The distribution of nitrogen ions in the pore and the overlying bottom waters in three important regions of Abu-Kir Bay, Alexandria, Egypt

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Abstract

This study aimed to access the concentration of N-ions (NO_2^-, NO_3^-, NH_4^+, DIN, DON and DTN) in sediment pore waters as well as in the corresponding overlying bottom waters, to see if the former is more or less enriched with these ions compared with those in the overlying waters in three important regions in Abu-Kir Bay (Tabia, Maadia and Rosetta regions). The data revealed that, the concentrations of N-ions in the pore water of grab sediments are higher than that in the overlying bottom water. The percentage of NO_3^- to DIN in pore water is greater than that of NO_2^- and much lower of $NH_4^{+.}$. In the overlying bottom water, the percentage of NH_4^+ > NO_3^->> NO_2^- in Tabia and Maadia regions, but in Rosette region NO_3^- > NH_4^+ >> NO_2^- referring that the role of reduction in the bottom water is greater than that of nitrification and less than that in the corresponding pore water, but in the bottom of Rosetta region the reverse was observed. The net diffusion flux of DIN is generally directed towards the overlying bottom water and mainly due to NH_4^+ where it represents 94.9, 95.7 and 93.6 % of DIN in Tabia , Maadia and Rosetta regions, respectively.

Key words: Nitrogen ions, Pore water, diffusion flux, bottom water, Abu-Kir Bay.

1. Introduction

Pore water plays an important role as a medium for chemical exchange between sediments and the overlying water and can help assess a number of important environmental concerns including: the redox state (oxic-suboxic-anoxic) in estuarine sediments, storage of nutrients and potentially toxic species and their release to the overlying water, reactions which control mineral formation in sediments, the chemical environment in contact with benthic ecosystems and oxidation or decomposition of organic matter (Goldhaber et al., 1977) . In coastal and continental shelf areas, sediments have been demonstrated to supply from 10% to > 100% of the nitrogen required for phytoplankton production in the overlying water (Wetzel, 1983). The release of nutrients from sediments is largely regulated by the rates at which organic detritus reaches the sediments, the rates at which this detritus is decomposed (mainly by bacteria), and the rates at which nutrients released to pore waters are transported to the overlying water by diffusion and bioturbation (Goldhaber et al., 1977). The present study aims to estimate the concentration of N-ions in the sediment pore waters as well as in the corresponding overlying bottom waters, to see if the former is more or less enriched with these ions compared with those in the overlying waters in three important regions in Abu-Kir Bay.

2. Materials and methods

2.1 study Area

Abu-Kir Bay (Fig. 1) is one of the Mediterranean coastal bays. It is a shallow semi-circular (mean depth 12m), and lies between longitudes 30˚ 5¯ and 30˚ 22¯ E and latitudes 31˚ 20¯ and 31˚ 29¯ N. The area of the bay is about 360 km^2 with a shoreline of about 50 km long (EL-Rayis and Faragallah, 2010). This bay receives a continuous runoff (totally of about 5 million m^3/d) mainly from three land-based sources (Fig. 1), namely from west to east Tabia pumping station (mainly industrial and agriculture waste waters), Maadia outlet (mainly agriculture water) and Rosetta mouth (mainly river Nile water mixed with agricultural drainage water). The bay is one of the major spawning, nursery and fishing grounds of the Egyptian Mediterranean waters.

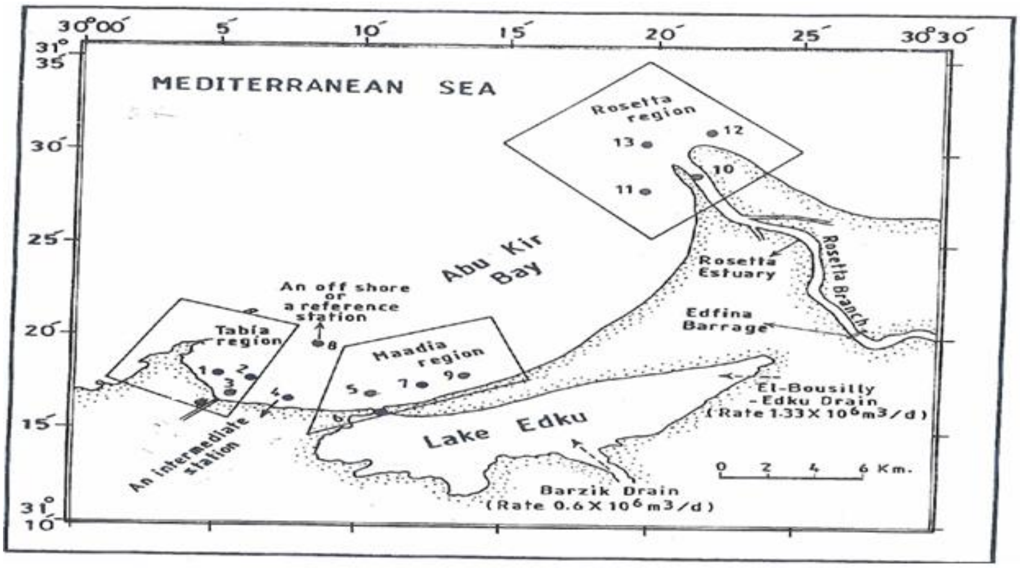

Fig. 1 Map of AKB showing positions of the sampling stations at the sources and the neighboring waters

2.2 Sampling

Bottom water samples were seasonally collected (winter 2013- winter 2014) from 14 selected stations (Fig. 1) using a two liters capacity plastic sampler. Grab sediment samples were collected at the same time from the same stations using Patterson grab sampler. Each of the sediment samples was used for the extraction of the pore water by centrifugation directly after sampling. The supernated (pore) waters and the bottom waters were filtered through Whatman GF/C glass fiber filter and used for the determination of different N forms.

2.3 Analytical Methods

Ammonia (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) were determined according to Grasshoff (1983) and total dissolved N (TDN) according to Valderrama (1981).Dissolved inorganic N (DIN) and dissolved organic N (DON) were calculated.

2.4 Data Treatment

- The obtained results are summarized by excel program and the distribution of the studied parameters is drawn using the same program.
- Enrichment factor between the pore water and the overlying bottom water for each of N ions is calculated according to the following equation:

  Enrichment factor (EF) = pore water / overlying bottom water
- The percentage for each NO_2^-, NO_3^- and NH_4^+ in the pore water and the overlying bottom water to the corresponding DIN are calculated.
- Eutrophication of the bay was determined according to Vollenwieder (1968), Giovanardi and Tromellini (1992).
- The diffusion flux (J_i) from sediment to the overlying water is estimated by Fick's law: $J_i = - D_0\, Ø^{2.5}\, (dc/dx)$

  Where D_0 = Molecular diffusion coefficient of a solute at in situ temperature,

  Ø = Porosity of the sediment

  dc/dx = The concentration gradient at the sediment – water interface

3. Results and discussion

3.1 Nitrite (NO_2^-)

At Tabia coastal region, dissolved nitrite in the pore water of grab sediment varies between 1.20 and 12.45 µM at Sts.1 and 3 in autumn and winter 2013 with a mean of 4.61 µM. Seasonally, autumn has the minimum value (1.64 µM) and the other seasons have values >4.63 µM (Fig. 2). At Maadia coastal region, the concentration ranges between 1.45 µM at Sts.5 and 9 in autumn and 6.45 µM in winter 2014 with a whole mean of 3.00 µM. Seasonally winter (2013 and 2014) has a concentration of > 4.52 and the other season has a value <3.21 µM (Fig .2). At Rosetta coastal region, Sts.12 and 11 have the minimum (1.08

µM) and maximum (9.70 µM) values in spring and winter (2013) with a whole mean of 4.06 µM. Winter (2014 and 2013) has low (2.28 µM) and high (9.70 µM) concentrations, respectively (Fig. 2).

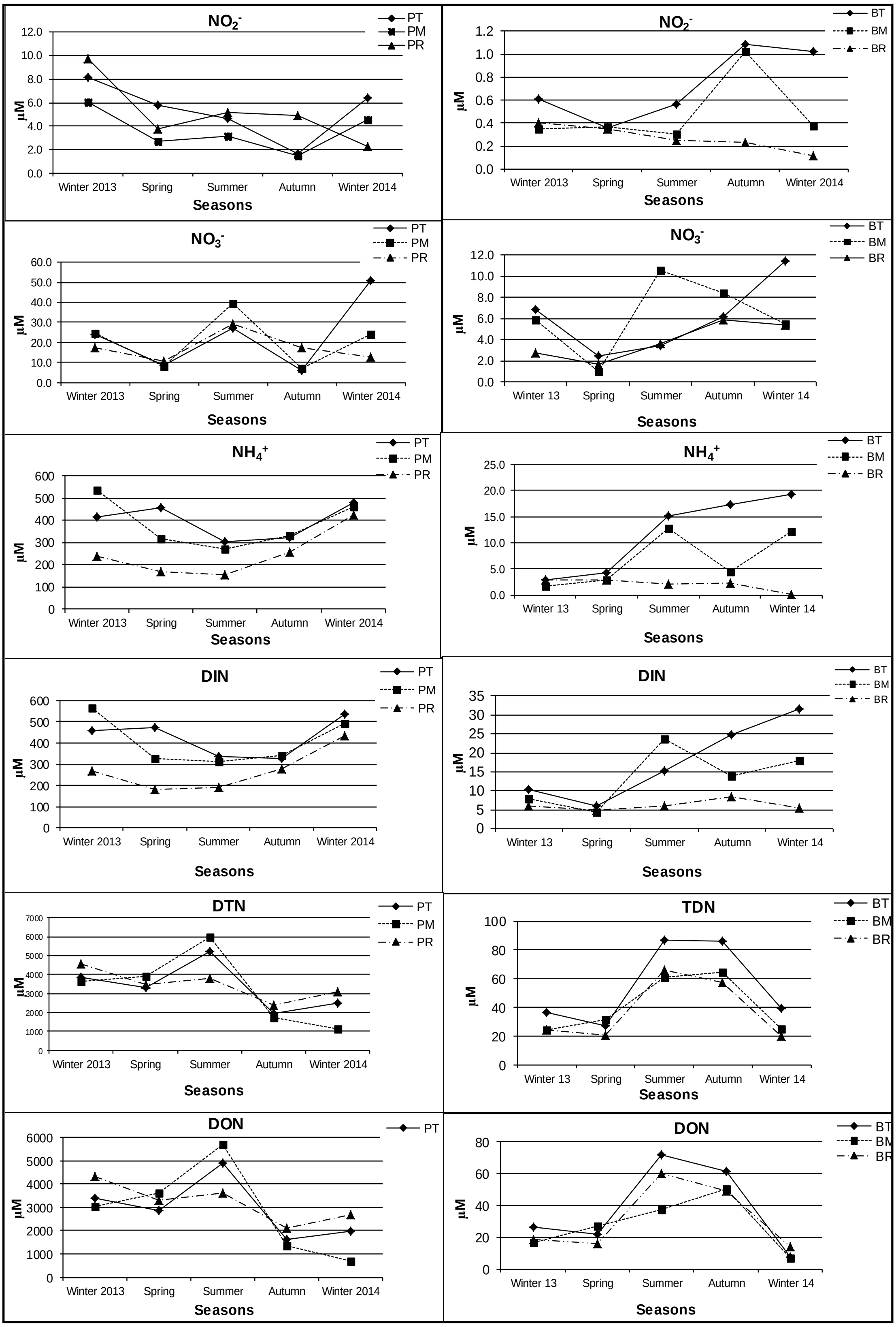

Fig. 2 Seasonal variation of Nitrogen ions (µM) in pore water (P) of grab sediment and in the overlying bottom water (B) in the three coastal regions Tabia (T), Maadia (M) and Rosetta (R) of Abu-Kir Bay (AKB) from 2013-2014

The high level in winter may be due to bacterial oxidation of some ammonia during nitrification. The low levels in the other seasons are mainly due to the consumption of nitrite during N-immobilization.

Generally, Tabia region has the average nitrite content in the pore water of grab sediment (4.61 µM) mostly equal to that in the Rosetta (4.06 µM) region and higher than that in the Maadia (3.00 µM) region. Also, the source of the Rosetta region (St.10) has the nitrite content (6.48 µM) higher than that in front of the Tabia pumping station 4.55 µM (St.3) and in the Maadia opening 3.66 µM (St.6). This means that nitrite contents increase from the south western side in AKB (Tabia and Maadia) 3.92 µM to the north east (Rosetta) 4.06 µM and off shore 4.30 µM (St,8). This is the opposite of that obtained in the overlying bottom water where the concentrations decrease from the south western of AKB 0.66 µM to the Rosetta region 0.24 µM.

Pore water has nitrite content higher than that of the overlying bottom water at all stations except Sts. 3 and 5 during autumn, where the enrichment factor (EF) in Tabia, Maadia and Rosetta regions are 6.09, 5.78 and 16.90 and in the three outlets are 4.17, 2.50 and 19.07, respectively. The decrease of EF value in the south western part of AKB in autumn (1.51) means that the concentration of nitrite in the pore water (1.59 µM) during this season is close to that in the overlying bottom water ((1.06 µM). This explains that nitrite is not the end product, its concentration in the water column or in the pore water is subjected to a number of factors working at the same time, or due to the decrease in the rate of diffusion flux from the sediment to the pore water.

3.2 Nitrate (NO_3^-)

At Tabia coastal region, nitrate content in the pore water of grab sediment ranges between 3.82 and 60.48µM at Sts.3 and 1 in autumn and winter (2014), respectively with a mean of 23.11 µM. Autumn and spring have the lowest seasonal average (<8.67 µM), summer and winter has have values > 23.88 µM (Fig. 2). In Maadia coastal region, St.5 in spring and summer has the minimum (4.29 µM) and the maximum (64.95 µM) values with a mean of 19.73 µM. At Tabia coastal region autumn and spring have the lowest nitrate content <8.29 µM, summer and winter have values >23.81 µM (Fig. 2). At Rosetta coastal region, St.12 has the minimum and maximum values 5.84 and 30.02 µM in winter (2014) and summer, respectively with a mean of 17.52 µM. Summer has a value of 29.23 µM which is higher than that of the other season < 17.40 µM (Fig. 2).

Tabia coastal region has mean value 23.11 µM which is higher than that of Maadia 19.73 µM and Rosetta 17.52 µM coastal regions. The concentration in AKB decrease from the south western side (Tabia and Maadia regions) 21.66 µM to the north east 17.52 µM (Rosetta) and this is different from that observed in nitrite, mainly due to the higher concentrations in Maadia opening 27.75 µM (St.6) and in front of Tabia pumping station 21.63 µM (St.3) than that inside of Rosetta mouth 13.19 µM (St.10). The off shore station (St.8) has a value of 13.38 where there is a low effect of the land based sources.

It is clear that the seasonal average of nitrate content at the three regions (Table 1) in the pore water of grab sediment is higher than that in the overlying bottom water where EF varies between 3.94, 3.10 and 4.22 in Tabia, Maadia and Rosetta regions, respectively. This may be due to the mineralization of organic matter in the bottom deposits which causes the pore water to be enriched with NO_3^- compared to the overlying bottom water. In many stations observed during winter 2014 (Sts.9, 10 and 12) and autumn (Sts.4, 5 and 11) show that the level of NO_3^- at the pore water is less than that in the overlying bottom water reflecting more consumption rate of NO_3^- during respiration or oxidation of organic matter or ammonia (Bender et al., 1989) by anaerobic denitrifying in the pore waters (Santschi et al., 1990). Faragallah (1995) pointed out this observation in the Eastern Harbor and reflect that NO_3^- in the pore waters is mostly used bacterially as terminal electron acceptor when DO becomes depleted.

Table (1). Regional averages of N- forms (µM) in pore water (P) of grab sediment and in the overlying bottom water (B) in the three coastal regions of Abu-Kir Bay (AKB) and their land runoff during the period from 2013-2014.

Region	**Station**	**Depth**	**mg O_2/l**	**NO_2^-**	**NO_3^-**	**NH_4^+**	**DIN**	**DON**	**DTN**
Tbia	1	B	6.69	0.96	4.96	21.31	27	29	56
		P		4.08	28.96	399.8	433	3389	3821
	2	B	6.05	0.52	3.45	10.96	15	40	55
		P		4.89	17.29	321.0	343	2571	2914
	3	B	1.47	1.09	8.86	26.91	23	47	70
		P		4.55	21.63	384.0	410	2156	2567
	4	B	6.92	0.46	6.18	5.52	12	46	58
		P		4.95	24.57	458.0	488	3201	3690
		Average B	4.41	0.76	5.86	14.03	19	41	60
		Average P		4.62	23.11	390.7	418	2829	3248
		EH=P/B		6.09	3.94	27.85	22	70	54
Maadia	5	B	7.38	0.95	10.04	7.50	18	38	57
		P		2.76	33.42	347.8	384	2969	3353
	7	B	6.92	0.34	4.60	7.87	13	25	38
		P		2.70	16.32	264.3	283	2845	3127
	9	B	7.47	0.27	4.42	8.78	14	28	42
		P		3.55	9.45	427.0	440	2672	3112
		Average B	7.76	0.52	6.35	8.05	15	31	46
		Average P		3.00	19.73	346.3	369	2829	3197
		EH=P/B		5.78	3.10	43.03	25	93	70
Maadia outlet	6	B	7.20	1.47	8.90	8.71	19	19	38
		P		3.68	27.75	303.8	335	2243	2578
		EH=P/B		2.50	3.12	34.86	18	118	68
The two regions mean		Average B	5.85	0.66	6.07	11.48	18	36	54
		Average P		3.92	21.66	371.7	397	2829	3226
		EH=P/B		5.99	3.57	32.39	23	78	60
AKB offfshore	8	B	6.74	0.26	3.77	3.84	8	36	44
		P		4.30	13.38	303.8	321	2459	2780
		EH=P/B		16.52	3.55	79.15	41	68	63

Region	Station	Depth	mgO_2/l	NO^{2-}	NO^{3-}	NH^{4+}	DIN	DON	DTN
Rosetta	11	B	6.82	0.24	4.01	1.72	6	31	37
		P		4.26	12.76	258.0	275	2932	3205
	12	B	9.04	0.22	4.02	1.98	6	42	48
		P		2.73	17.92	246.8	262	3150	3418
	13	B	7.71	0.26	4.44	1.80	7	32	39
		P		5.17	21.89	249.8	277	2686	2960
		Average B	7.86	0.24	4.15	1.83	6	35	41
		Average P		4.06	17.52	251.5	271	2923	3194
		EH=P/B		16.90	4.22	137.2	44	84	78
Rosetta mouth	10	B	6.82	0.34	3.42	1.29	5	44	49
		P		6.49	13.19	236.5	256	2949	3207
		EH=P/B		19.07	3.86	183.7	51	67	65

Table 1 cont.

where EF= P/B = Enrichment Factor

Also, denitrification process seems to be occurring in both the bottom water by rate lower than that in the pore water. Further, the production of $NH_4^+$from the sediment organic matter is mostly due to the use of NO_3^- for oxidation and NH_4^+ produced is not nitrified. This process is accompanied by the release of N_2 molecules as well.

Generally, the level of NO_3^- is greater than that of NO_2^- and much lower than that of NH_4^+. This observation confirms the prevailing reducing conditions due to depletion of DO (EL-Rayis and Faragallah, 2010). Also, the denitrification or/and N-immobilization are the main processes controlling nitrate concentration.

3.3 Ammonia (NH_4^+)

Ammonia in the pore water of Tabia coastal region ranges between 162 and 744 µM at Sts.2 and 4 in autumn and spring, respectively with a mean of 391 µM. Winter and spring have seasonal values (> 414 µM), summer and autumn have values < 321 µM. At Maadia coastal region, Sts.7 and 9 have the minimum 192 µM and maximum 642 µM values in autumn and winter 2014 with a mean of 346 µM. Seasonally, winter has values > 462 µM and the other seasons have values < 334 µM (Fig. 2). At Rosetta region, the absolute minimum and maximum values 102 and 572 µM are detected in St. 12 at summer and winter 2014, respectively with a mean of 252 µM.

Ammonia concentration in the pore water of grab sediment at Tabia coastal region (391 µM) is higher than that at Maadia (346 µM) and Rosetta (252 µM) regions. Also, in front of Tabia pumping station 384 µM (St.3) is higher than that inside Maadia opening 304 µM (St.6) and inside Rosetta mouth 237 (St.10). The concentrations decrease from the south western side of AKB 372 µM (Tabia and Maadia regions) to the sea ward 304 µM (St.8) and north east 252 µM (Rosetta region).

Generally, the concentration of NH_4^+ in the pore water is much higher than that in the overlying bottom water (Table 1). Enrichment factors at the three regions are 28, 43 and 137, indicating that NH_4^+ is accumulated more in the pore water. The increase in NH_4^+ content in the pore water gives indication that, the diffusion flux from the sediment to the water column is slow. The assimilation of NH_4^+ in the sediment by bacteria was small and also due to the fact that most of the ammonia detected in the sediment is adsorbed to sediment particles and thus it is not readily available for the bacteria. Faragallah (2009) pointed out that in Edku Lake the pore water at the lake has much more ammonia content than in the overlying bottom water reflecting the lake bottom water in the side of organic decomposition. Also, it is due to the decomposition of plants remains and detrital organic matter present in the sediment. Mineralization of organic matter in bottom deposits causes the pore water to be enriched in various nutrients as compared to the overlying water (Henderson-Seller and Markland, 1987). As will be seen latter, the level of NH_4^+ in the pore water at any time is always more dominant than the other N-ions; NO_2^- and NO_3^-. This observation indicates that the environmental conditions in the pore waters are encouraging formation and accumulation of the reduced N-forms, NH_4^+, i.e., the oxidation reduction of burial organic matter in the sediments mostly steps at the NH_4^+fraction. Therefore, processes of deamination or ammonification as well as N- immobilization and denitrification are expected to be the dominant processes (Santschi et al., 1990).

3.4 Dissolved inorganic nitrogen (DIN)

Dissolved inorganic nitrogen, in the pore water of grab sediment at Tabia coastal region ranges between 172.4 and 757.5µM at Sts.2 and 4 in autumn and spring, respectively, with a mean of 418.4 µM. At Maadia coastal region the minimum (201 µM) and maximum (653 µM) of DIN was detected in Sts.7 and 9 in autumn and winter (2014) with a mean of 369 µM. At Rosetta region, the concentration varies between 120 and 580 µM in Sts 11 and 12 in spring and winter (2014), respectively, with a of mean 273 µM. In all stations of AKB region, DIN content in the pore water of grab sediment is greater than that in the overlying bottom water (EF= 21.5, 24.8 and 43.9 in Tabia, Maadia and Rosetta regions, respectively), also the concentration decreases from the south western side 397.3 µM (Tabia and Maadia regions) to off shore 321.4 µM (St.8) and to the north east 273.1 µM (Rosetta region). Seasonally, winter and spring have the maximum seasonal average at Tabia region; while at Maadia and Rosetta regions winter and autumn have the highest values (Fig. 2). This distribution is similar to that observed in $NH4^+$.

It is clear that the abundance of the percentage ratio of NH_4^+, NO_3^- and NO_2^- to DIN in the pore water of grab sediment in Tabia, Maadia and Rosetta regions of AKB are in the following order:

Tabia region NH_4^+ (93.19) >> NO_3^- (5.57) >NO_2^- (1.24%)

Maadia region NH_4^+ (93.25) >> NO_3^- (5.92) >NO_2^- (0.84%)

Rosetta region NH_4^+ (89.51) >> NO_3^- (8.73) >NO_2^- (1.76%)

This means that at the three regions the reduction of nitrate to ammonia is much greater than that nitrification process.

The percentage ratios of NH_4^+, NO_3^- and NO_2^- to DIN in the overlying bottom water in the three regions are as follows:

Tabia region NH_4^+ (58.65) > NO_3^- (34.19) >>NO_2^- (7.16%)

Maadia region NH_4^+ (54.57) > NO_3^- (41.12) >>NO_2^- (4.32%)

Rosetta region NO_3^- (66.50) > NH_4^+ (28.52) >> NO_2^- (4.98%)

This indicates that in Tabia and Maadia regions the rate of reduction is greater than that of nitrification and is less than that in the corresponding pore water, while in Rosetta region the opposite was observed. In the three regions the percentage of ammonia to DIN in the pore water of grab sediment is higher than that in the overlying bottom water, but the opposite was observed for nitrate and nitrite confirming the occurrence of deamination and denitrification or/and N-immobilization rather than nitrification in the pore water.

3.5 Dissolved organic nitrogen (DON)

The concentration of DON in the pore water of grab sediment is higher than that overlying bottom water (EF= 70, 92 and 84 for Tabia, Maadia and Rosetta regions, respectively). Tabia and Maadia coastal regions have the same value (2828 µM) and increase in Rosetta coastal region (2922 µM).

3.6 Dissolved total nitrogen (DTN)

At Tabia coastal region, DTN in the pore water of grab sediment varies between 1378 and 7560 µM at Sts.2 and 1 in autumn and summer, respectively with a mean of 3248 µM. Summer and autumn have the maximum (5240 µM) and minimum (1950 µM) seasonal average values (Fig. 2). At Maadia coastal region, the minimum (938 µM) and the maximum (6501 µM) are detected at St.9 in winter (2014) and summer, respectively with a mean of 3198 µM. Summer has the maximum seasonal average (5996 µM) and the minimum values

(< 3618 µM) were detected in autumn and winter (Fig.2). At Rosetta, St.11 has the minimum (1704 µM) and maximum (4577 µM) values in autumn and winter (2013) respectively with a mean of 3196 µM. Autumn and spring have the minimum (2362 µM) and maximum (4179 µM) seasonal averages (Fig. 2).

The concentration of DTN in the pore water of grab sediment is much higher than that in the overlying bottom water (EF= 54, 70 and 78 in the three regions) and decreases from the south west side of AKB 3226 µM to the off shore 2788 µM and to the north east 3196 µM. The concentration of DON in the pore water of grab sediment is more dominant than that of DIN where it is represented by 87, 88 and 91 % in Tabia, Maadia and Rosetta regions, respectively.

3.6 Trophic status of the three regions

According to the preliminary classification of the trophic state of shallow marine water bodies based on the level of TDN, the south west part of AKB (Tabia and Maadia regions) can be considered as eutrophic while its north east part (Rosetta region) as mesotrophic.

3.7 Diffusion flux of N- ions

The benthic flux is calculated using the diffusive flux equation of Fick's law that depends mainly on pore water profile. All the studied N-ions (NH_4^+, NO_2^- and NO_3^-) in the three regions (Table 2) show negative values i.e the diffusion is generally directed towards the overlying bottom water. The maximum flux of NH_4^+ in AKB (-6.40 mg N/m^2 /d) was in Tabia region and decreases toward Maadia (-5.75 mg N/m^2 /d) and Rosetta (-4.25 mg N/m^2 /d) regions. The diffusion of NO_2^- to the overlying bottom water is low compared to that from NH_4^+. Tabia and Rosetta regions which have the same NO_2^- benthic flux (-0.063 mg N/m^2 /d) that is higher than that in Maadia region (-o.o4 mg N/m^2 /d). Tabia region has NO_3^- a flux (-0.279 mg N/m^2 /d) higher than that of Maadia and Rosetta regions (-0.217 mg N/m^2 /d).

Table (2). Diffusion flux of N-ions (mg N/m^2/d) in the three regions.

Region	**NH_4^+**	**NO_2^-**	**NO_3^-**	**DIN**
Tabia	-6.404	-0.063	-0.279	-6.746
Maadia	-5.751	-0.041	-0.217	-6.01
Rosetta	-4.245	-0.063	-0.217	-4.534
AKB	5.467-	-0.056	-0.238	-5.763

Therefore the net percentage of DIN diffused to the overlying bottom water is mainly due to NH_4^+, where it represents 94.9, 95.7 and 93.6% from DIN in Tabia, Maadia and Rosetta region, respectively. This is virtually due to the fact that NH_4^+ is the dominant form of DIN. Shreadahet al., (2015) reported that in EL-Mex Bay the diffusion flux of -7.24 and 1.36 mg N/m^2 /d for NO_3^- and NO_2^-, Abu El-Khair et al., (2010) reported the values of -0.053 mg N/m^2 /d for NO_3^- in AKB and Faragallah (1995) reported the values of -0.014, + 0.014 and -1.21 mg N/m^2 /d for NO_2^-, NO_3^- and NH_4^+ in the Eastern Harbor. Comparing the results of the present study with that reported in the other regions revealed that N-ions upward diffusive fluxes in AKB has value higher than that in the Eastern Harbor and lower in El-Mex Bay.

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