

Effects of Surface Microlayer and Sediment Water Interface Layer on the Nutrient Species in the Eastern Harbour of Alexandria

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Abstract

The Eastern Harbor (EH), a small shallow semicircular basin surrounded by Alexandria, has an area of 2.53 million m², with an average depth of 6.5 m and water volume of 16.44 million m³. It is sheltered from the Mediterranean Sea by a water break leaving two openings through which the harbor water is connected to the open seawater. The EH is mainly influenced by sewage disposal from Alexandria. Water samples were collected seasonally at three selected stations from the surface microlayer (SML) to sediment water interface layer (SWIL) for studying the effects of SML and SWIL on the distribution of nutrient species in the rest of the water column; middle water layer (MWL). Contrary to nitrate and particulate nitrogen, the annual means of the rest of parameters (nitrite, ammonium, dissolved organic nitrogen, dissolved inorganic, organic and particulate phosphorus and silicate) in the SML were higher than the corresponding means in the SWIL, confirming that contribution of these nutrient species from the SML to the MWL was more than that from the SWIL to the MWL, which generally gave intermediate annual means. Accordingly, it could be concluded that most of the nutrient species in the EH originated mainly from an allochthonous source (untreated domestic wastes) floating over the surface harbor water rather than from the autochthonous sources; decomposition of organic remains and release from the harbor sediments.

Key words: surface microlayer, sediment water interface layer, nutrient species, Mediterranean harbor.

INTRODUCTION

The surface microlayer (SML) is defined as the topmost layer that has varying composition and thickness from tens to hundreds micrometers, depending on the nature and abundance of materials present. Its study is important in understanding fluxes of heat, energy and materials between ocean and atmosphere, as it is considered as a microenvironment at the air-sea water interface. A number of reviews showed an increasing awareness of the importance of exchange processes in the sea-surface microlayer.

The air-sea water interface, unlike sediment - seawater and particle - seawater interfaces, is a subject to a number of unique and dynamic non-equilibrium processes, such as wind stress, water transpiration, solar energy flux and atmospheric inputs. These processes in conjunction with the concentration of surface active organic matter at the interface can result in relatively rapid changes in the chemical, biological and physical properties of the sea surface microlayer.

Definitive studies on the chemical composition and physico-chemical properties of sea surface films began during 1960s. Of the most important difficulty facing studies on the sea surface film is the sampling techniques.

The sediment water interface layer (SWIL), being one of the richest water layers in nutrients and trace metals, is the most important part of the water column. The main cause of this richness is its adhering to the bottom sediments from which diffusion of most elements according to their concentration gradients takes place. Although such diffusion is in an antigravitational direction, it is still effective on the few centimeters covering the bottom sediments. The enrichment of SWIL by elements depends not only on the type of sediments but mainly on the extent of interstitial water enriched with these elements.

The exchange of dissolved elements across the SWIL is an important process affecting the chemical composition of the coastal oceans [1], seas [2], estuaries [3] and lakes [4]. This process is particularly important for estuarine and coastal marine environments, where nutrient regeneration in the benthic sediments can supply a significant fraction of the nutrient requirements for the primary producers in the overlying water [5]. Molecular diffusion within interstitial water is of fundamental importance in affecting the exchange of dissolved constituents across the sediment-water interface, but mass balance calculations and in situ benthic flux studies have shown that other processes can enhance the diffusive flux. Mechanisms responsible for this enhancement include physical stirring of sediments by currents [6] and by benthic invertebrates [7], as well as irrigation of sediments by macrobenthos [8] and transport through bubble tubes [1].

Benthic nutrient fluxes are important in the nutrient balance of many aquatic systems. Migration out of sediments supplying about 80% of nutrients from the 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 are released to pore waters and transported to the overlying waters by diffusion and bioturbation [9].

All investigations on the local and seasonal distribution of nutrients in the Egyptian marine environments did not consider the SML and the effect of this top most water layer, as well as the SWIL on the levels of nutrients in the rest of the water column. Because of the immense importance of these two seawater layers on the distribution of nutrient species in the water column, a research project was carried out to highlight this fact in two coastal Mediterranean semi enclosed basins subjected to different levels of pollution. It is hoped that this pioneer study will be followed by similar investigations on other elements, not only in the two study areas, but also in the other Egyptian Mediterranean coastal waters to reach a more or less integrated understanding of the role played by these two important micro water layers on the water column. The first paper of this project entitled "effects of surface microlayer and sediment water interface layer on the distribution of nutrient species in the polluted Abu-Kir Bay, Egypt" was published by Saad et.al., [10]. The present study, the second part of this project, deals with the effects of the SML and SWIL on the distribution of nutrient species in the Eastern Harbor of Alexandria.

STUDY AREA

The Eastern Harbor (EH) of Alexandria, a relatively small, shallow and semicircular basin generally surrounded by Alexandria, lies between longitudes $29^{\circ} 53'$ and $29^{\circ} 54.4'$ E and Latitudes $31^{\circ} 12'$ and $31^{\circ} 13'$ N. Its area is about $2.53 \times 10^6 \text{ m}^2$, with an average depth of 6.5 m and water volume of $16.44 \times 10^6 \text{ m}^3$. The harbor is sheltered from the Mediterranean Sea by an artificial water break, about 750 m in length, leaving two openings through which the harbor's water is freely connected with the open seawater; El Boughaz and El-Silsila (Fig. 1).

The EH is mainly influenced by sewage disposal of the central part of Alexandria City, which is pumped into the Mediterranean Sea. The main sewage tube begins at Kayet Bay Pumping Station (Fig. 1), which is the main metropolitan sewage pumping station of the central part of Alexandria. It discharged to the sea about $96 \times 10^6 \text{ m}^3/\text{yr}$ during 1985-1986 [11]. This amount increased successively with progress of time following the successive increase in population. Besides, small 11 sewage openings discharged about 15,000 and 10,000 m^3/day of untreated sewage wastes directly to the harbor in winter and summer, respectively [12]. Also, large quantities of different wastes of the fishing and sailing boats anchoring inside the harbor were dumped into its north-western part.

MATERIAL AND METHODS

Sampling of seawater was carried out seasonally during January, April, July and November 1989, representing winter, spring, summer and autumn, respectively. Three stations were chosen to represent different regions in the harbor (Fig. 1).

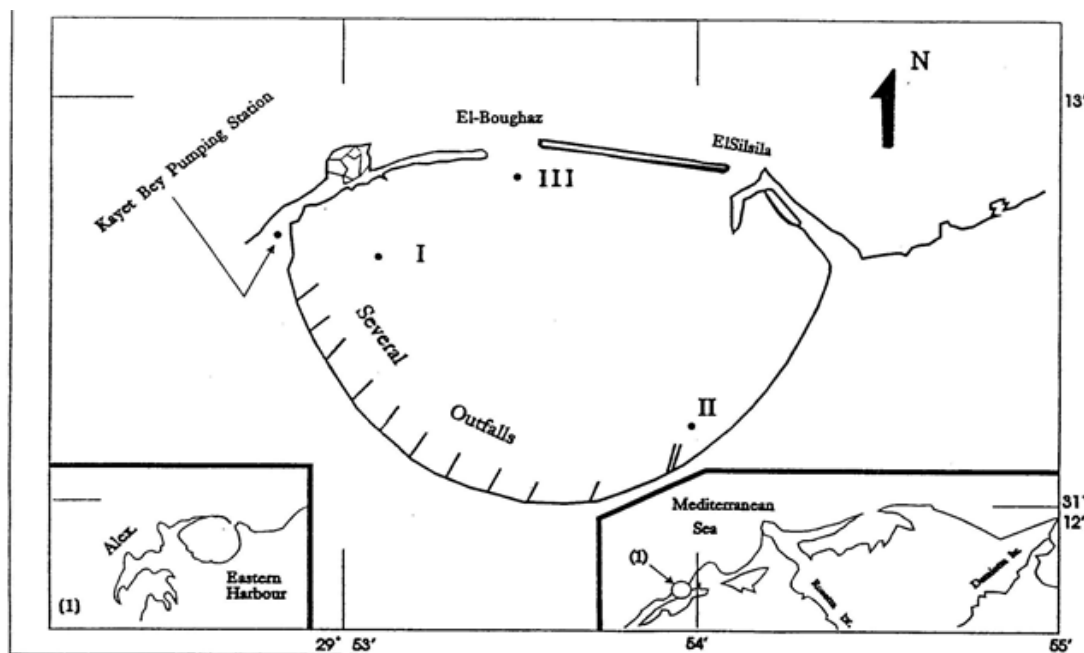


Figure 1: Map of the Eastern Harbor, showing position of stations.

At each station, water samples were collected from seven depths; surface micro layer (SML), upper 30 cm water layer (30 cm UWL), upper one meter water layer (1 m UWL), middle water layer (MWL), lower one meter water layer (1 m LWL), lower 30 cm water layer (30 cm LWL) and sediment water interface layer (SWIL).

Before and during sampling, the conditions of the sea and surface water were recorded to assure accurate sampling during calm weather. About 2 liters of the SML samples were collected by the Garette [13] technique, as this method is inexpensive and simple. During 130 minutes, about 200 dips were needed to yield the required volume at each station. The screen was rinsed with seawater before sampling and the first few dips were rejected.

The screen was immersed in the seawater and withdrawn horizontally through the water surface and the water which adhered to it was drained into the polyethylene sampling bottles. The material from the top 150 μm of seawater was sampled with an efficiency of about 75%. The loss than 100% is due to irreversible adsorption of some micro layer material onto the mesh when it was first immersed in the water. This material did not drain into the sampling bottles and deactivated a fraction of the screen for subsequent immersion.

The SWIL was collected by pumping it, using a polyethylene siphon and a left hand pump (5 gpm). The siphon was lowered in the water column until settled on the sea bottom, using a sufficient weight. Then, it was raised up carefully to a few cm to prevent possible disturbance from the bottom sediments. The SWIL was pumped for collecting about two liters of seawater at each station; sampling was repeated when the collected seawaters were turbid.

The 30 cm UWL, 30 cm LWL and 1 m LWL were collected by pumping the water samples similar to the SWIL. The 1 m UWL and MWL were collected by a PVC Nisken sampler. All samples were kept in 5 liters polyethylene bottles.

Water samples were filtered, using 0.45 μm Millipore filter. The filtered samples were kept in polyethylene well stoppered bottles and freezed at -20°C until analysis. Samples for determination of total nitrogen and total phosphorus were frozen without filtration.

Dissolved inorganic nitrogen (DIN) and phosphorus (DIP) species, as well as reactive silicate were determined spectrophotometrically according to the methods described by Strickland and Parsons [14]. Total dissolved nitrogen (TDN) was determined following the technique of Koroloff [15] and modified by Valderrama [16]. Dissolved organic nitrogen (DON) was calculated from the equation:

$\text{DON} = \text{TDN} - \text{DIN}$. Total nitrogen (TN) was determined by the same technique of TDN but on unfiltered seawater samples. Particulate nitrogen (PN) was calculated from:

$$\text{PN} = \text{TN} - \text{TDN}.$$

Total dissolved phosphorus (TDP) was determined by the persulphate method described by the International Council for Exploration of the Sea [17].

Dissolved organic phosphorus (DOP) was calculated from the equation:

$\text{DOP} = \text{TDP} - \text{DIP}$. Analysis of total phosphorus (TP) was the same as that for TDP but using unfiltered samples. Particulate phosphorus (PP) was calculated from: $\text{PP} = \text{TP} - \text{TDP}$.

RESULTS AND DISCUSSION

To reduce the text, presentation and discussion of the data are concentrated principally on the regional and seasonal average concentrations, as well as on the annual means of the investigated parameters in the three water layers of the harbor (SML, MWL and SWIL). The regional average values are averages of all seasons at each station. The seasonal average values are averages of all stations in each season.

Nitrate variations

In the SML and SWIL, nitrate showed an enrichment at station I in January (rainy season) and III in April. Lewis [18] stated that mixing of water column during winter would bring nitrate rich deeper water to the surface. The highest absolute value at station III in April selected at El – Boughaz might be due to the entrance of considerable amounts of untreated sewage wastes from Kayet Bay Out- falls into the EH via El-Boughaz. This highest value caused the maximum regional average concentration at this station (Table 1) and the maximum seasonal averages that month (Table 2), despite the relative increase in nitrate uptake in spring. However, the

minimum seasonal average value in July in the SML (Table 2) resulted mainly from the increase in phytoplankton uptake in summer. In the SWIL, the release of nitrate from the sediments and its regeneration from decomposition of the descending plankton must be considered as autochthonous sources of this nutrient to the SWIL.

Table 1. Regional average values of nutrient species ($\mu\text{g-at} / \text{l}$) in the surface microlayer (SML), middle water layer (MWL) and sediment water interface layer (SWIL) in the Eastern Harbor.

Stations	Water layers	Nitrate	Nitrite	Ammonium	DON	PN	DIP	DOP	PP	SiO ₃
I	SML	4.566	0.520	9.579	25.956	8.309	0.285	0.650	0.372	10.770
II		1.952	0.687	8.474	16.211	6.789	0.493	0.738	0.629	12.195
III		5.831	0.751	5.232	18.970	14.414	2.462	6.078	3.557	10.623
I	MWL	5.85	0.491	7.344	17.541	8.081	0.601	1.055	0.847	6.458
II		4.284	0.469	4.060	16.394	4.618	0.350	0.990	0.239	8.706
III		4.853	0.568	2.742	19.503	9.414	0.541	1.569	0.589	4.571
I	SWIL	4.925	0.279	11.881	15.388	8.247	0.308	0.594	0.181	4.486
II		4.497	0.583	3.439	19.964	14.803	0.288	2.090	0.090	7.853
III		6.032	0.321	1.882	18.027	13.143	0.229	1.582	0.643	4.041

Nitrite variations

In the SML, nitrite gave the highest absolute concentration at station III in January, leading to the maximum regional average value at this station (Table 1) and the maximum seasonal average value that month (Table 2). This resulted possibly from the entrance of considerable amounts of nitrite enriched sewage wastes from kayet Bay Outfalls into El-Boughaz. Saad and Antoine [19] suggested that the increased value of nitrite resulted from the input of nitrite from rain. Mortinson and Brooks [20] pointed out that the increasing values of nitrite resulted from reduction of nitrate, the oxidation of ammonium and extra cellular release of nitrite by phytoplankton. The lowest seasonal average nitrite value in July (Table 2) resulted from the increase in phytoplankton uptake in summer and thus its depletion at stations I and III.

The high absolute values in the SWIL at station II in January and April might be due to the increase in the amounts of sewage discharged from Shambilion Pump in those months compared with the amounts discharged in the other two months. These highest values caused the maximum regional average value at this station (Table 1) and the highest seasonal averages in January and April, despite the high uptake in spring.

Table 2. Seasonal average concentrations and annual mean values of the nutrient species ($\mu\text{g-at/l}$) in the surface microlayer (SML), middle water layer (MWL) and sediment water interface layer (SWIL) in the Eastern Harbor.

Parameters	Water layers	Jan.	April	July	Nov.	Annual means
Nitrate	SML	4.792	6.368	0.611	4.693	4.116
	MWL	7.530	3.778	3.310	5.365	4.996
	SWIL	7.384	8.390	2.862	1.968	5.151
Nitrite	SML	1.261	0.755	0.065	0.529	0.653
	MWL	0.937	0.458	0.314	0.328	0.509
	SWIL	0.564	0.562	0.196	0.255	0.394
Ammonium	SML	13.909	6.432	9.370	1.335	7.762
	MWL	9.428	1.145	7.350	0.937	4.715
	SWIL	5.797	1.615	14.313	1.211	5.734
DON	SML	40.750	22.614	9.836	8.315	20.379
	MWL	40.296	18.601	6.746	5.609	17.813
	SWIL	40.177	25.782	1.883	3.329	17.793
PN	SML	4.200	3.251	29.978	1.920	9.837
	MWL	3.283	2.539	22.587	1.074	7.371
	SWIL	4.024	4.258	39.432	0.544	12.064
DIP	SML	1.023	0.242	0.311	2.744	1.080
	MWL	0.717	0.223	0.429	0.621	0.497
	SWIL	0.481	0.304	0.248	0.068	0.275
DOP	SML	1.331	0.114	0.492	8.017	2.489
	MWL	1.895	0.190	0.865	1.869	1.205
	SWIL	2.379	0.312	2.796	0.199	1.422
PP	SML	0.653	0.260	0.264	4.901	1.519
	MWL	0.420	0.267	0.410	1.136	0.558
	SWIL	0.403	0.205	0.488	0.122	0.305
SiO ₃	SML	15.633	12.036	9.281	7.834	11.196
	MWL	13.632	4.172	4.645	3.864	6.578
	SWIL	8.936	4.750	3.869	4.285	5.460

Contrary to nitrate, the regional average values of nitrite at the three stations in the SML were markedly higher than the corresponding averages in the SWIL (Table 1) leading to the assumption that contribution of nitrite from the SML to the MWL was more than that from the SWIL to the MWL. This is confirmed from the gradual decrease in the annual means from 0.653 $\mu\text{g-at N/l}$ in the SML to 0.509 $\mu\text{g-at N/l}$ in the MWL to 0.394 $\mu\text{g-at N/l}$ in the SWIL (Table 2).

Ammonium variations

In the SML, the high level at station II might be due to the increase in the discharge of ammonium enriched wastes from Shambilion Outfall. The absolute maximum at station I in July causing the maximum regional average at this station (Table 1) resulted mainly from the increase in nitrate reduction in summer, as confirmed from nitrate depletion in the same water sample and the increase in the rate of decomposition of organic remains at this stagnant area of the shipyard during summer. According to William *et al.*, [21], ammonium tended to be abundant from phytoplankton excretion and lyses of microplanktonic organisms. The high ammonium concentrations at the three stations in January (rainy season and decrease in phytoplankton uptake) caused the highest seasonal average value that month (Table 2).

In the SWIL, an increase in ammonium level was observed at station II in January and at station I in July. The explanation of these highest values might be similar to that described for the SML data, beside the release of ammonium from the sediments. According to MacCaffery *et al.*, [8], ammonium tended to be high from organic matter decomposition and diffusion into the water. The highest absolute amount at station I in July caused the maximum regional average value at this station (Table 1) and the highest seasonal average value that month (Table 2).

The annual mean concentration of 7.762 $\mu\text{g-at N/l}$ for the SML was noticeably higher than that of 5.734 $\mu\text{g-at N/l}$ for the SWIL, confirming that contribution of ammonium from SML to the MWL was more than that from the SWIL to the MWL, which gave intermediate mean of 4.715 $\mu\text{g-at N/l}$ (Table 2).

Dissolved organic nitrogen (DON) variations

In the SML, the vertical variations of DON showed enrichment at station I in the four seasons, giving the maximum regional average value (Table 1). This is mainly due to its position in the fishing shipyard, where considerable amounts of organic wastes were discharged from the vessels anchored at this location, beside the autochthonous decomposition of organic remains in this stagnant area. Riley and Chester [22] showed that most of organic nitrogen compounds probably enter the water as a result of decomposition of protein during the decay of organic tissues. According to Wetzel [23], release of DON by aquatic vegetation constitutes a major source of organic nitrogen to the water. The highest seasonal average DON value in January (Table 2) resulted from the markedly high DON concentrations at the three stations, resulting from the considerable amounts of organic wastes discharged from the vessels at the area of station I, from Shambilion Outfalls affecting station II and from kayet Bay Outfalls affecting station III. According to Riely and Chester [22], the increased rate in decomposition of organic content increased the DON concentration. Also, the stirring up of the bottom sediments in the shallow EH by strong winds prevailed in winter accelerated the release of DON from bottom sediments to the overlying water column.

The horizontal distribution at the three stations in the SWIL was mostly similar to that in the SML; the absolute values at the three stations in January were in general markedly higher than the corresponding values in the other three seasons, leading also to the maximum seasonal average value that month (Table 2). The explanation given for the higher values in the SML can be also applied to those for the SWIL. Besides, the release of DON from the sediments affected directly the SWIL before its influence on the SML. The increase in the absolute DON value at station II in April with the high value at the same station in January caused the maximum regional average value at this station (Table 1).

The annual mean concentration showed a decrease from 20.379 $\mu\text{g-at N/l}$ in the SML to 17.813 $\mu\text{g-at N/l}$ in the MWL to 17.793 $\mu\text{g-at N/l}$ in the SWIL. These data confirm that contribution of DON to the MWL was mainly from the SML.

Particulate nitrogen (PN) variations

Variations of PN in the SML showed a considerable enrichment in July, giving the maximum seasonal average concentration (Table 2). According to Riely and Chester [22], the exceedingly high PN content originates mostly from the organic fraction of nitrogen (bacteria, plant or animal nitrogen) and some particularly stable organic nitrogen compounds resist bacterial attack and remain in the water. This might explain the highest PN values in summer, when biota was abundant. The absolute maximum at station III in July leading to the maximum regional average value at this station (Table 1) reflects its position near El-Boughaz, when PN enriched domestic wastes from Kayet Bay Outfalls might be introduced into the harbor.

Similar to variations of the absolute values in the SML, the values in the SWIL were also highest in July, giving the maximum seasonal average concentration that month (Table 2). The same explanation given for the SML can be also given for the SWIL for such seasonal maximum in the hot season. The absolute highest PN value at station II in July has led to the maximum regional average at this station (Table 1).

As shown in Table 2, The annual mean PN value of 12.064 $\mu\text{g-at N/l}$ for the SWIL was noticeably higher than that of 9.837 $\mu\text{g-at N/l}$ for the SML, confirming that the contribution of PN from the SWIL to the MWL was more than that from the SML to the MWL, which gave an intermediate annual mean of 7.371 $\mu\text{g-at N/l}$.

Dissolved inorganic phosphorus (DIP) variations

The vertical variations in the SML gave at station III an absolute maximum in November and relatively high values in the other months, causing the maximum regional average value at this station (Table 1). This resulted from the enrichment of DIP in the sewage input discharged from Kayet Bay Outfalls and introduced into the harbor. This highest absolute value caused the maximum seasonal average concentration in November (Table 2). Marty *et al.*, [24] stated that the increase in DIP in the SML is probably due to an input from the atmosphere and lateral input from

pollution. Hansson [25] pointed out that DIP concentration was influenced by several factors, including an impact from adjacent water bodies, detergent impacts, less uptake and production of the phosphorus fractions in water.

Variations of DIP in the SWIL showed enrichment at station I in January, causing the maximum regional average value at this station (Table 1) and the maximum seasonal average that month (Table 2). This might be due to the increase in the amounts of wastes discharged from the anchored ships enriched with DIP and the possible increase in the rate of DIP released from the sediments accelerated by the effect of wind action in stirring up the shallow water column in winter. Williams *et al.*, [21] pointed out that the hydrolysis of polyphosphate might release phosphorus from the sediments.

As shown from Table 2, the annual mean concentrations of DIP showed a gradual decrease from 1.080 μg - at P/1 in the SML to 0.497 μg - at P/1 in the MWL to 0.275 μg - at P/1 in the SWIL, confirming that the contribution of DIP to the MWL was mainly from the SML rather than from the SWIL.

Dissolved organic phosphorus (DOP) variations

Similar to DIP, DOP gave the maximum absolute value at station III in November leading to the maximum regional average at this station (Table 1) and the highest seasonal average that month (Table 2). The other DOP levels in the SML were comparatively low and thus such abnormal absolute maximum definitely reflects the flow of domestic wastes enriched with phosphates during November into the EH.

The SWIL showed an increase in values at station II in January and July leading to the maximum regional average (Table 1) possibly reflecting the effect of sewage wastes discharged through Shambilion Outfalls. The markedly high concentrations at stations II and III directly affected by sewage wastes in January and July gave the highest seasonal averages (Table 2), despite the considerable difference in water temperatures in winter and summer affecting the different activities of aquatic organisms.

As shown in Table 2, the annual mean concentration of DOP showed an increase in the SML (2.489 μg - at P/1) compared to that in the SWIL (1.422 μg - at P/1), confirming that contribution of the DOP from the SML to the MWL was more than that from the SWIL. This is in agreement with the conditions of the DIP.

Particulate phosphorus (PP) variations

Horizontal variations of PP in the SML showed an absolute maximum at station III in November, giving the maximum regional average at this station (Table 1) and the highest seasonal average that month (Table 2). This is in agreement with DIP and DOP reflecting the position of this station in the vicinity of El - Boughaz, when high amounts of phosphate enriched sewage wastes were discharged from Kayet Bay Outfalls. However, the SWIL showed an increase in PP at station III in January and July, but leading to the maximum regional average value at this station (Table 1).

These highest absolute values gave the highest seasonal averages those months (Table 2).

The annual mean values of PP showed a sharp drop from 1.519 μg - at P/I in the SML to 0.558 μg - at P/I in the MWL to 0.305 μg - at P/I in the SWIL (Table 2), confirming that PP in the MWL originated mainly from the SML rather than from the SWIL.

Silicate variations

In the SML, the highest absolute value at station I in April, in spite of phytoplankton abundance in spring, suggests the influence of the anchoring vessels at this location. Excluding the absolute maximum, the highest absolute values at station II in the different seasons caused the maximum regional average at this station (Table 1), directly influenced by sewage waste discharges. El wakeel and Wahby [26] suggested that the high concentrations of silicate resulted from the influx of drainage water enriched with silica. The high absolute value at station II influenced by waste discharges and III affected by Kayet Bay Outfalls in January (rainy season) causing the maximum seasonal average concentration that month (Table 2), resulted from draining the soil material enriched with silica into the receiving water. The decrease in silicate uptake by diatoms in winter also played a role in increasing its content that month. According to Hamza [27], silicon tended to be high due to the decrease in uptake by low phytoplankton crop.

In the SWIL, The highest absolute value at station II in January caused the maximum regional average value (Table 1) and supplemented by the second highest silicate concentration at station III also in January in giving the maximum seasonal average value (Table 2). The explanation given to the increase in silicate content at stations II and III in the SML can be also applied for these two stations in the SWIL. Regeneration of silicate from dissolution of the deposited diatom frustules, a process accelerated by the stirring up of the bottom sediments by prevailing wind in winter, also played a significant role in increasing the silicate content in the SWIL in January.

The sources of silicate into the SML exceeded those into the SWIL at the three stations, giving an annual mean value of 11.196 μg - at Si/l for the SML which was more than double that of 5.460 μg -at Si/l for the SWIL. Accordingly, the contribution of silicate from the SML to the MWL exceeded that from the SWIL (Table 2).

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