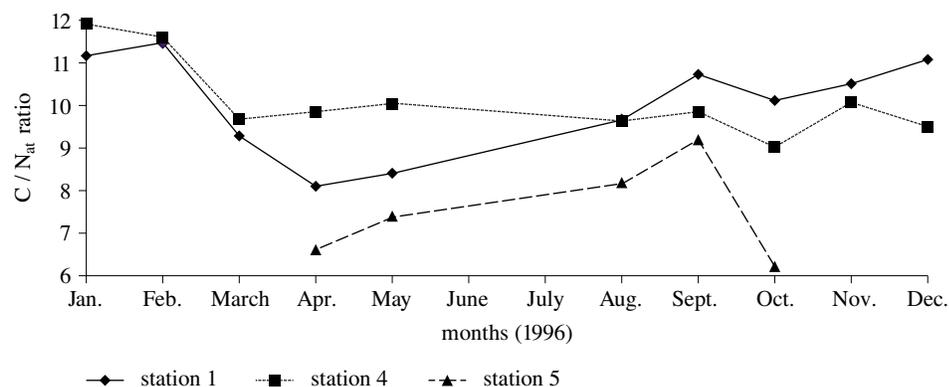


Fig. 2. Seasonal variations in the C/N atomic ratio in sedimentary organic matter deposited in the 0–1 cm layer of surface sediment (station 1 – silty-clays, station 4 – fine sand, and station 5 – silty-sand)

The redox potential (Eh) is one of the most important parameters characterising surface sediments, since it reflects the intensity of organic matter degradation and of bacterial activity, and indicates changes in the oxidation of organic material (Stumm 1978). This results from the fact that the successive redox reactions occurring during the degradation of organic matter proceed within certain Eh values (Stumm 1978). Based on Boyd's (1995) criterion, reducing conditions were usual ($Eh < 100$ mV,

Tables 1 and 2) in the surface sediments of the Gulf of Gdańsk. Similar values had been previously found in the western part of the Gulf (Bolałek & Kowalewska 1997). Eh values differed significantly ($p < 0.05$) between sediment types and sampling stations (from -365 to $+246$ mV; Table 2), indicating that the lithological properties of sediments constitute one of the parameters influencing the conditions of organic matter degradation. Higher Eh values in sandy sediments reflect their better oxygenation with respect to silty-clay sediments.

The seasonal variability in the redox potentials of most of the sediments studied (stations 1, 2, 3, and 4; Table 2) is high ($p < 0.05$): elevated Eh values were recorded mainly at the beginning of the year, before the spring phytoplankton bloom. The better oxygenation of the sediment in this period was probably caused by the absence of labile organic matter deposited from the water column and the presence of highly degraded refractory organic matter in the sediments ($C/N > 10$), which is less susceptible to microbial degradation (Henrichs 1993). Slower degradation lessened the utilisation of oxidants, which resulted in their higher pore-water concentrations and in an increase of Eh. The decrease in the rate of organic matter degradation and the better oxygenation were also induced by the low temperature of the near-bottom waters during this period (Fig. 3a); temperature is one of the principal factors influencing organic matter degradation rates. After the spring bloom (March–April), sediment Eh started to fall (Table 2); this drop was particularly marked in silty-clays (stations 1 and 2). Changes in Eh due to the inflow of organic matter into the sediments were preceded by intensive phytoplankton blooms in surface waters. In sandy sediments (stations 3 and 4), the decrease in Eh did not begin before May, reflecting the depletion of the most effective oxidants of organic matter. This could have been due to the higher potential oxidation capacity of sands as compared to silty-clays, and the considerably lower accumulation of organic matter in sandy sediments. In summer, a further decrease in Eh was noted and was simultaneous with the temperature increase in the near-bottom waters (Fig. 3a; Table 2). Similar changes in Eh, connected with organic matter inflow into the sediment and temperature changes, have been recorded in other coastal areas, e.g. the Mediterranean Sea (Buscail et al. 1995) and the North Sea (Lohse et al. 1996).

In the silty-sands of Puck Lagoon, Eh varied only slightly in comparison with other sediments (from -70 mV to $+51$ mV; Tables 1 and 2). The surface sediments in this area are sites of intensive production of microphytobenthos and macrofauna. The activity of both microphytobenthos and zoobenthos

Table 2. Eh values (mV) in surface sediments of the Gulf of Gdańsk

Station and sediment type	Level [cm]	Eh [mV]									
		January	February	March	April	May	August	September	October	November	December
1 s-c	0-1	61	70	55	-101	-74	-83	-134	-123	-37	-72
	1-2	50	-3	-89	-97	-92	-59	-179	-136	-63	-159
	2-3	40	-28	-78	-110	-88	-82	-259	-131	-121	-189
	3-4	37	-37	-85	-88	-106	-123	-252	-131	-198	-298
	4-5	50	-4	-102	-42	-120	-159	-309	-137	-195	-318
	0-5	47.6	-0.4	-59.8	-86.7	-96.0	-101.2	-226.6	-131.6	-122.8	-207.2
2 s-c	0-1	50	54	49	7	-55	-130	33	-242	-99	-168
	1-2	-30	-297	-89	-101	-86	-160	-127	-217	-167	-152
	2-3	-150	-112	-103	-109	-126	-210	-180	-188	-180	-337
	3-4	-190	-156	-138	-162	-102	-240	-278	-194	-315	-333
	4-5	-120	-142	-186	-203	-163	-300	-317	-212	-338	-365
	0-5	-88.0	-130.6	-93.4	-113.6	-106.4	-208.0	-173.8	-210.6	-219.8	-271.0
3 f.s.	0-1	123	118	113	24	10	-16	-8	-46	64	-25
	1-2	119	106	101	86	12	-16	-25	-148	69	-4
	2-3	134	95	87	73	14	-98	-63	-143	68	-63
	3-4	112	106	76	61	-8	-206	-85	-43	13	-31
	4-5	93	87	51	33	-5	-206	-112	-73	-4	36
	0-5	116.2	102.4	85.6	55.4	4.6	-108.4	-58.6	-90.6	42.0	-17.4

Table 2. (continued)

Station and sediment type	Level [cm]	Eh [mV]									
		January	February	March	April	May	August	September	October	November	December
4	0-1	-20	46	152	246	21	15	26	-53	32	-
f.s.	1-2	-120	21	80	225	25	-18	12	21	68	-
	2-3	197	68	24	233	-36	-110	-26	26	51	-
	3-4	-123	5	74	237	-85	-146	-42	58	90	-
	4-5	30	-81	183	-127	-106	-16	-18	86	68	-
	0-5	-7.2	11.8	102.6	162.8	-36.2	-55.0	-9.6	27.6	61.8	-
5	0-1	-	-	-	1	16	10	20	20	-	-
s-s	1-2	-	-	-	9	17	-12	14	-12	-	-
	2-3	-	-	-	5	9	-8	-50	-31	-	-
	3-4	-	-	-	25	15	-21	-70	-10	-	-
	4-5	-	-	-	51	18	-32	52	-5	-	-
	0-5	-	-	-	18.2	15.0	-12.6	-6.8	-7.6	-	-

Abbreviations: s-c – silty-clay, f.s. – fine sand, s-s – silty-sand.

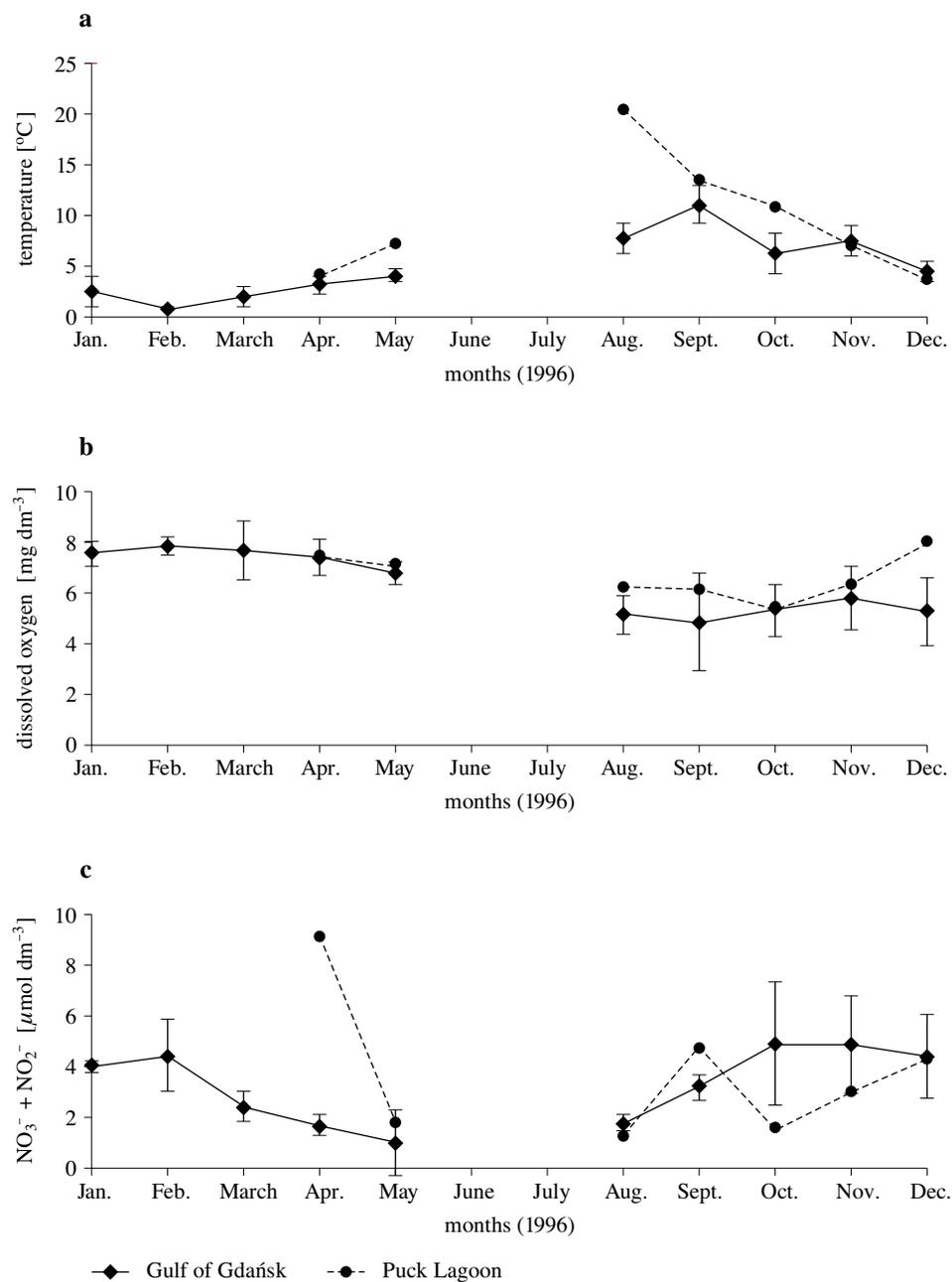


Fig. 3. Seasonal variations in temperature (a), concentrations of dissolved oxygen (b), concentrations of the sum of nitrates and nitrites (c) in the near-bottom waters of the Gulf of Gdańsk. (The data for the open Gulf of Gdańsk are represented by mean values from stations 1, 2, 3 and 4 with standard deviation; the data for Puck Lagoon are represented by the values from station 5)

increase oxygen concentrations in sediments. The phytobenthos does so through oxygen production, the zoobenthos through bioturbation and irrigation, which facilitates the transport of oxidants into the deeper sediment layers (Henrichs 1993) and stabilises Eh in surface sediments.

4.2. Ammonium in interstitial waters – seasonal changes

High variations of ammonium concentrations in interstitial waters were influenced by sediment type and sampling station ($p < 0.05$). Low concentrations of NH_4^+ were recorded in sediments with a large sand fraction located in shallow areas of the Gulf (Fig. 4; Table 3).

In anoxic layers of bottom sediments the production of ammonium is stoichiometrically related to the consumption of organic matter and the utilisation of anaerobic oxidants, thus, N-NH_4^+ concentrations increase exponentially with sediment depth (Berner 1974, Christensen et al. 1988). However, during winter in all of the sediments investigated and during all the sampling periods in the sediments of Puck Lagoon (station 5), pore-water ammonium profiles displayed a slightly rising gradient (Fig. 4). Such a profile shape suggests a zone of net ammonium consumption. Several biological processes could be responsible for this consumption: nitrification, ammonium consumption by benthic algae, assimilation by bacteria of nitrogen-poor organic material (with C/N between 10 and 20) (Fenchel & Blackburn 1979). In sediments from the deeper (>15 m) part of the Gulf (stations 1–4) consumption of N-NH_4^+ by phytobenthos is unlikely because the light necessary for primary production is lacking. In these sediments in winter, all of the other processes could be responsible for N-NH_4^+ consumption. In contrast, in the Puck Lagoon sediments (station 5), which are colonised by microphytobenthos (Witkowski 1993), similar N-NH_4^+ concentrations in the surface 5-cm sediment layer could also be influenced by the consumption of N-NH_4^+ by benthic algae. However, on the basis of our data it is not known which of these processes plays the most important role.

The increase in ammonium concentration within the sediment profile during the growing season (April–October) was due to intensifying degradation of organic matter; this was also reflected in a decrease in Eh (Fig. 4; Table 2). The increase in N-NH_4^+ concentrations could also be partially due to the diminishing role of nitrification (microbial oxidation of ammonium), because this process is limited by oxygen concentrations (Kaplan 1983), and usually proceeds only in the top few millimetres of surface sediments. It has been shown that at $\text{Eh} = -100$ mV nitrification is much reduced, while when Eh is about -200 mV, it is totally inhibited (Kemp et al. 1990). Nitrification is also inhibited by the presence of hydrogen sulphide

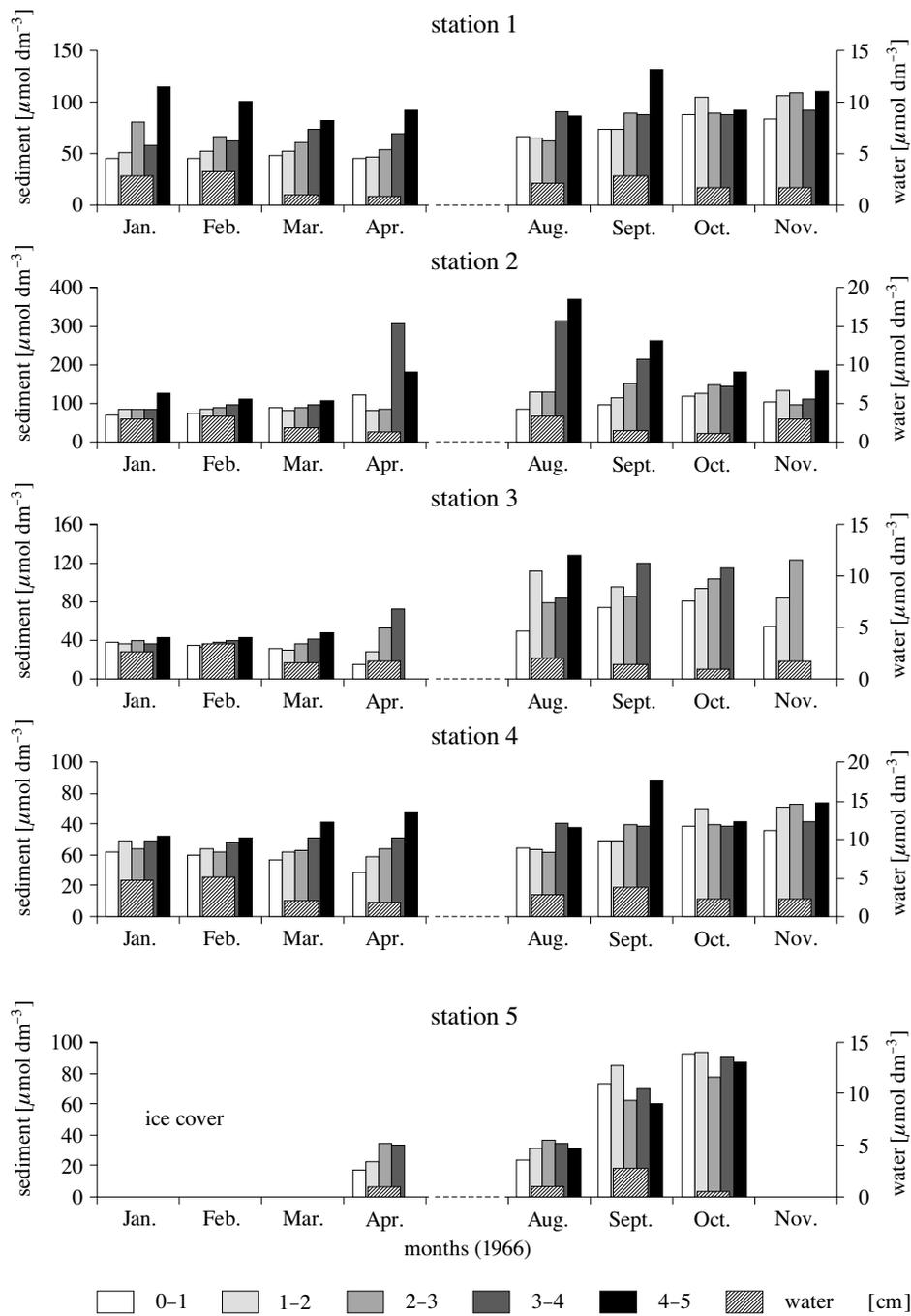


Fig. 4. Seasonal variations in the concentration of ammonium nitrogen in near-bottom waters and interstitial waters (0–5 cm levels) in the Gulf of Gdańsk (stations 1–5)

Table 3. Characteristics of near-bottom waters and interstitial waters (data are presented as mean annual values with standard deviation and numbers of samples)

Sampling station	Bottom-water temperature [°C]	O ₂ bottom water [mg dm ⁻³]	NO ₃ ⁻ + NO ₂ ⁻ bottom water [μmol dm ⁻³]	NH ₄ ⁺ bottom water [μmol dm ⁻³]	NH ₄ ⁺ (0–5 cm) pore waters [μmol dm ⁻³]	Diffusive NH ₄ ⁺ fluxes [μmol m ⁻² day ⁻¹]
1	5.1 ± 3.8 (10)	6.9 ± 1.4 (10)	2.2 ± 1.0 (10)	2.1 ± 0.9 (10)	77.1 ± 22.1 (40)	767 ± 333 (10)
2	4.6 ± 2.0 (10)	5.1 ± 2.1 (10)	2.4 ± 1.0 (10)	2.3 ± 1.0 (10)	134 ± 70.1 (40)	1286 ± 457 (10)
3	4.8 ± 3.5 (10)	6.5 ± 1.4 (10)	2.5 ± 1.3 (10)	1.9 ± 0.7 (10)	62.9 ± 32.3 (40)	201 ± 111 (10)
4	4.9 ± 3.2 (10)	6.6 ± 1.1 (10)	3.2 ± 2.0 (10)	2.9 ± 1.4 (10)	53.4 ± 15.2 (40)	204 ± 101 (10)
5	9.6 ± 5.9 (7)	6.3 ± 1.2 (7)	3.2 ± 2.7 (7)	1.2 ± 1.0 (7)	55.6 ± 27.2 (20)	362 ± 264 (7)

in interstitial waters. According to Henriksen & Kemp (1988), hydrogen sulphide concentrations of 0.01–1.0 mmol dm⁻³ are sufficient to inhibit nitrification in sediments. In the surface sediments of the deepest area investigated (station 2), nitrification was unlikely to occur because Eh was usually lower than -100 mV (Tables 1 and 2), and hydrogen sulphide was present here during the whole year in amounts higher than 0.01 mmol dm⁻³ (Janas 1998). The statistically significant negative correlation ($p < 0.05$) between Eh and pore water NH₄⁺ confirms the lack of nitrification in these sediments. In anoxic sediments, where NH₄⁺ is not consumed, the decrease in Eh accompanies NH₄⁺ concentration increases (Berner 1974, Christensen et al. 1988). Nitrification may occur here, but only in the superficial sediment layer in periods of low organic matter accumulation and high oxygen concentrations in near-bottom waters (at the beginning of the year – Fig. 3b). This is indicated by a slight increase in pore water NH₄⁺ concentrations with sediment depth, the highest values of Eh, and the highest nitrate concentrations in near-bottom waters, which could to some extent be due to their inflow from sediments (Figs. 3c, 4; Table 2).

In the silty-clays of shallower areas (station 1) nitrification could be more important in the surface sediment layer because Eh values are generally higher than -100 mV (Tables 1 and 2), hydrogen sulphide is absent (Janas 1998), and there is no correlation ($p > 0.05$) between Eh and pore water ammonium concentrations (data not shown). In sands and silty-sands (stations 3, 4, 5) N-NH₄⁺ concentrations were considerably lower and Eh values were higher than in silty-clays (Fig. 4, Table 2) and could indicate active nitrification in the superficial sediment layers.

4.3. Diffusive benthic ammonium fluxes

In this work we estimated benthic ammonium fluxes proceeding only by molecular diffusion. Molecular diffusion within interstitial waters is of fundamental importance in effecting the exchange of dissolved constituents across the sediment–water interface, although mass balance calculations and *in situ* benthic flux measurements have shown that other processes enhance the flow of dissolved nitrogen at the sediment–water interface. These processes include physical mixing of sediments by currents and benthic biota, irrigation and bioturbation of sediments by the macrobenthos, and transport through bubble tubes; disregarding them leads to the underestimation of benthic fluxes (Klump & Martens 1981, Callender & Hammond 1982). Callender & Hammond (1982) showed that these processes could increase the nutrient flux even twenty fold, although opinions concerning dissimilarities between the real and diffusive (estimated from concentration gradients) ammonium fluxes differ considerably. According to some of the research results, advective

fluxes in the coastal zone (connected with the transport of dissolved constituents by water and sediment transport induced by organisms) are almost as important as diffusive fluxes, and therefore, fluxes calculated on the basis of Fick's law are seriously underestimated (Klump & Martens 1981, Callender & Hammond 1982). However, other authors have shown that in the case of ammonium the main process responsible for the flow at the sediment–water interface is molecular diffusion (McCaffrey et al. 1980, Bolalek & Graca 1996). Bolalek & Graca (1996) showed that in the western part of the Gulf of Gdańsk, calculations of ammonium fluxes based on concentration gradients and *in situ* ammonium fluxes measured using benthic chambers yield similar results. Bearing the conclusions of all these authors in mind, we estimated the diffusive ammonium fluxes on the assumption that they approximately reflect the real fluxes at the sediment–water interface of the Gulf of Gdańsk.

Diffusive ammonium fluxes in the Gulf of Gdańsk always moved in the direction from the sediment into the water column and were significantly different in relation to sampling station and sediment type ($p < 0.05$).

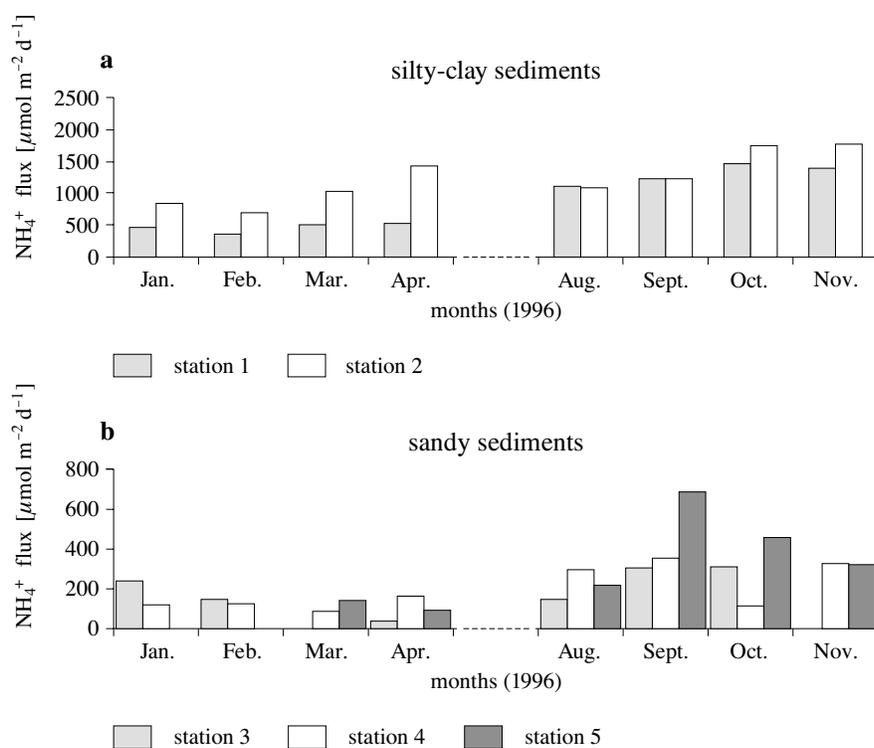


Fig. 5. Seasonal variations in benthic diffusive fluxes of ammonium-nitrogen: silty-clay sediments (a), sandy sediments (b)

Their values were highest (mean: $1286 \mu\text{mol m}^{-2} \text{d}^{-1}$) in sediment with the largest silty-clay fraction (station 2; Fig. 5, Table 3). NH_4^+ release intensified in all sediments simultaneously as the temperature of the near-bottom waters increased ($p < 0.05$; Fig. 6). Values were highest from August to October. This could have been the result of intensified ammonification and nitrate reduction during the increase in temperature of the near-bottom waters (Terry & Nelson 1975). In other areas of the world ocean, as in the Gulf of Gdańsk, the highest ammonium fluxes were most often found in summer, during the warmest periods (e.g. Seitzinger 1987, Simon 1988, Kemp et al. 1990, Lerat et al. 1990). Moreover, in the silty-clay sediments of the Gulf, there was a strong negative correlation ($p < 0.05$) between ammonium fluxes and dissolved oxygen concentration in the near-bottom waters (Fig. 7). It seems, therefore, that elevated ammonium release may not only indicate intensifying ammonification of organic matter in the sediments, but may also reflect the less important role of nitrification, which results from a decreasing oxygen concentration. This has been already mentioned by Kemp and co-workers (1990), who found a strong negative correlation between the temperature of near-bottom waters and the nitrification rate in surface sediments. This is due to the general decrease in oxygen concentration, essential for the maintenance of nitrification, with increasing temperature.

Generally low NH_4^+ concentrations and low values of ammonium fluxes from sandy sediments in the Gulf of Gdańsk may suggest that the part played by ammonification in this type of sediments is negligible. However, low ammonium concentrations and fluxes may have been caused by the fact that part of the NH_4^+ produced in sandy sediments was immediately oxidised to nitrates during nitrification. It has been already emphasised (Rosenfeld 1979, Canfield et al. 1993) that even if ammonium concentrations are low, ammonification and nitrate reduction are relatively intense in sandy sediments.

We estimated the annual release of ammonium nitrogen from the sediments of the western part of the Gulf of Gdańsk. For the purposes of this research, the western part of the Gulf (approximately 20% of the whole area of the Gulf of Gdańsk) was the area delineated in the north by the Hel Peninsula as far east as the 19°E meridian, which is the eastern border of this area (Fig. 1). Estimates were made on the assumption (i) that the mean annual ammonium flux is $5.24 \text{ tonnes km}^{-2} \text{ y}^{-1}$ from silty-clays, $1.85 \text{ tonnes km}^{-2} \text{ y}^{-1}$ from silty-sands and $1.03 \text{ tonnes km}^{-2} \text{ y}^{-1}$ from sandy sediments (this study), and (ii) that the bottom of this part of the Gulf is

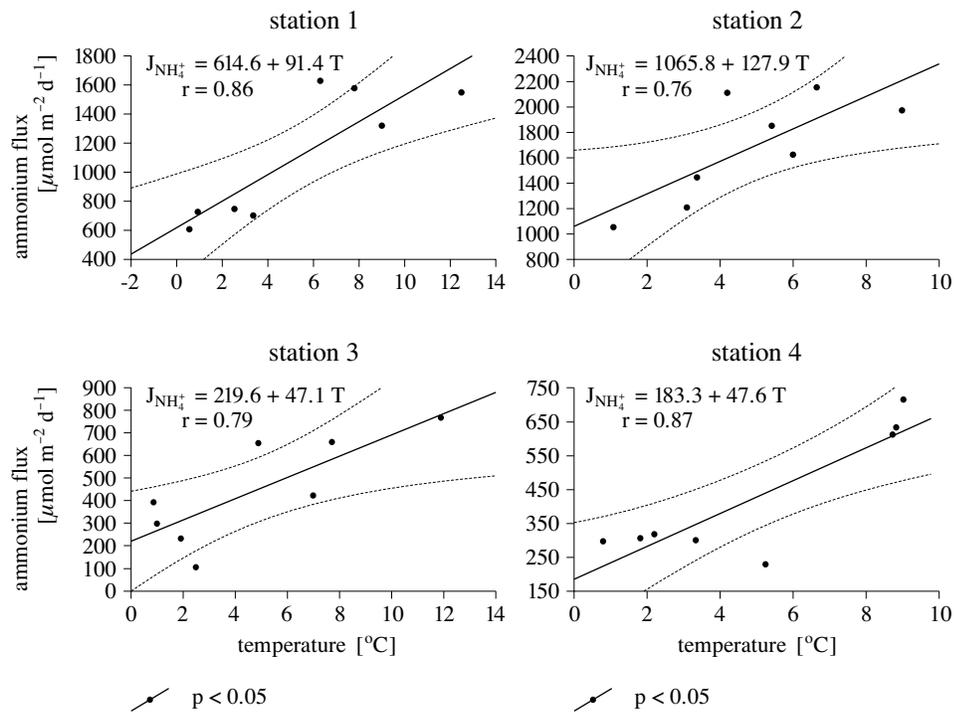


Fig. 6. Correlation between the temperature of near-bottom waters and benthic diffusive fluxes of N-NH_4^+ [$\mu\text{mol m}^{-2} \text{d}^{-1}$] at particular sampling stations 1–4 ($p < 0.05$)

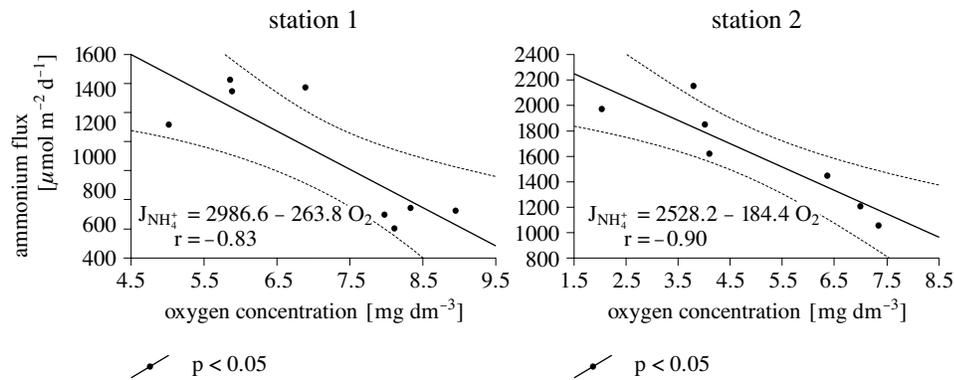


Fig. 7. Correlation between oxygen concentration [mg dm^{-3}] in near-bottom waters and benthic diffusive fluxes of N-NH_4^+ [$\mu\text{mol m}^{-2} \text{d}^{-1}$] at particular sampling stations 1–2 ($p < 0.05$)

covered with the above-mentioned sediments in the respective proportions: 38.8, 5.4 and 55.8% (Szczepańska & Uścińowicz 1994). We estimated that 2681 tonnes of N-NH_4^+ are released annually from the sediments of the investigated area.

In order to determine the influence of remineralised N-NH_4^+ inflow on phytoplanktonic primary production in the western part of the Gulf of Gdańsk, we compared the magnitude of ammonium release with the inorganic nitrogen demand of phytoplankton. Assuming that (i) primary production in the Gulf of Gdańsk is $190 \text{ gC m}^{-2} \text{ y}^{-1}$ (Renk 1997), (ii) the mean N-NH_4^+ flux from sediments is estimated at $2.71 \text{ gN m}^{-2} \text{ y}^{-1}$ (this study), and (iii) C:N:P is assimilated by phytoplankton in a ratio of 106:16:1 (Redfield et al. 1963), we calculated that regenerated benthic ammonium is responsible for approximately 9.5% of primary production in the western part of the Gulf. According to our estimates, the inflow of remineralised ammonium-nitrogen from surface sediments is an important component of the total inorganic nitrogen flow to the western part of the Gulf of Gdańsk, which is further assimilated during primary production. In the whole Gulf of Gdańsk this contribution should be greater owing to the higher participation of silty-clay sediments, which produce the largest quantity of ammonium. It should be pointed out that our results are certainly underestimated as we disregarded advective ammonium fluxes, caused mostly by irrigation and bioturbation of surface sediments by macrofauna, as well as by mechanical disturbance of the sediment structure (resuspension). Their magnitude could well be comparable to diffusive fluxes (Klump & Martens 1981, Callender & Hammond 1982, Morin & Morse 1999).

5. Conclusions

The mean annual diffusive fluxes of ammonium nitrogen from the sediments of the western part of the Gulf of Gdańsk to the near-bottom water was estimated at $5.24 \text{ tonnes km}^{-2} \text{ y}^{-1}$ for silty-clays, $1.85 \text{ tonnes km}^{-2} \text{ y}^{-1}$ for silty-sands and $1.03 \text{ tonnes km}^{-2} \text{ y}^{-1}$ for sandy sediments. Ammonium fluxes underwent considerable seasonal variation, the greatest values being recorded in summer and early autumn, when the temperature of the near-bottom water was the highest. On the basis of these estimates, 2681 tonnes of ammonium nitrogen is released annually from the sediments of the western part of the Gulf of Gdańsk.

We have demonstrated that the surface sediments of the western part of Gulf of Gdańsk are an important source of ammonium nitrogen for the water column, providing a minimum of 10% of the nitrogen salts essential for primary production. However, in order to balance the nitrogen cycle in the

Gulf of Gdańsk, it is necessary to have accurate quantitative calculations of the nitrogen transformation processes in the sediments, with special regard to ammonification, nitrification and denitrification.

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References

- Berner R. A., 1971, *Principles of chemical sedimentology*, McGraw-Hill Book Comp., New York-St. Louis-San Francisco-Toronto-London-Sydney, 245 pp.
- Berner R. A., 1974, *Kinetic models for the early diagenesis of nitrogen, sulfur, phosphorus, and silicon in anoxic marine sediments*, [in:] *The sea*, E. D. Goldberg (ed.), Wiley, New York, 427-450.
- Billen G., 1978, *A budget of nitrogen recycling in North Sea sediments off the Belgian coast*, *Estuar. Coast. Mar. Sci.*, 7, 127-146.
- Bolałek J., Graca B., 1996, *Ammonium nitrogen at the water-sediment interface in Puck Bay (Baltic Sea)*, *Estuar. Coast. Shelf Sci.*, 43, 767-779.
- Bolałek J., Kowalewska M., 1997, *Oxidation conditions in the bottom sediments of Puck Bay*, *Oceanol. Stud.*, 2/3, 117-126.
- Bordovskiy O. K., 1965, *Accumulation and transformation of organic substances in marine sediment*, *Mar. Geol.*, 3, 3-114.
- Boyd C. E., 1995, *Bottom soils, sediment, and pond aquaculture*, Chapman & Hall, New York, 368 pp.
- Buscaïl R., Pocklington R., Germain C., 1995, *Seasonal variability of the organic matter in a sedimentary coastal environment: sources, degradation and accumulation (continental shelf of the Gulf of Lions - Northwestern Mediterranean Sea)*, *Cont. Shelf Res.*, 15, 843-869.
- Callender E., Hammond D. E., 1982, *Nutrient exchange across the sediment-water interface in the Potomac River Estuary*, *Estuar. Coast. Shelf Sci.*, 15, 395-413.
- Canfield D. E., Thamdrup B., Hansen J. W., 1993, *The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction*, *Geochim. Cosmochim. Acta*, 57, 3867-3883.
- Christensen J. P., Smethie W. M., Devol A. H., 1988, *Benthic nutrient regeneration and denitrification on the Washington continental shelf*, *Deep-Sea Res.*, 34, 1027-1047.
- Cyberska B., 1990, *Salinity of waters in the Gdańsk Basin*, [in:] *The Gulf of Gdańsk*, A. Majewski (ed.), Wyd. Geol., Warszawa, 237-255, (in Polish).
- Fenchel T., Blackburn T. H., 1979, *Bacteria and mineral cycling*, Acad. Press, New York-London, 225 pp.

- Feuillet-Girard M., Gouleau D., Blanchard G., Joassard L., 1997, *Nutrient fluxes on an intertidal mudflat in Marennes-Oléron Bay, and influence of the emersion period*, *Aquat. Liv. Resour.*, 10, 49–58.
- Grasshoff K., 1976, *Methods of seawater analysis*, Verlag Chem., Weinheim, 103 pp.
- Hedges J.I., Stern J.H., 1984, *Carbon and nitrogen determinations of carbonate containing solids*, *Limnol. Oceanogr.*, 29, 657–663.
- Henrichs S.M., 1993, *Early diagenesis of organic matter: the dynamics (rates) of cycling of organic compounds*, [in:] *Organic geochemistry, principles and applications*, M.H. Engel & S.A. Macko (eds.), Plenum Press, New York–London, 101–118.
- Henriksen K., Kemp W.M., 1988, *Nitrification in estuarine and coastal marine sediments*, [in:] *Nitrogen cycling in coastal marine environments*, T.H. Blackburn & J. Sorensen (eds.), Proc. SCOPE Symp. Univ. Aarhus, 3–7 June 1985, Wiley & Sons, Chichester, 207–243.
- Heybowicz E., Borkowski T., 1997, *The characteristic of water quality*, [in:] *Environmental conditions in the Polish coastal zone of the Southern Baltic Sea in 1996*, B. Cyberska, A. Trzosińska & Z. Lauer (eds.), Mater. Oddz. Mor. Inst. Meteor. i Gosp. Wod., Gdynia, 65–177, (in Polish).
- Janas U., 1998, *Effect of oxygen deficiency and presence of hydrogen sulfide on macrozoobenthos of the Gulf of Gdańsk*, Ph.D. thesis, Inst. Oceanogr., Uniw. Gdańsk, Gdynia, 158 pp., (in Polish).
- Jankowska H., 1993, *The bottom deposits of Puck Bay*, *Stud. i Mater. Oceanol.*, 64, 163–171.
- Jędrasik J., Kowalewski M., Ołdakowski B., 1994, *Transport of nutrients in Gdańsk Bay*, Proc. Int. Congr.: Baltic Sea and Mediterranean Sea, a comparative ecological approach of coastal and pelagic ecosystems, Montpellier (France).
- Kaplan W.A., 1983, *Nitrification*, [in:] *Nitrogen in the marine environment*, E.J. Carpenter & D.G. Capone (eds.), Acad. Press, New York–London, 139–190.
- Kemp W.M., Sampou P., Caffrey J., Mayer M., Henriksen K., Boynton W.R., 1990, *Ammonium recycling versus denitrification in Chesapeake Bay sediments*, *Limnol. Oceanogr.*, 35, 1545–1563.
- Kępińska U., Wypych K., 1990, *Bottom sediments*, [in:] *The Gulf of Gdańsk*, A. Majewski (ed.), Wyd. Geol., Warszawa, 55–65, (in Polish).
- Klump J.V., Martens C.S., 1981, *Biogeochemical cycling in an organic rich coastal marine basin – II. Nutrient sediment–water exchange processes*, *Geochim. Cosmochim. Acta.*, 45, 101–121.
- Koop K., Boynton W.R., Wulff F., Carman R., 1990, *Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea*, *Mar. Ecol. Prog. Ser.*, 63, 65–77.
- Krom M.D., Berner R.A., 1980, *The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments*, *Limnol. Oceanogr.*, 25, 327–337.

- Lerat Y., Lasserre P., le Corre P., 1990, *Seasonal changes in pore water concentrations of nutrients and their diffusive fluxes at the sediment-water interface*, J. Exp. Mar. Biol. Ecol., 135, 135–160.
- Li Y-H., Gregory S., 1974, *Diffusion of ions in sea water and in deep-sea sediments*, Geochim. Cosmochim. Acta., 38, 703–714.
- Loeff van der M.M., Van Es F.B., Helder W., De Vries R.T.P., 1981, *Sediment-water exchanges of nutrients and oxygen on tidal flats in the Ems-Dollar Estuary*, Neth. J. Sea Res., 15, 113–129.
- Lohse L., Epping E.H.G., Helder W., van Raaphorst W., 1996, *Oxygen pore water profiles in continental shelf sediments of the North Sea: turbulent versus molecular diffusion*, Mar. Ecol. Prog. Ser., 145, 63–75.
- Majewski A., 1994, *Natural environmental conditions of the Gulf of Gdańsk and its coastline*, [in:] *The pollution and renewal of the Gulf of Gdańsk*, J. Błażejowski & D. Schuller (eds.), Mater. Seminar. – Gdynia 1991, Wyd. Uniw. Gdańsk, Gdynia, 22–35, (in Polish).
- Manheim F.T., 1970, *The diffusion of ions in unconsolidated sediments*, Earth Planet. Sci. Lett., 9, 307–309.
- McCaffrey R.J., Myers A.C., Davey E., Morrison G., Bender M., Luedtke N., Cullen D., Froelich P., Klinkhammer G., 1980, *The relation between pore water chemistry and benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island*, Limnol. Oceanogr., 25, 31–44.
- Morin J., Morse J.W., 1999, *Ammonium release from resuspended sediments in the Laguna Madre Estuary*, Mar. Chem., 65, 97–110.
- New Baltic Manual*, 1972, Cooper. Res. Rep., Ser. A (29).
- Niemirycz E., Borkowski T., 1996, *Characteristics of water quality*, [in:] *Environmental conditions in the Polish zone of the Southern Baltic Sea in 1995*, B. Cyberska, Z. Lauer & A. Trzosińska (eds.), Mater. Oddz. Mor. Inst. Meteor. i Gosp. Wod., Gdynia, 173–184, (in Polish).
- Nixon W.S., Oviat C.A., Garber J., Lee V., 1976, *Diel metabolism and nutrient dynamics in a salt marsh embayment*, Ecology, 57, 740–750.
- Nowacki J., 1993, *Morphometry of the Bay*, [in:] *The Puck Bay*, K. Korzeniewski (ed.), Fund. Rozw. Uniw. Gdańsk, Gdańsk, 71–78, (in Polish).
- Redfield A.C., Ketchum B.H., Richard F.A., 1963, *The influence of organisms on the composition of the sea water*, [in:] *The Sea*, M.N. Hill (ed.), Wiley, New York, 2, 26–49.
- Renk H., 1997, *Primary production of the Gulf of Gdańsk*, Wyd. Uniw. Gdańsk, Gdańsk, 102 pp., (in Polish, summary in English).
- Roman M.R., 1980, *Tidal resuspension in Buzzards Bay, Massachusetts. III. Seasonal cycle of nitrogen and carbon: nitrogen ratios in the seston and zooplankton*, Estuar. Coast. Sci., 11, 9–16.
- Rosenfeld J.K., 1979, *Ammonium adsorption in near-shore anoxic sediments*, Limnol. Oceanogr., 24, 356–364.

- Seitzinger S.P., 1987, *Nitrogen biogeochemistry in an unpolluted estuary: the importance of benthic denitrification*, Mar. Ecol. Prog. Ser., 41, 177–186.
- Simon N.S., 1988, *Nitrogen cycling between sediment and the shallow-water column in the transition zone of the Potomac river and estuary. I. Nitrate and ammonium fluxes*, Estuar. Coast. Shelf Sci., 26, 483–497.
- Stumm W., 1978, *What is the pε of the sea?*, Thalassia Jugosl., 14 (1/2), 197–208.
- Szczepańska T., Uścińowicz S., 1994, *Geochemical atlas of the southern Baltic*, Polish Geol. Inst., Sopot–Warszawa, (in Polish).
- Terry R.E., Nelson D.W., 1975, *Factors influencing nitrate transformation in sediments*, J. Environm. Qual., 4, 549–554.
- UNEP/IOC/IAEA, 1988, *Standard chemical methods for marine environmental monitoring. Reference methods for marine pollution studies*, Nairobi–Monaco, 50, 50 pp.
- Witkowski A., 1993, *Microphytobenthos*, [in:] *The Puck Bay*, K. Korzeniewski (ed.), Fund. Rozw. Uniw. Gdańsk, Gdańsk, 181–206, (in Polish).