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Evaluation of Linear Alkyl Benzene Sulfonate (LAS) and Physicochemical Properties of Water in Manzala Lake, Egypt

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ABSTRACT

Detergents are commonly used as essential products in our lives. Linear alkyl benzene sulfonate (LAS) is one of the main synthetic anionic surfactants used in detergents all over the world for domestic and industrial applications. Nervetheless, detergents are one of the most prevalent contaminants in all bodies of water. They enter through sewage outfalls, household garbage, and municipal waste, and they pose serious risks to aquatic life. This study focused on the determination of the physicochemical characteristics, and the concentration of linear alkyl benzene sulfonates (LAS) at ten different sites throughout the Manzala Lake, Egypt, on a seasonal basis (2021–2022). The results revealed that pH varied from 6.93 to 9.70, and a very significant difference was detected in temperature between the seasons ($P \le 0.001$). However, no significant differences were found between lake sites (P>0.05). The highest salinity value was recorded at the southern sites of the lake. The fluctuations of oxidizable organic matter during the four seasons can be organized as follows: spring > winter > summer > autumn, while the annual mean concentrations of LAS fluctuated between 0.08 and 0.62mg/l. The summer season had the highest level of LAS (1.07 mg/l). In addition, pollution of LAS had highly positive significant correlations with ammonium (r = 0.475, P<0.01) and silicate (r = 0.405, p<0.01), while it had a highly negative significant correlation with dissolved oxygen (r= -0.642, P<0.01) and a negative significant correlation with total suspended solids (r= -0.317, P<0.05). The outcomes of the present study can help researchers and policymakers effectively manage and control the Manzala Lake's water, which is negatively affected by the high concentrations of LAS.

INTRODUCTION

Contamination of aquatic resources with various types of pollutants has become a matter of concern over the last few decades. Uncontrolled wastewater discharged from agricultural, household, and industrial sites into water bodies result in ecological risk and an increased mortality rate of aquatic organisms (Sener et al., 2023).

Water contamination has recently escalated as a major issue in Egypt and other developing nations.







One of the principal reasons is the many toxic and bioaccumulative chemicals such as detergents (**Esenowo & Ugwunba, 2010**). Large quantities of detergents, cleaning agents, and cosmetics that we use every day are complex mixtures of various compounds containing substances, which affect the environment, irritate the skin, and even cause allergies (**Clausen** *et al.*, 2020). Due to the huge scale of detergent and surfactant production, they easily enter aquatic ecosystems, with a global annual production exceeding 15 million tons (**Trivedi & Yadav, 2018**).

Detergents are cleaning products made of synthetic organic compounds. The cheapness of detergent production from petrochemical sources and its great capacity to foam when used in acidic or hard water give it an advantage over soaps (**Keshwani** *et al.*, **2015**).

The essential component of a detergent is its surfactant content, which can account for up to 50% of its weight and is principally in charge of its cleaning activity. The additional ingredients consist of builders, soil-suspending agents, foam stabilizers, anti-redeposition agents, zeolite, alkaline agents, corrosion inhibitors, perfume, oxygen bleach, colorants, fragrances, dyes, optical brighteners, fillers, enzymes, and other minor constituents intended to improve the surfactant action (Mousavi & Khodadoost, 2019).

Detergents are commonly used as essential products in our lives, containing anionic surfactants such as linear alkylbenzene sulfonates (LAS) that contribute as the major ingredient of household cleaning supplies (such as laundry detergent and dishwashing liquid), personal care products, textiles, food industries, and industrial applications due to their ease of manufacture, low cost, and ease of biodegradability. LAS can be biologically degraded under oxygenic conditions and removed by suspended particles or sediment adsorption (Badmus et al., 2021).

Detergents and surfactants can enter aquatic ecosystems through wastewater treatment plant discharged into rivers, lakes, and seas as well as through direct discharge of raw sewage. Surfactant pollution in aquatic environments is mostly caused by human activities, such as runoff and the direct discharge of effluents from urban and industrial areas. In lake ecosystems, surfactant adsorption on the water surface can significantly speed up the water eutrophication process, preventing oxygen from being transported to deeper parts of the body (Markowski et al., 2017).

LAS has been considered the most harmful pollutant for aquatic life since its low concentrations cause the appearance of a foam-insulating layer that leads to a reduction of dissolved oxygen (Atici, 2021). This produces the hypoxia condition, which causes the death of many microorganisms, leading to the deterioration of water bodies (Chandanshive, 2014; Luo et al., 2023).

Pollution in the Egyptian coastal lakes is one of the most dangerous risks, affecting not only Egypt but also the entire Mediterranean Sea basin aquatic system, causing harsh threats to the coastal and marine environment and negative socio-economic consequences on fisheries, maritime activities, tourism, and ecosystem services (**Abdelbaki**, 2022).

The northern delta lakes of Egypt, especially the Manzala Lake, are receiving high attention as pivotal water resources in Egypt. They are one of Egypt's most valuable fish sources (producing more than 40% of all Egyptian fish) and important conservation areas for Egyptian flora and migratory birds. However, they are threatened by problems of increased freshwater via various agricultural drains, as well as eutrophication, pollution, and environmental deterioration. These environmental changes have reduced commercial fish species capture and have had an important impact on the local fishery. Furthermore, the rising levels of lake pollution have a negative effect on both the human and environment (Aly-Eldeen et al., 2023; Shalloof et al., 2023).

Lake Manzala, the largest Egyptian coastal lake and one of Egypt's most lucrative fish sources (~14% of the total annual Egyptian fisheries production), has been evaluated with various pollutants. However, to the best of our knowledge, there were no reported studies on the determination of LAS in Manzala Lake. Therefore, the present study aimed to evaluate the physicochemical characteristics and determine the levels of linear alkylbenzene sulfonates (LAS) in Manzala Lake water.

MATERIALS AND METHODS

1. Study area description

The current investigation was conducted in a lake with brackish water (8–13 ‰) that is rather shallow and has three inlets (boughazes) leading to the Mediterranean Sea named Manzala in northeastern Egypt on the Nile Delta near the city of Port Said (Elshinnawy & Almaliki, 2021; Shalloof et al., 2023). It is the largest coastal lake (about 1000km²) of the northern deltaic lakes of Egypt, on the fringe of the Mediterranean Sea. It is 50km long and 30km wide, situated between latitudes of 31°07°N and 31°30°N and longitudes 31°48°E and 32°17'E (Fig. 1) (Al-Agroudy & Elmorsi, 2022). Manzala Lake serves as an important habitat for a variety of aquatic wildlife and endangered bird species and is also thought to be a feeding ground for migratory birds. It produces 32% of the fish generated by the Egyptian lakes and 44% of the fish produced by the northern lakes (Mirdan, 2019; Shalloof et al., 2023).

Manzala Lake receives water from the Al-Sufra (North), Al-Jamil, Bughaz Al-Raswa, and Al-Qubouti (East) canals. Five major drains—the Bahr El-Baqar, Hadous, El-Serw, Mataria, and Faresquer drains provide the lake with around 5.5 BCM of fresh water annually (**Thompson** *et al.*, **2017**). The drains transport urban, industrial, and agricultural trash from six governorates; namely, Port Said, Demietta, El-Sharqia, El-Daqahlia, El-Qalubia, and the Great Cairo (**Rasmussen** *et al.*, **2009**).

2. Climatology

The lake's Mediterranean environment, which is hot and dry in the summer and rainy in the winter, has a significant impact on its water budget. The rate of evaporation rises from north to south, peaking in the summer and declining in the winter, and varying between 2.8mm/day in December and 5.4mm/day in June (**Elnaggar & El-Alfy, 2016**). The minimum air temperature ranges from 8.4°C in January to 21.4°C in August, while

the maximum air temperature fluctuates from 18.3°C in January to 31°C in August. The relative humidity ranges between 68% in May and 76% in August. The total annual precipitation reaches about 107mm.

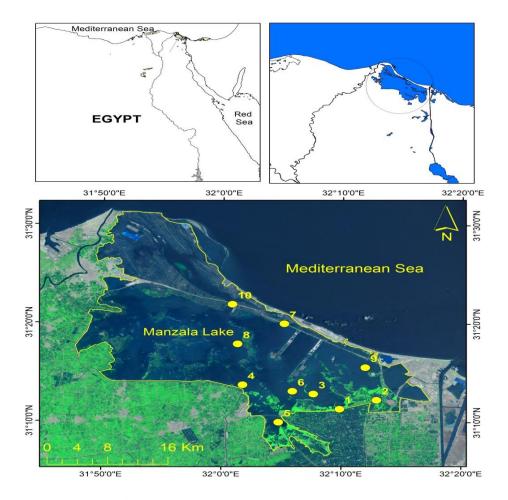


Fig.1. Sampling sites along the Manzala Lake

Sites:

1 (Bashtir) 6 (Bahr kromolos)

2 (Bahr El- Baqr) 7 (Temsah) 3 (Legan) 8 (Alhomra)

4 (Deshdi) 9 (Boughaz Ashtom Al-Jamil)

5 (Genka) 10 (Triangle Open)

3. Sampling and analysis

Using a motor boat, ten surface water samples were seasonally obtained from Manzala Lake from spring 2021 to winter 2022 (Fig. 1). In order to minimize temperature-related oscillations in physical and chemical parameters, measurements were always made in the same order throughout the sample day. On that same day, water

samples were collected in plastic jars and delivered to the lab. Upon arrival, the samples were stored in a refrigerator at 4°C before examination.

3.1. Physicochemical parameters and nutrient salts

Water depth and transparency were measured in situ according to the methods described by APHA (1999). A regular Schmidt thermometer and a portable digital pH meter (HANNA equipment, research model 211) were used to take instantaneous measurements of the water's temperature and pH in the field. The salinity was estimated using a salinity-conductivity meter (Thermo, Orion 150A+ advanced conductivity). Using a conductivity meter (Corning, NY 14831, USA), electrical conductivity was directly measured. Dissolved oxygen concentration was measured using the traditional Winkler method, and total alkalinity was determined using the titration method (APHA, 1999). Oxidizable organic matter was measured using the permanganate oxidation method (FAO, 1975). Total suspended solids (TSS) were measured in the lab as the difference in the dry weight of the standard Whatman filter paper No. 1 under vacuum before and after filtration of 100ml subsamples of a well-mixed water sample (dried at 105°C to constant weight (APHA, 1989). The preferred method for assessing total hardness is the ethylene diamine tetra-acetic acid titrimetric method, which was described by APHA (1999).

The procedures outlined by **Grasshoff** *et al.* (1999) were used to determine the nutrient salts in water samples. The developed colors were spectrophotometrically measured, and all concentrations were expressed as mg/l.

3.2. Linear alkyl bnzene sulfonates (LAS)

Koga *et al.* (1999) investigated the spectrophotometer approach for the quick detection of surfactants (LAS), using methylene blue (MB) as a cationic dye. The method was established on the production of an associated ion pair (LAS-MB ion pair) in water at a 1:1 molar ratio between linear alkylbenzene sulfonates, an anionic surfactant, and methylene blue, a cationic dye, which could then be easily extracted into the organic phase (chloroform). LAS measurements were carried out using a UV-150-02 Shimadzu double-beam spectrophotometer.

4. Statistical analysis

The one-way ANOVA test was employed to detect the differences in analyses of all parameter concentrations in water between study stations and different seasons. Furthermore, differences between each pair of study sites and seasons were examined using multiple range comparisons (post-hoc tests: Tukey HSD). Probability values \leq 0.001 were very highly significant, \leq 0.01 were highly significant, \leq 0.05 were significant, and > 0.05 were not significant.

As a measure of similarity, hierarchical cluster analysis (HCA) was utilized. This technique was used to determine any similarity between the sampling sites and identify reasonably homogeneous groups of samples with similar attributes. A Pearson correlation

test was also utilized to investigate the relationship between the measured variables. SPSS 16.0 was employed to conduct the statistical analysis.

RESULTS AND DISCUSSION

1. Physicochemical characteristics and nutrients of Manzala Lake

1.1. Depth of the lake

The Manzala Lake has a shallow water depth, with the minimum value (10 cm) at site 10 during spring and the maximum value (190 cm) at site 7 during winter. Its variation (Table 1) in the lake depends on the diverse topography of the lake bottom. Depth is an important measure of hydrology because it influences other environmental elements like as nutrient content, temperature variation, and the intensity of underwater light. Increased water depth decreases light intensity, which restricts the photosynthesis of submerged aquatic plants in shallow lakes (**Zouh** et al., 2017). The one-way ANOVA test and multiple range comparisons (post-hoc tests: Tukey HSD) revealed that there was no significant difference in the lake's depth between different seasons or sites (P > 0.05). These results are consistent with those of previous studies (Elshinnawy & Almaliki,

2021; Al-Agroudy & Elmorsi, 2022).

1.2. Temperature

Our results showed that the Manzala Lake's water temperature fluctuated between 14°C in the autumn and 30°C in the summer and spring, with hardly detectable variances between the sampling stations (Table 1). Water temperature influences the photosynthesis process in water, the degradation of organic matter, and the rate of biochemical activity and respiratory rate of the inhabitant organisms (Ravn et al., 2020). Therefore, it can be influenced by turbidity since these suspended particles absorb heat from solar radiation. Additionally, high water temperatures can increase the solubility of toxic elements, including heavy metals as well as compounds such as ammonia (Dey et al., 2021).

The one-way ANOVA test's statistical results showed that there was a highly significant change in the lake's water temperature between the seasons ($P \le 0.001$). Very significant differences ($P \le 0.001$) between all seasons were found using multiple range comparisons, except for high significant differences between autumn and winter $(P \le 0.01)$ and significant differences between spring and summer ($P \le 0.05$). However, no significant differences were found between Manzala Lake sites (P>0.05).

The lake's water temperature can be categorized as follows: summer > spring > winter > autumn. This variation in water temperature is mostly influenced by the seasons' varying air temperatures, such as deeper water, time of collection, length of day, season, waves, wind, and solar radiation (Elsayed et al., 2019; Heneash et al., 2021). The results described above are in line with the investigations of **Mahmoud** et al. (2022), and **Serag** et al. (2022). The obtained temperature values in all studied sites in the present study harmonize with Egyptian standard regularities (temperature not exceeding 35°C) (EEAA, 2003).

1.3. Transparency

In the present study, water transparency appeared at its lowest value (5cm) at site 10 during the summer and autumn seasons and at site 4 during the winter season; however, the highest transperancy (25cm) was recorded at site 6 during the spring and autumn seasons, at site 8 during the autumn season, and at site 9 during the spring season. The annual mean values varied between 9.50 ± 3.07 cm at site 10 and 20.50 ± 2.10 cm at site 9 (Table 1). No significant change was found in water transparency across seasons or between sites according to the one-way ANOVA test (P > 0.05). Tukey HSD tests also revealed no discernible variations across all seasons and sites.

Water transparency, which affects primary productivity, is the depth at which light can penetrate water. It is measured by the quantity of organic and inorganic particles, including suspended solids, sediment from erosion, algae, and phytoplankton (Goher et al., 2018). It was noticed that there are low transparency values at all sites, which indicate turbidity in the lake water due to massive amounts of various wastes discharged into the lake. Moreover, decreased values of water transparency in the present study may be linked to the shallowness of the lake and the wind shear effect's ongoing disruption of the mud bottom (Bek et al., 2018). The obtained results coincide with those of Abd El-Hamid et al. (2017) and Goher et al. (2017).

Table 1. Seasonal fluctuations of water depth, surface water temperature, and transparency value (Annual mean ±Standard Error) in Manzala Lake during spring 2021 to winter 2022

| Parameter | Sites | Spring | Summer | Autumn | Winter | Min. | Max. | Annual mean | P value |
|------------------|-------|--------|--------|--------|--------|------|------|----------------|---------|
| | 1 | 40 | 120 | 60 | 50 | 40 | 120 | 67.50±17.97 | |
| | 2 | 120 | 75 | 80 | 130 | 75 | 130 | 101.25±13.90 | |
| | 3 | 90 | 60 | 120 | 80 | 60 | 120 | 87.50±12.50 | |
| (n) | 4 | 70 | 100 | 130 | 110 | 70 | 130 | 102.50±12.50 | |
| (cr | 5 | 80 | 90 | 130 | 100 | 80 | 130 | 100.00±10.80 | 0.525 |
| Depth (cm) | 6 | 120 | 100 | 120 | 100 | 100 | 120 | 110.00±5.77 | 0.535 |
| De | 7 | 60 | 27 | 50 | 190 | 27 | 190 | 81.75±36.74 | |
| | 8 | 110 | 110 | 130 | 100 | 100 | 130 | 112.50±6.29 | |
| | 9 | 80 | 80 | 160 | 35 | 35 | 160 | 88.75±26.01 | |
| | 10 | 10 | 15 | 30 | 150 | 10 | 150 | 51.25±33.19 | |
| Range | | 10-120 | 15-120 | 30-160 | 35-190 | | | | |
| P value | | | 0.2 | 283 | | | | | |
| | 1 | 24 | 29 | 16 | 19 | 16 | 29 | 22.00±2.86 | |
| O | 2 | 24 | 29 | 17 | 18 | 17 | 29 | 22.00 ± 2.80 | |
| °) | 3 | 26 | 28 | 14 | 18 | 14 | 28 | 21.50±3.30 | |
| tur | 4 | 24 | 27 | 15 | 19 | 15 | 27 | 21.25 ± 2.66 | 1.000 |
| era | 5 | 26 | 27 | 15 | 19 | 15 | 27 | 21.75±2.87 | 1.000 |
| Temperature (°C) | 6 | 26 | 27 | 15 | 18 | 15 | 27 | 21.50±2.96 | |
| Te | 7 | 28 | 29 | 17 | 18 | 17 | 29 | 23.00±3.19 | |
| | 8 | 30 | 27 | 16 | 19 | 16 | 30 | 23.00±3.29 | |

| | 9 | 26 | 30 | 18 | 19 | 18 | 30 | 23.25±2.87 | |
|-------------------|----|-------|-------|-------|-------|----|----|------------|-------|
| | 10 | 29 | 29 | 18 | 19 | 18 | 29 | 23.75±3.04 | |
| Range | | 24-30 | 27-30 | 14-18 | 18-19 | | | | |
| P value | | | 0.0 | 000 | | | | | |
| | 1 | 20 | 10 | 15 | 10 | 10 | 20 | 13.75±2.39 | |
| | 2 | 10 | 10 | 18 | 10 | 10 | 18 | 12.00±2.00 | |
| Ê | 3 | 20 | 11 | 15 | 15 | 11 | 20 | 20.00±1.84 | |
| Transparency (cm) | 4 | 20 | 20 | 20 | 5 | 5 | 20 | 16.25±3.75 | |
| enc | 5 | 20 | 15 | 20 | 15 | 15 | 20 | 17.50±1.44 | 0.200 |
| par | 6 | 25 | 15 | 25 | 10 | 10 | 25 | 18.75±3.75 | 0.209 |
| sue | 7 | 10 | 17 | 10 | 20 | 10 | 20 | 14.25±2.53 | |
| Ţ | 8 | 20 | 20 | 25 | 8 | 8 | 25 | 18.25±3.61 | |
| | 9 | 25 | 15 | 20 | 22 | 15 | 25 | 20.50±2.10 | |
| | 10 | 10 | 5 | 5 | 18 | 5 | 18 | 9.50±3.07 | |
| Range | | 10-25 | 5-20 | 5-25 | 5-22 | | | | |
| P value | | | 0.1 | 66 | | | | | |

1.4. The pH values

The pH values in the present study varied from a minimum of 6.93 at site 6 during winter to a maximum of 9.70 at site 10 during autumn, with an annual mean range of 7.91 ± 0.34 at site 5 and 8.60 ± 0.44 at site 10. There was a high significant difference between the spring and winter seasons and between the winter and autumn seasons ($P\le0.001$), and a significant difference was detected between winter and summer ($P\le0.01$). No significant difference existed across the sites (P>0.05). Numerous waterbased life processes depend heavily on pH. The toxicity of heavy metals is immobilized by a slightly alkaline pH because the acidity of the medium encourages and improves their solubility and movement in water, allowing the metals to adsorb on algae and other plants within the aquatic food web (**Loucif** *et al.*, **2020**).

The pH values can be listed in the following order: spring, autumn, summer, and winter. Its variation depends on interactions between different chemicals dissolved in water, aquatic plant photosynthetic activity, aquatic organism respiration, organic matter decay, precipitation and/or dissolution of CO2 components, and oxidation-reduction reactions (Ahmed, 2020). The obtained values of pH in all investigated sites (Table 2) reside between neutral and moderately alkaline. The relative rise in pH values during spring can be related to photosynthesis and aquatic plants growth, where photosynthesis consumes CO2 and causes pH values to increase. While the relative decrease in pH values during winter may be attributed to an increase in carbon dioxide solubility due to a decrease in water temperature and thus causing an increase in bicarbonate ions (Goher et al., 2017); these results agreed with the finding of Deyab et al. (2020) while exceeding the Egyptian standard.

1.5. Salinity

The lowest salinity value was 0.78 ‰ at site 2 during autumn, while the highest value was 39.95 ‰ at site 10 during the summer. The annual mean fluctuated between 1.58±0.25 ‰ at site 5 and 19.86±7.64 ‰ at site 10. Statistically, there were no significant differences between seasons or sites. Salinity is the primary supporting factor that influences fish growth, density, and aquatic population growth (Vermal et al., 2022). It influences organism growth by osmoregulating body minerals with those of the surrounding water (Heneash et al., 2021).

The high salinity values (Table 2) were recorded at the southern sites of the lake caused by freshwater flowing through the northern drainage channels, and the lowest ones were in the southern area due to the influence of the Mediterranean Sea and the lack of freshwater (Bek et al., 2018). These results coincide with those of Abd El-Hamid et al., (2017) and Devab et al. (2020).

1.6. Electrical conductivity

Electrical conductivity (EC) is directly proportional to dissolved ion concentrations. It was noticed that EC in the Manzala Lake can be arranged in the following order: summer > autumn > spring > winter. EC ranged between the lowest value of 2.88mmhos/cm at site 5 in spring and the highest value of 54.50mmhos/cm at site 10 in summer (Table 2). The one-way ANOVA test recorded a highly significant difference in lake water conductivity between different sites ($P \le 0.001$). Multiple range comparisons showed significant differences between site 10 and sites 1, 2, 3, and 5 ($P \le 0.05$). However, there were no major seasonal differences.

EC is affected by the concentration and level of ion dissociation, temperature, and ion migration speed in the electric field (Soliman et al., 2022). Its high values affect the permeability, irrigation, and soil structure; these negative effects are recognized as salinity hazards, which harm the growth of plants (Tekade et al., 2011). The northern sector of the lake had the highest conductivity measurement during summer due to the increase in seawater intrusion into the lake, while the low values were in the east and south sectors during winter as a result of low temperatures and the entrance of brackish water and freshwater through the drains (Mahmoud et al., 2022). These results are in agreement with the finding of Hafez et al. (2019).

1.7. Total suspended solids

Total suspended solids (TSS) fluctuated between 28.50mg/l at site 3 and 164mg/l at site 10. The annual mean extended from 51.50 ± 8.26 mg/l at site 5 to 100.88 ± 24.48 mg/l at site 10. Analysis of variance (ANOVA) results showed a significant difference between seasons. Multiple range comparisons detected a significant difference between summer and autumn ($P \le 0.05$). Suspended solids enter the water column as tiny organic particles as a result of the breakdown of animals, plants, and algae. Turbidity levels had a direct impact on TSS concentrations, where increased turbidity causes higher water column TSS content, and vice versa (Morsy et al., 2020). The obtained results (Table 3) of the concentration of TSS at all studied sites are within the permitted limits for

estuarine water and also agree with those of **Afifi** (2015), but lower than the data recorded in the study of **Ismail and Hettiarachchi** (2017), which may be due to the increased fresh runoff from drains and canals.

Table 2. Seasonal fluctuations of pH, salinity, and electrical conductivity value (mean \pm SE) in Manzala Lake during spring 2021 to winter 2022

| Parameter | Sites | Spring | Summer | Autumn | Winter | Min. | Max. | Annual mean | P value |
|--------------|----------|----------------|----------------|----------------|----------------|-------|-------|-----------------|------------|
| | 1 | 8.68 | 7.70 | 7.70 | 8.05 | 7.70 | 8.68 | 8.30±0.23 | |
| | 2 | 8.16 | 7.70 | 7.80 | 8.26 | 7.70 | 8.26 | 7.98±0.14 | |
| | 3 | 8.87 | 8.50 | 8.20 | 7.30 | 7.30 | 8.87 | 8.22±0.34 | |
| | 4 | 8.86 | 7.80 | 8.80 | 7.36 | 7.36 | 8.86 | 8.21±0.37 | |
| = | 5 | 8.83 | 8.00 | 7.40 | 7.40 | 7.40 | 8.83 | 7.91±0.34 | |
| Hd | 6 | 8.88 | 9.00 | 9.10 | 6.93 | 6.93 | 9.10 | 8.48 ± 0.52 | |
| | 7 | 8.77 | 9.00 | 8.50 | 7.75 | 7.75 | 9.00 | 8.51±0.27 | |
| | 8 | 8.78 | 8.50 | 9.30 | 7.15 | 7.15 | 9.30 | 8.43 ± 0.46 | 0.883 |
| | 9 | 8.73 | 8.50 | 9.50 | 7.40 | 7.40 | 9.50 | 8.53±0.43 | |
| | 10 | 8.43 | 8.70 | 9.70 | 7.58 | 7.58 | 9.70 | 8.60 ± 0.44 | |
| Range | | 8.16-8.88 | 7.70-9 | 7.40-9.70 | 7.15-8.26 | | | | |
| P value |) | | 0.0 | 000 | | | | | |
| | 1 | 1.80 | 2.35 | 1.00 | 1.80 | 1.00 | 2.35 | 1.74 ± 0.28 | |
| | 2 | 1.80 | 2.25 | 0.78 | 1.60 | 0.78 | 2.25 | 1.61±0.31 | |
| | 3 | 3.30 | 5.35 | 1.25 | 2.50 | 1.25 | 5.35 | 3.10±0.86 | |
| (0% | 4 | 2.70 | 5.45 | 3.75 | 1.50 | 1.50 | 5.45 | 3.35 ± 0.84 | |
| Salinity (‰) | 5 | 1.50 | 2.20 | 1.00 | 1.60 | 1.00 | 2.20 | 1.58±0.25 | |
| <u>iii</u> | 6 | 4.60 | 4.10 | 6.13 | 2.30 | 2.30 | 6.13 | 4.28±0.79 | |
| S | 7 | 7.20 | 36.65 | 10.25 | 7.30 | 7.20 | 36.65 | 15.35±7.14 | |
| | 8 | 9.50 | 27.15 | 8.18 | 6.70 | 6.70 | 27.15 | 12.88±4.79 | 0.013 |
| | 9 | 8.00 | 6.15 | 9.18 | 27.70 | 6.15 | 27.70 | 12.76±5.02 | |
| | 10 | 23.50 | 39.95 | 8.68 | 7.30 | 7.30 | 39.95 | 19.86±7.64 | |
| Range | | 1.80- 23.50 | 2.20- 39.95 | 0.78- 10.25 | 1.50- 27.70 | | | | |
| P value | • | | 0.215 | | | | | | |
| | 1 | 3.48 | 4.10 | 3.78 | 3.47 | 3.47 | 4.10 | 3.71±0.15 | |
| cm) | 2 | 3.49 | 3.61 | 3.74 | 3.21 | 3.21 | 3.74 | 3.51±0.11 | |
| (mmhoS/cm) | 3 | 6.18 | 8.56 | 7.13 | 4.72 | 4.72 | 8.56 | 6.65±0.81 | |
| mh | 4 | 5.09 | 8.61 | 13.66 | 2.96 | 2.96 | 13.66 | 7.58±2.34 | |
| | 5 | 2.88 | 3.76 | 3.66 | 3.21 | 2.88 | 3.76 | 3.38±0.02 | |
| vity | 6 | 8.26 | 6.74 | 15.46 | 4.39 | 4.39 | 15.46 | 8.71±2.39 | |
| ıcti | 7 | 12.52 | 49.40 | 22.60 | 12.92 | 12.52 | 49.40 | 24.36±8.67 | |
| Conductivity | 8 | 16.24 | 39.00 | 20.40 | 12.02 | 12.02 | 39.00 | 21.92±5.95 | 0.001 |
| ప | 9 | 13.87 | 9.66 | 25.80 | 44.00 | 9.66 | 44.00 | 23.33±7.69 | |
| | 10 | 37.30 | 54.50 | 24.25 | 12.88 | 12.88 | 54.50 | 32.23±8.94 | |
| Range | | 2.88- 37.30 | 3.61- 54.50 | 3.66- 25.80 | 2.96- 44.00 | | | | |
| P value | <u> </u> | | 0.511 | | | | | | |

1.8. Dissolved oxygen

The results revealed that the dissolved oxygen (DO) experienced pronounced variations between the sampling stations, falling within a range of 0–18mg/l. It was noticed that the variation of DO (Table 3) concentrations during the four seasons in the Manzala Lake can be arranged as spring > summer > autumn > winter. Decreased DO concentrations during the winter may be due to the low photosynthesis activity during this season. The increased DO concentrations during spring were due to the increase in photosynthetic activity that releases a significant amount of O_2 to the surrounding water ecosystem (Elsayed *et al.*, 2019). Multiple range comparisons detected a very high significant difference between site 2 and site 8 ($P \le 0.001$), high significant differences between site 1 and site 8; site 2 and site 6; and between site 2 and site 9 ($P \le 0.01$), and significant differences were detected between site 1 and site 4; site 1 and site 9; site 2 and site 3; site 2 and site 10; site 2 and site 7, and between site 5 and site 8 ($P \le 0.05$). However, multiple range comparisons recorded no significant differences between all sites.

The amount of dissolved oxygen in the water is a crucial water quality measure for assessing the health of an aquatic environment given that it is essential for life and the existence of aquatic life. The majority of the oxygen in solution is derived from the atmosphere, while some also originates from plants through photosynthesis and diffusion in the water (Heneash *et al.*, 2021). The complete depletion of DO at sites 1 and 2 (the southern sector of the lake) in almost all seasons was as a result of the effect of domestic waste and sewage from the Bahr El-Baqar drain; these results match those of Elnaggar and El-Alfy (2016). Furthermore, the concentration of DO at northern sites was within the allowable limits of the Egyptian standard regularities (DO≥ 5mg/l) and WHO standards, and vice versa with respect to the southern sites.

1.9. Oxidizable organic matter

The oxidizable organic matter (OOM) value ranged between the minimum value of 6.72 mg/l at site 4 in autumn and at site 9 in winter and the maximum value of 28.80 mg/l at site 2 in spring (Table 3). The annual mean fluctuated between 12.16 ± 2.21 mg/l at site 9 and 17.12 ± 0.56 mg/l at site 10. Organic matter is crucial in aquatic systems. It influences biological availability, nitrogen cycle, chemical transport, and interactions as well as biogeochemical processes. Organic matter can come from both autochthonous and allochthonous sources. Autochthonous sources include the excretion of organic matter, which is driven by living organisms, and the decomposition of dead organisms and detritus through long chains of decomposition processes. Allochthonous sources include river runoff that enters aquatic systems, with less air transport (**Shreadah** *et al.*, **2014**). Remarkably, an extremely high significant difference was found between spring and autumn ($P \le 0.001$), as well as highly significant differences between spring and summer and between autumn and winter ($P \le 0.01$). While, no significant difference was found between sites (P > 0.05).

The fluctuations in the concentration of oxidizable organic matter during the four seasons in the Manzala Lake can be arranged as follows: spring> winter > summer > autumn. The decrease in OOM in autumn was a result of the reduction of biological activities owing to the low water temperature, as well as the decrease in the rate of

bacterial organic matter decomposition, while the increase in OOM value in spring was due to the organic supply introduced into the drains and the lake itself (**Darwish**, 2017). These results agree with those of **Shreadah** *et al.* (2014) and **Basiony** (2015).

Table 3. Seasonal fluctuations of TSS, DO and OOM values (mean \pm SE) in Manzala Lake during spring 2021 to winter 2022

| Parameter | Site | Spring | Summer | Autumn | Winter | Min. | Max. | Annual mean | P value |
|-------------------------------|------|----------------|----------------|----------------|---------------|-------|--------|------------------|---------|
| | 1 | 65.00 | 43.50 | 68.50 | 33.50 | 33.50 | 68.50 | 52.63±8.44 | |
| Total suspended solids (mg/l) | 2 | 109.00 | 44.50 | 76.00 | 28.50 | 28.50 | 109.00 | 64.50±17.82 | |
| s (n | 3 | 113.00 | 65.00 | 112.00 | 52.00 | 52.00 | 113.00 | 85.50±15.81 | |
| olide | 4 | 83.00 | 38.50 | 86.50 | 104.67 | 38.50 | 104.67 | 78.17±14.05 | |
| g g | 5 | 55.50 | 44.00 | 72.50 | 34.00 | 34.00 | 72.50 | 51.50±8.26 | |
| nde | 6 | 73.00 | 39.00 | 61.00 | 77.00 | 39.00 | 77.00 | 62.50±8.54 | 0.533 |
| spe | 7 | 43.50 | 69.50 | 160.00 | 41.00 | 41.00 | 160.00 | 78.50±27.92 | |
| l su | 8 | 83.50 | 64.50 | 61.50 | 77.50 | 61.50 | 83.50 | 71.75±5.23 | |
| ota | 9 | 41.50 | 60.50 | 72.00 | 97.00 | 41.50 | 97.00 | 67.75±11.60 | |
| H | 10 | 89.50 | 104.50 | 164.00 | 45.50 | 45.50 | 164.00 | 100.88±24.48 | |
| Range | | 41.50- | 38.50- | 61.00- | 28.50- | | | | |
| | | 113.00 | 104.50 | 164.00 | 104.67 | | | | |
| P value | | 0.10 | 0.027 | 0.10 | 0.00 | 0.00 | 0.40 | 207.202 | |
| | 1 | 8.10 | 0.00 | 0.10 | 0.00 | 0.00 | 8.10 | 2.05±2.02 | |
| (V) | 2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00±0.00 | |
| Dissolved oxygen (mg/l) | 3 | 10.50 | 6.10 | 14.20 | 5.10 | 5.10 | 14.20 | 8.98±2.10 | |
| gen | 4 | 9.40 | 13.30 | 12.50 | 9.90 | 9.40 | 13.30 | 11.28±0.96 | |
| S X | 5 | 9.30 | 6.40 | 0.20 | 0.00 | 0.00 | 9.30 | 3.98±2.31 | 0.000 |
| p _a | 6 | 10.80 | 10.20 | 10.80 | 7.20 | 7.20 | 10.80 | 9.75±0.86 | 0.000 |
| olve | 7 | 10.00 | 11.00 | 8.20 | 8.00 | 8.00 | 11.00 | 9.30±0.72 | |
| Oiss | 8 | 15.10 | 18.00 | 9.50 | 6.70 | 6.70 | 18.00 | 12.33±2.57 | |
| _ | 9 | 16.40 | 9.80 | 11.00 | 5.20 | 5.20 | 16.40 | 10.60±2.30 | |
| | 10 | 8.00 | 8.80 | 9.50 | 6.60 | 6.60 | 9.50 | 8.23±0.62 | |
| Range | | 0.00- 16.40 | 0.00- 18.00 | 0.00- 14.20 | 0.00- 9.90 | | | | |
| P value | e | 10.10 | 0.162 | 11.20 | 7.70 | | | | |
| | 1 | 17.92 | 9.92 | 7.36 | 16.32 | 7.36 | 17.92 | 12.88±2.52 | |
| c matter (mg/l) | 2 | 28.80 | 10.88 | 8.00 | 19.52 | 8.00 | 28.80 | 16.80±4.69 | |
| ter | 3 | 20.80 | 12.80 | 11.84 | 14.08 | 11.84 | 20.80 | 14.88±2.03 | |
| nat | 4 | 18.56 | 10.56 | 6.72 | 17.92 | 6.72 | 18.56 | 13.44±2.88 | |
| uic 1 | 5 | 18.56 | 11.84 | 8.96 | 16.00 | 8.96 | 18.56 | 13.84±2.14 | |
| | 6 | 17.28 | 11.84 | 7.36 | 17.28 | 7.36 | 17.28 | 13.44 ± 2.40 | |
| e or | 7 | 16.32 | 16.96 | 12.16 | 16.32 | 12.16 | 16.96 | 15.44±1.10 | |
| Oxidizable organi | 8 | 17.92 | 16.00 | 14.40 | 17.60 | 14.40 | 17.92 | 16.48 ± 0.81 | 0.842 |
| idiz | 9 | 17.28 | 13.44 | 11.20 | 6.72 | 6.72 | 17.28 | 12.16±2.21 | |
| Oxi | 10 | 16.00 | 17.92 | 16.32 | 18.24 | 16.00 | 18.24 | 17.12±0.56 | |
| Range | | 16.00- | 9.92- | 6.72- | 6.72- | | | | |
| | | 28.80 | 17.92 | 16.32 | 19.52 | | | | |
| P value | e | | 0.000 | | | | | | |

1.10. Total hardness

In the current study, the lowest value of total hardness was 184mg/l at site 6 during winter, while the highest value 480 was recorded at site 3 during winter. The annual mean extended between 292.00±36.43mg/l at site 7 and 363.50±51.37mg/l at site 3 (Table 4). There were extremely high significant differences between winter and spring, winter and summer and, on the other hand, between winter and autumn ($P \le 0.001$) in addition to thet a high significant difference between spring and autumn ($P \le 0.01$). It is worthnoting that, no significant differences were detected between sites. The higher total hardness levels at the studied sites could be due to industrial waste, which facilitates carbonate dissolution (Devab et al., 2020); these results are in agreement with those obtained in the study of Beheary et al. (2019). Water hardness was attributed to the presence of Ca and Mg sulphates and chlorides. However, in rare circumstances, permanent hardness is generated by sulphates and chlorides of Fe, Mn, and Al. Water hardness is defined as its capacity to react with detergent. The increasing hardness is essentially the result of more detergents being added on a regular basis in housing areas that drain into stream bodies. All stages of cleaning, from laundry and dishwashing to bathing and grooming, come into contact with hard water. Although hard water is not dangerous, dealing with it at home can be inconvenient (**Dey** et al., 2021).

1.11. Total alkalinity

The total alkalinity values (Table 4) showed a wide range (20–140mg/l), with highly significant differences between seasons. No significant differences were found between sites. The greatest total alkalinity value in the Manzala Lake could be attributed to the decomposition of organic compounds caused by various effluents released into the lake, such as increased sewage and household, agricultural, and industrial drainage water (Elnaggar & El-Alfy, 2016). These results concur with those of Elmorsi et al. (2017). Total alkalinity is significant as it affects the chemistry of CO₂, the speciation of trace metals, the buffering ability of water, the study of mixing processes between various water masses, and hydrographic features. It is influenced by various processes, including respiration, photosynthesis, CaCO₃ dissolution, sulfide oxidation, sulfide reduction, nitrification, and denitrification (Ahmed, 2020).

1.12. Ammonium

The lowest value of ammonium (NH4) was 0.07mg/1 at site 4 during summer, and the highest was 2.31mg/1 at sites 1 and 5 in autumn. The concentration of ammonium at most sites in the present study (Table 5) exceeds the permissible limit of Law 48 of 1982 (<0.5 mg/l). Statistically, there was no significant difference between seasons but highly significant differences between sites. Ammonia is a toxic byproduct of nitrogenous organic matter breakdown in water. It can be produced naturally through waste decomposition, gas exchange, or protein catabolism. It can also be found in surface water systems due to forest fires, nitrogen fixation processes, and industrial applications (**Ibearugbulam** *et al.*, **2021**). The increased concentrations of ammonium in the southern

| | | | | | | | | | P |
|-------------------------|------|---------|---------|---------|---------|------|------|--------------------|-------|
| Parameter | Site | Spring | Summer | Autumn | Winter | Min. | Max. | Annual mean | value |
| | 1 | 324 | 340 | 366 | 202 | 202 | 366 | 308.00±36.38 | |
| (| 2 | 460 | 328 | 270 | 190 | 190 | 460 | 312.00 ± 56.87 | |
| mg | 3 | 480 | 364 | 380 | 230 | 230 | 480 | 363.50±51.37 | |
| () 83 | 4 | 420 | 370 | 380 | 200 | 200 | 420 | 342.50 ± 48.71 | |
| nes | 5 | 290 | 350 | 320 | 210 | 210 | 350 | 292.50±30.10 | |
| Total hardness (mg/l) | 6 | 430 | 332 | 370 | 184 | 184 | 430 | 329.00 ± 52.37 | |
| ha | 7 | 356 | 354 | 234 | 224 | 224 | 356 | 292.00±36.43 | |
| tal | 8 | 370 | 424 | 254 | 194 | 194 | 424 | 310.50±52.59 | 0.984 |
| Tc | 9 | 318 | 390 | 280 | 230 | 230 | 390 | 304.50±33.72 | |
| | 10 | 420 | 366 | 258 | 234 | 234 | 420 | 319.50 ± 44.12 | |
| Range | | 290-480 | 328-424 | 234-380 | 184-234 | | | | |
| <i>P</i> value |) | | 0.000 | | | | | | |
| | 1 | 80 | 120 | 80 | 90 | 80 | 120 | 92.50±9.46 | |
| <u> </u> | 2 | 70 | 100 | 50 | 90 | 50 | 100 | 77.50±11.09 | |
| mg | 3 | 60 | 110 | 20 | 100 | 20 | 110 | 72.50±20.56 | |
| 3 | 4 | 80 | 110 | 40 | 80 | 40 | 110 | 77.50 ± 14.36 | |
| i.i. | 5 | 80 | 110 | 70 | 90 | 70 | 110 | 87.50±8.54 | |
| kal | 6 | 90 | 110 | 40 | 90 | 40 | 110 | 82.50 ± 14.93 | |
| Te Te | 7 | 70 | 90 | 50 | 80 | 50 | 90 | 72.50 ± 8.54 | |
| Total alkalinity (mg/l) | 8 | 100 | 100 | 80 | 80 | 80 | 100 | 90.00±5.77 | 0.807 |
| \mathbf{T}_0 | 9 | 80 | 100 | 70 | 50 | 50 | 100 | 75.00±10.41 | |
| | 10 | 80 | 90 | 140 | 90 | 80 | 140 | 100.00 ± 13.54 | |
| Range | | 60-100 | 90-120 | 20-140 | 50-100 | | | | |
| P value | • | | 0.001 | | | | | | |

Table 4. Seasonal fluctuations of total hardness and total alkalinity values (mean±SE) in Manzala Lake during spring 2021 to winter 2022

parts of the lake, especially at sites 1 and 2, may be corresponding to the direct influence of domestic sewage input into this area of the lake via the Bahr El-Baqr drain (Elnaggar & El-Alfy, 2016); these results agree with the findings in the study of Mahmoud *et al.* (2022).

1.13. Nitrite

Nitrite (NO2) levels in the Manzala Lake vary between sites, ranging from 0mg/1 at site 8 during summer to 0.54mg/1 at sites 3 during autumn, and similarly at site 6 During the winter (Table 5), with a significant difference observed between seasons. Nitrite, a naturally occurring intermediate product in bacterial nitrification and denitrification processes, is known as the "invisible killer of fish" due to its ability to oxidize hemoglobin, turn blood and gills brown, and impede breathing. Nitrite is created by the Nitrosomonas bacteria when ammonia and oxygen are combined (Ahmed, 2020). The study found no significant differences between sites, indicating that nitrite is a crucial intermediate product in the nitrogen transformation process. There were highly significant differences between seasons. The results in this study can be related to the nature of nitrite having a short lifetime in water since it is quickly converted to nitrate by bacteria. Due to this fact, pollution with nitrite is relevant for aquatic organisms; these results agree with the study of Ismail and Hettiararchchi (2017).

1.14. Nitrate

The concentrations of nitrate (NO3) in the Manzala Lake vary between 0.23mg/l at site 1 in autumn and 7.12mg/l at the same site in spring, with an annual mean of 2.34±1.18mg/l at site 5 (Table 5). Statistical analysis showed a significant difference in nitrate concentrations between seasons, with no significant differences between sites. Excess nitrate concentrations in aquatic systems may result from agricultural fertilizers, algae blooms, and ecosystem function changes (Singh & Craswell, 2020). The increased concentration of nitrate at site 1 (south part) may be due to domestic, industrial, and agricultural runoff from fertilizers. Increased concentrations of nitrate in hot seasons are attributed to the high activity of nitrifying bacteria, which convert nitrite to nitrate ions. These results support the investigation of Bek et al. (2018).

Table 5. Seasonal fluctuations of ammonium, nitrite and nitrate values (mean \pm SE) in Manzala Lake from spring 2021 to winter 2022

| Parameter | Site | Spring | Summer | Autumn | Winter | Mi n. | Max. | Annual mean | P value |
|-------------------|------|-----------|-----------|-----------|-----------|----------|------|-----------------|------------|
| | 1 | 2.21 | 2.21 | 2.31 | 2.24 | 2.21 | 2.31 | 2.24±0.02 | |
| | 2 | 2.26 | 2.21 | 2.30 | 2.23 | 2.21 | 2.30 | 2.25 ± 0.02 | |
| E | 3 | 0.20 | 1.19 | 2.18 | 2.11 | 0.20 | 2.18 | 1.42±0.46 | |
| gm) | 4 | 0.20 | 0.07 | 0.75 | 2.13 | 0.07 | 2.13 | 0.79 ± 0.47 | |
| H | 5 | 0.16 | 2.02 | 2.31 | 2.27 | 0.16 | 2.31 | 1.69±0.51 | |
| onii | 6 | 0.19 | 0.75 | 0.61 | 2.15 | 0.19 | 2.15 | 0.93 ± 0.42 | 0.000 |
| Ammonium (mg/l) | 7 | 0.18 | 0.10 | 0.29 | 0.08 | 0.08 | 0.29 | 0.16 ± 0.05 | |
| An | 8 | 0.17 | 0.10 | 0.37 | 0.11 | 0.10 | 0.37 | 0.19 ± 0.06 | |
| | 9 | 1.08 | 2.20 | 0.54 | 0.24 | 0.24 | 2.20 | 1.01±0.43 | |
| | 10 | 0.14 | 0.10 | 0.48 | 0.09 | 0.09 | 0.48 | 0.20 ± 0.09 | |
| Range | | 0.14-2.26 | 0.07-2.21 | 0.29-2.31 | 0.08-2.27 | | | | |
| P value | | | 0. | 434 | | | | | |
| | 1 | 0.14 | 0.02 | 0.24 | 0.19 | 0.02 | 0.24 | 0.15 ± 0.05 | |
| | 2 | 0.04 | 0.02 | 0.33 | 0.22 | 0.02 | 0.33 | 0.15 ± 0.07 | |
| | 3 | 0.03 | 0.15 | 0.54 | 0.50 | 0.03 | 0.54 | 0.30 ± 0.13 | |
| (I/g | 4 | 0.03 | 0.08 | 0.41 | 0.43 | 0.03 | 0.43 | 0.24 ± 0.10 | |
| (B | 5 | 0.02 | 0.22 | 0.28 | 0.19 | 0.02 | 0.28 | 0.18 ± 0.06 | 0.606 |
| Nitrite (mg/l) | 6 | 0.04 | 0.31 | 0.43 | 0.54 | 0.04 | 0.54 | 0.33 ± 0.11 | 0.606 |
| Ä | 7 | 0.03 | 0.01 | 0.28 | 0.21 | 0.01 | 0.28 | 0.13 ± 0.07 | |
| | 8 | 0.03 | 0.00 | 0.29 | 0.22 | 0.00 | 0.29 | 0.14 ± 0.07 | |
| | 9 | 0.02 | 0.16 | 0.34 | 0.25 | 0.00 | 0.34 | 0.19 ± 0.07 | |
| | 10 | 0.02 | 0.01 | 0.22 | 0.23 | 0.01 | 0.23 | 0.12 ± 0.06 | |
| Range | | 0.02-0.14 | 0.00-0.31 | 0.22-0.54 | 0.19-0.54 | | | | |
| P value | | | | 000 | | | | | |
| T) | 1 | 7.12 | 4.97 | 0.23 | 1.94 | 0.23 | 7.12 | 3.57±1.54 | |
| Nitrate (mg/l) | 2 | 2.11 | 5.25 | 0.28 | 2.02 | 0.28 | 5.25 | 2.42±1.03 | |
| Z | 3 | 3.54 | 5.84 | 0.68 | 1.24 | 0.68 | 5.84 | 2.83±1.18 | |

| | 4 | 4.04 | 4.31 | 0.65 | 1.02 | 0.65 | 4.31 | 2.50±0.97 | |
|---------|----|-----------|------------|-----------|-----------|------|------|---------------|-------|
| | 5 | 2.37 | 5.65 | 0.33 | 1.02 | 0.33 | 5.65 | 2.34±1.18 | |
| | 6 | 3.95 | 6.01 | 0.66 | 1.12 | 0.66 | 6.01 | 2.94±1.26 | 1.000 |
| | 7 | 3.55 | 6.96 | 0.27 | 0.90 | 0.27 | 6.96 | 2.92±1.52 | 1.000 |
| | 8 | 2.40 | 6.78 | 0.29 | 0.65 | 0.29 | 6.78 | 2.53 ± 1.49 | |
| | 9 | 3.78 | 5.55 | 0.46 | 0.93 | 0.46 | 5.55 | 2.68±1.21 | |
| | 10 | 3.24 | 6.19 | 0.25 | 0.83 | 0.25 | 6.19 | 2.63 ± 1.35 | |
| Range | | 2.11-7.12 | 4.321-6.96 | 0.23-0.68 | 0.65-2.02 | | | | |
| P value | | | 0.00 | 00 | | | | | |

1.15. Orthophosphate

In this study, the values of orthophosphate (PO₄) were irregularly distributed and fluctuated from 0mg/l at site 7 during autumn and site 8 during summer and autumn to 0.57mg/l at site 9 in spring. The annual mean oscillated from 0.03±0.02mg/l at site 8 to 0.22±0.08mg/l at site 5 (Table 6). Multiple range comparisons showed very high significant differences between spring and summer and between spring and autumn ($P \le$ 0.001) and a high significant difference between spring and winter ($P \le 0.01$). However, no significant differences were found between the different sites. Orthophosphate is the most stable form of phosphate and is used by plants when naturally produced and found in sewage (Mallin & Cahoon, 2020). The increase and decrease of orthophosphate value depend on the source of phosphate, which can be divided into non-point sources of phosphate, including agricultural runoff, stormwater runoff, erosion and sedimentation, atmospheric deposition, and direct animal and wildlife input in addition to point sources, viz wastewater treatment plants, detergents, as well as allowed industrial effluent (Fagbohun et al., 2017; Alimohammadi et al., 2021). The slight increase of orthophosphate in the northern sites of the Manzala Lake during spring is due to sewage overflow from homes, fish farms, and agriculture (Deyab et al., 2020). These results are in agreement with those of **Hafiz** et al. (2019).

1.16. Reactive silicate

The Manzala Lake's silicate (SiO₃) concentrations vary between 0.03mg/l in winter and 7.49mg/l in summer. The annual mean ranges from 1.34 ± 0.49 mg/l at site 4 to 2.75 ± 1.64 mg/l at site 10 (Table 6). Multiple range comparisons revealed very high significant differences ($P \le 0.001$) between summer and spring, summer and autumn, and winter and summer, as well as a high significant difference ($P \le 0.01$) between spring and winter and a significant difference ($P \le 0.05$) between winter and autumn. However, there was no significant difference between the sites. Silicate is a vital nutrient used by diatoms in coastal water to form their siliceous cell walls. It enters the water system through weathering processes on land, transport by water, or biogenic silica dissolution. Reduced river inputs may reduce primary production or alter phytoplankton species composition, which is considered a natural feeding source for certain fish species (**Zhang** *et al.*, **2020**). Increased concentrations of silicates could be a result of modifications in sewage, industrial, and agricultural effluents.

| | ~ | | | | | | | Annual | P |
|--------------------------|------|-----------|-----------|-----------|-----------|------|------|-----------------|-------|
| Parameter | Site | Spring | Summer | Autumn | Winter | Min. | Max. | mean | value |
| | 1 | 0.04 | 0.11 | 0.14 | 0.20 | 0.04 | 0.20 | 0.13±0.03 | |
| | 2 | 0.16 | 0.10 | 0.16 | 0.23 | 0.10 | 0.23 | 0.16 ± 0.03 | |
| ng/ | 3 | 0.39 | 0.04 | 0.08 | 0.19 | 0.04 | 0.39 | 0.17 ± 0.08 | |
| œ (I | 4 | 0.42 | 0.01 | 0.01 | 0.11 | 0.01 | 0.42 | 0.14 ± 0.10 | |
| hat | 5 | 0.43 | 0.08 | 0.15 | 0.21 | 0.08 | 0.43 | 0.22 ± 0.08 | _ |
| dsou | 6 | 0.46 | 0.05 | 0.02 | 0.15 | 0.02 | 0.46 | 0.17 ± 0.10 | 0.635 |
| Orthophosphate (mg/l) | 7 | 0.15 | 0.01 | 0.00 | 0.02 | 0.00 | 0.15 | 0.05 ± 0.04 | |
| rth | 8 | 0.09 | 0.00 | 0.00 | 0.01 | 0.00 | 0.09 | 0.03 ± 0.02 | |
| 0 | 9 | 0.57 | 0.06 | 0.01 | 0.02 | 0.01 | 0.57 | 0.16 ± 0.14 | |
| | 10 | 0.17 | 0.01 | 0.00 | 0.01 | 0.00 | 0.17 | 0.05 ± 0.04 | |
| Range | | 0.04-0.57 | 0.00-0.11 | 0.00-0.16 | 0.01-0.23 | | | | |
| P value | • | | 0.0 | 000 | | | | | |
| | 1 | 1.13 | 4.27 | 2.38 | 0.53 | 0.53 | 4.27 | 2.08±0.83 | |
| | 2 | 2.83 | 4.36 | 2.54 | 0.60 | 0.60 | 4.36 | 2.58 ± 0.77 | |
| ng/l | 3 | 2.21 | 3.06 | 0.45 | 0.25 | 0.25 | 3.06 | 1.49±0.68 | |
| te (I | 4 | 1.75 | 2.50 | 0.76 | 0.34 | 0.34 | 2.50 | 1.34 ± 0.49 | |
| Reactive silicate (mg/l) | 5 | 0.42 | 3.29 | 2.63 | 0.82 | 0.42 | 3.29 | 1.79±0.69 | |
| s sil | 6 | 3.19 | 4.79 | 1.41 | 0.54 | 0.54 | 4.79 | 2.48 ± 0.95 | 0.960 |
| tive | 7 | 2.77 | 2.90 | 1.72 | 0.04 | 0.04 | 2.90 | 1.86±0.66 | |
| reac | 8 | 1.71 | 3.53 | 1.79 | 0.04 | 0.04 | 3.53 | 1.77 ± 0.71 | |
| ~ | 9 | 1.78 | 3.11 | 1.22 | 0.06 | 0.06 | 3.11 | 1.54±0.63 | |
| | 10 | 1.36 | 7.49 | 2.13 | 0.03 | 0.03 | 7.49 | 2.75 ± 1.64 | |
| Range | | 0.42-3.19 | 2.50-7.49 | 0.45-2.63 | 0.03-0.82 | | | | |
| P value | • | | 0.0 | 000 | | | | | |

Table 6. Seasonal fluctuations of orthophosphate and silicate values (mean \pm SE) in Manzala Lake during the period from spring 2021 to winter 2022

2. Linear alkylbenzene sulphonate in Manzala Lake

Table (7) displays the concentration of linear alkyl benzene sulphonate (LAS) in water samples collected from the Manzala Lake. It varies from $0.03 \, \text{mg/}\ 1$ at site 4 in spring to $1.07 \, \text{mg/}\ 1$ at site 2 in summer, with annual mean ranges of $0.08 \pm 0.02 \, \text{mg/}\ 1$ at site 4 and $0.62 \pm 0.21 \, \text{mg/}\ 1$ at site 2. The one-way ANOVA test revealed that there was a significant difference in LAS in the Manzala Lake between different sites ($P \le 0.01$). Multiple range comparisons (PostHoc tests: Tukey HSD) also detected a highly significant difference between sites 2 and 4 ($P \le 0.05$). Furthermore, no significant differences were found between sites.

Surfactant-rich wastewater from the utilization of synthetic detergents is released into the environment, resulting in the formation of persistent water foams that serve as an insulating layer by appearing as bubbles that do not quickly disperse. This layer decreases the surface tension of the water, which increases the concentration of insoluble or soluble water pollutants in the water. In addition, this layer weakens the exchange between the

water body and gas atmosphere, causing a reduction in dissolved oxygen, killing microorganisms, and inhibiting the degradation of toxic substances (**Latef & Al-Azawey**, **2020**). The increasing concentration of LAS in the summer may be attributable to the increase in population density and human activities, leading to an increase in household loading during this season. These results are higher than those recorded by **Okbah** *et al.* (**2022**) in Burullus Lake water, Edku Lake water, and the Nile River water because of the excess domestic wastes and sewage discharged to Manzala Lake surface water, especially from the Bahr El-Baqr drain.

Table 7. Seasonal fluctuations of LAS value (mean \pm SE) in Manzala Lake during spring 2021 to winter 2022

| Parameter | Site | Spring | Summer | Autumn | Winter | Min. | Max. | Annual mean | P |
|--------------|------|-----------|-----------|-----------|-----------|------|------|---------------|-------|
| | | | | | | | | | value |
| | 1 | 0.18 | 0.93 | 0.76 | 0.43 | 0.18 | 0.93 | 0.57 ± 0.17 | |
| | 2 | 0.15 | 1.07 | 0.42 | 0.86 | 0.15 | 1.07 | 0.62 ± 0.21 | |
| | 3 | 0.22 | 0.26 | 0.09 | 0.24 | 0.09 | 0.26 | 0.20 ± 0.04 | |
| - | 4 | 0.12 | 0.11 | 0.03 | 0.06 | 0.03 | 0.12 | 0.08 ± 0.02 | |
| LAS (mg/l) | 5 | 0.09 | 0.09 | 0.60 | 0.68 | 0.09 | 0.68 | 0.36±0.16 | |
| VS (| 6 | 0.19 | 0.13 | 0.08 | 0.10 | 0.08 | 0.19 | 0.12 ± 0.02 | 0.010 |
| Γ | 7 | 0.17 | 0.37 | 0.07 | 0.07 | 0.07 | 0.37 | 0.17 ± 0.07 | |
| | 8 | 0.17 | 0.30 | 0.09 | 0.05 | 0.05 | 0.30 | 0.15 ± 0.06 | |
| | 9 | 0.16 | 0.18 | 0.08 | 0.08 | 0.08 | 0.18 | 0.13 ± 0.03 | |
| | 10 | 0.30 | 0.60 | 0.10 | 0.10 | 0.10 | 0.60 | 0.28 ± 0.12 | |
| Range | | 0.09-0.30 | 0.11-1.07 | 0.03-0.76 | 0.05-0.86 | | | | |
| P value | ; | 0.272 | | | | | | | |

3. Correlation between LAS and physicochemical parameters

The pearson correlation coefficient based on the relationship between concentrations of the investigated LAS, nutrients and physicochemical parameters of Manzala Lake is summarized in Table (8).

The correlation coefficient showed that pollution of LAS had highly positive and significant correlations with ammonium (r= 0.475, P< 0.01) and silicate (r= 0.405, P< 0.01). While, LAS concentration had a negative significant correlation with total suspended solids (r= -0.317, P <0.05), and a highly negative significant correlation with dissolved oxygen (r= -0.642, P <0.01). The negative significant correlation between LAS and total suspended solids can be enlightened by the fact that the LAS can be removed by suspended particles or sediment adsorption (**Badmus** *et al.*, 2021). The extremely negative association between LAS and DO may be explained by the high amount of dissolved oxygen enhancing the rate of biodegradation of surfactants added into a natural system. As a result, the biodegradable compounds introduction causes the depletion of DO in water. Sometimes, foaming prevents reaeration at the air-water interface from addressing this oxygen deficiency, and as a result, the reduced content of dissolved

oxygen may be too low for higher species of aquatic life to survive. These data coincide with the information gathered at sites 1 and 2, where municipal wastewater was dumped through the Bahr El-Baqr drain without any kind of treatment. However, at the other sites, the oxidizing conditions and high dissolved oxygen concentrations favored bacterial action on a large number of organic compounds easily biodegradable in such conditions, resulting in lower LAS concentrations (**Okbah** *et al.*, **2013**). In addition, the positive relationships indicate that the source of nutrients and LAS in Manzala Lake are similar. These results are also confirmed in the study of **Atici** (**2021**).

Table 8. Pearson correlation between LAS and physicochemical parameters in Manzala Lake water

| | Тетр. | Depth | Transparency | pН | EC | Salinity | Total hardness | DO | ООМ | TSS | Total alkalinity | NH ₃ | NO ₂ | NO ₃ | SiO ₃ | PO ₄ | LAS |
|------------------|--------|--------|--------------|--------|--------|----------|-------------------|--------|--------|--------|---------------------|-----------------|-----------------|-----------------|------------------|-----------------|-----|
| Temp. | 1 | | | | | | | | | | | | | | | | |
| Depth | 349* | 1 | | | | | | | | | | | | | | | |
| Transparency | -0.076 | .362* | 1 | | | | | | | | | | | | | | |
| РН | 0.247 | -0.138 | 0.266 | 1 | | | | | | | | | | | | | |
| EC | 0.187 | 396* | -0.003 | .325* | 1 | | | | | | | | | | | | |
| Salinity | .320* | 447** | -0.043 | 0.225 | .970** | 1 | | | | | | | | | | | |
| Total hardness | .545** | -0.123 | 0.253 | .441** | 0.115 | 0.153 | 1 | | | | | | | | | | |
| DO | 0.235 | 0.052 | .378* | .524** | .380* | .329* | .335* | 1 | | | | | | | | | |
| OOM | 0.298 | -0.01 | -0.235 | 0.113 | -0.038 | 0.042 | 0.075 | 0.076 | 1 | | | | | | | | |
| TSS | -0.207 | 312* | -0.276 | 0.238 | .329* | 0.223 | 0.141 | 0.196 | 0.106 | 1 | | | | | | | |
| Total alkalinity | .500** | -0.148 | 316* | 0.01 | -0.037 | 0.035 | -0.072 | -0.087 | 0.208 | -0.269 | 1 | | | | | | |
| NH ₃ | -0.235 | 0.056 | -0.288 | 475** | 597** | 543** | -0.196 | 621** | -0.12 | -0.203 | 0.024 | 1 | | | | | |
| NO_2 | 792** | .315* | -0.029 | -0.284 | -0.242 | 344* | 493** | -0.066 | 407** | 0.131 | 374* | .356* | 1 | | | | |
| NO ₃ | .848** | 356* | -0.03 | 0.244 | 0.194 | .342* | .506** | 0.231 | 0.18 | -0.278 | .458** | -0.078 | 613** | 1 | | | |
| SiO3 | .601** | -0.281 | -0.193 | 0.276 | 0.259 | .339* | .524** | -0.005 | -0.061 | 0.008 | .365* | -0.026 | 469** | .644** | 1 | | |
| PO ₄ | 0.187 | -0.041 | 0.25 | 0.057 | 376* | -0.311 | 0.191 | -0.019 | .355* | -0.157 | -0.049 | 0.077 | 316* | 0.041 | -0.087 | 1 | |
| LAS | 0.146 | -0.127 | -0.295 | -0.274 | -0.104 | -0.011 | -0.015 | 642** | -0.145 | 317* | 0.254 | .475** | -0.283 | 0.188 | .405** | 0.091 | 1 |

^{*}Correlation is significant at the 0.05 level (2-tailed).









4. Cluster analysis

A cluster analysis was carried out to study the spatial variation of all measured parameters in the Manzala Lake. Cluster results revealed that the sites could be classified into four groups (Fig. 2). Group 1 included sites 1, 2, and 5; group 2 included sites 3, 4, and 6; group 3 comprised sites 7, 8, and 10; and group 4 included only site 9. Group 1 is the southern section of the lake and is categorized by agricultural, industrial, and sewage discharge from the Bahr El-Baqr drain. Group 2 included sites 3 and 6, which are open water in the middle of the lake, and included site 4, which is influenced by agricultural discharges from the El-Gamaliyah and El-Matariya drains. Group 3 is the northern section of the lake. Group 4 is Boughaz Ashtom-Al Jamil, which is affected by seawater.

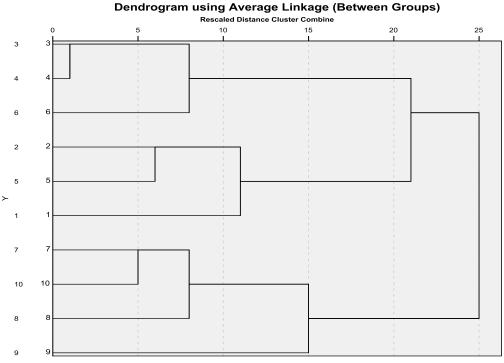


Fig. 2. Dendrogram of hierarchical clustering (CLUSTER) using average group abundance of each sampling site

5. Variation of some reported water quality parameters in Manzala Lake

Table (9) shows the comparison of some major water quality characteristics of Manzala Lake, including depth, temperature, clarity, pH, salinity, EC, DO, ammonium, nitrite, nitrate, silicate, and phosphate levels. Depth and transparency are lower than values recorded in previous studies. Temperatures are greater than the value recorded by **Hafiz** *et al.* (2019) while lower than in previous studies. The pH value of the present study is lower than that recorded in the study of **Abd El-Hamid** *et al.* (2017) and that of **El-Mezayen** *et al.* (2018). However, the current value is higher than those recorded in prior studies. EC is higher than that recorded in earlier research by **El-Sonbati** *et al.* (2012) and **Elnaggar and El-Alfy** (2016) but lower than in other investigations. DO is







lower than that recorded by Elnaggar and El-Alfy (2016) and Abd El-Hamid et al. (2017), but higher than in earlier investigations. Salinity levels in the current study is higher than that obtained in the work of El-Sonbati et al. (2012) while the value is lower than in earlier research. On the other hand, nitrate levels are higher than in prior investigations. Ammonium levels are lower than in the Deyab et al. (2020) study but greater than that recorded in prior studies. Nitrite levels are lower than those assessed in the prior study of Hafiz et al. (2019) but greater than those registered in other previous studies. Silicate levels are higher than that of in Elnaggar and El-Alfy (2016) but lower than that recorded in previous research. Phosphate levels are comparable to those of Hafiz et al. (2019). While, they are greater than those of Elnaggar and El-Alfy (2016) and El-Mezayen et al. (2018), and lower than those recorded in earlier research. Except for ammonium, which was higher than the permitted limits, and nitrate and silicate, which were lower than the permissible limits, all parameters were within the permissible limits.

Table 9. Comparison among some physicochemical parameters for Manzala Lake

| Parameter | El-Sonbati et al. (2012) | Elnaggar and El- Alfy (2016) | Abd-El Hamid et al. (2017) | El- Mezayen et al. (2018) | Hafiz et al. (2019) | Deyab <i>et</i> <i>al</i> . (2020) | The Present study | Permissible limits* |
|-------------------|--------------------------------|---------------------------------------|-------------------------------------|------------------------------------|---------------------|--|-------------------------|---------------------|
| Depth (cm) | 150 | 130 | - | - | - | - | 90.30 | - |
| Temperature (°c) | - | 19.5 | 15.3 | 21.9 | 30.6 | 19.35 | 22.30 | <35 |
| Transparency (cm) | - | 32 | 25 | - | - | - | 16.08 | - |
| pН | 8.03 | 8.3 | 8.7 | 8.42 | 8.15 | 8.1 | 8.32 | 6-9 |
| EC (mmhos/cm) | 7.2 | 10.9 | - | 40.6 | 20.5 | - | 13.54 | - |
| DO (mg/l) | 7.5 | 10.57 | 9.2 | 5.01 | - | 7.33 | 7.65 | >4 |
| Salinity (‰) | 4.7 | - | 15.6 | 25.4 | 8.75 | 26.08 | 7.65 | >4 |
| Ammonium (mg/l) | 0.457 | 0.753 | 0.050 | 0.004 | - | 2.77 | 1.09 | <0.5 |
| Nitrite (mg/l) | 0.126 | 0.082 | 0.180 | - | 0.280 | 1.13 | 0.19 | <0.3 |
| Nitrate (mg/l) | 0.136 | 0.232 | 0.370 | 0.001 | - | 1.50 | 2.74 | 11.3-45 |
| Silicate (mg/l) | - | 2.241 | 0.560 | - | 0.934 | - | 1.97 | - |
| Phosphate (mg/l) | - | 0.049 | 0.200 | 0.008 | 0.130 | 0.508 | 0.13 | 1 |

^{*}Permissible limits of Egypt legislation of the national law 48/1982.

6. Comparison of LAS levels in the studied water samples to those of national and international studies

In contrast to LAS levels in other locations in Egypt and around the world (Table 10), it is worth noting that the levels of LAS are greater than those recorded in all prior studies except those of and Macit (2010) and Ekmekyapar and Barut (2017).







| Location | LAS value (mg/l) | Reference |
|--|--------------------------|---------------------------|
| Manzala Lake | 0.03-1.07 | The present study |
| Burullus Lake | 0.135-0.518 | |
| Edku Lake | 0.162-0.752 | Okbah <i>et al</i> . 2022 |
| Nile River | 0.069-0.256 | - |
| Alexandria City (El-Max Bay) | 0.03-0.48 | Okbah <i>et al</i> . 2013 |
| Baghdad/Iraq (Tigris River) | 0.205-0.553 | Hassan et al. 2017 |
| Turkey (Morali, Akkopru, and Kurbas Rivers | (0.026-0.347),(0.023- | Atici 2021 |
| that flowing into Van Lake) | 0.137) and (0.109-0.401) | |
| Turkey (Karasu Stream) | 0.005-0.973 | Gündoğdu et al. 2018 |
| Poland (Klodnica River) | 0.2105±0.0023 | Ruman <i>et al</i> . 2017 |
| Turkey (Ergene Basin) | 0.014-3.09 | Ekmekyapar and Barut 2017 |
| Turkey (Sapanca Lake) | 0.003-1.122 | Macit 2010 |
| China (Dinachi Lake) | 0.018-0.260 | Wang <i>et al.</i> 2010 |

Table 10. Comparison of LAS concentrations in water of different locations

CONCLUSION

It is clear from the study that exposure to Lake Manzala had quality problems with physicochemical parameters and linear alkyl benzene sulfonates (LAS), particularly in the southern portion, due to the excessive sewage and residential wastes discharged into the surface water of the lake from the Bahr El-Baqr drain. As a result, the examination of Lake Manzala water quality should be regularly continued, the reasons that reduce the quality should be discovered, and the required safeguards should be adopted.

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