Original Research Article

Relation of selected hydrochemicals with hydrogen sulphide levels in sediments of Lake Burullus, Egypt.

Abstract

Lake Burullus, one of the northern deltaic lakes in Egypt, is an important economic, recreational and fish breeding reservoir. The study used nine georeferenced stations to assess hydrogen sulphide (H_2S) levels, its relationship with selected hydrochemical parameters, and the implication on this lake's biota.

The study reveals that areas mostly affected by drainage water with high load of organic matter, aid to the production of H_2S into sediments and dispersion to water. The present results indicate that H_2S in lake sediment ~~is~~ increase with increasing water temperature, biological oxygen demand (BOD) and load of organic matter (OM) in water. On the other hand areas with high oxygen levels and clear water aid in reducing sulphide levels in sediments as proved from correlation analysis. The distribution maps of H_2S, OM and BOD reveal positive correlation of variables of organic matter and H_2S. The ~~huge~~ amount of different wastes, particularly when in large quantities, increase the level of H_2S, and therefore negatively affected on biota badly so it is highly recommended to treat wastewater to conserve the biodiversity of this lake.

Keywords: Lake Burullus, Pollution, Hydrochemicals, Hydrogen Sulphide

Comment [111]: please re-insert this

Comment [112]: Since this is a scientific paper, please be consistent: use H_2S? Since, it's about H_2S, retain it as such. The usage here is critical because the current sentence is contrasting the preceding one.

Comment [113]: here be specific: what does "badly" mean? You can use terms like "reduce" "diminish" ...use a term that reveals what this "negatively... and badly" mean.

Introduction

The bottom sediments of Lake Burullus are mainly derived from the suspended load (i.e. the total suspend particulate matter in water), clay and silt (citation needed). These sediments are carried annually into the lake through the drain water, sea water and wind. The lake's bottom along the northern shores extending from the lake-sea connection westwards is mainly clayey-sand; silty sand with some patches formed molluscan shells. The eastern and western regions of the lake are silty clay. The southern shore sediments which receive directly the drain discharges which formed from clay and silt with small areas covered with molluscan shells (Med. Wet. Coast Project, 2005).

Abdo (2005) explains that the total organic matter in sediments plays an important role in the accumulation and release of pollutants in lagoon water, and it is a source of nutrient for the living fauna in the lagoon.

Hydrogen sulphide concentration in water and sediment in many aquatic system is considered good indicator of oxygen levels in the water and sediment as regards assessing the lake’s water suitability for supporting biota (Golterman, 1975). Naturally, hydrogen sulfide occurs in the process of decomposing organic substances containing sulfur used by bacteria in anaerobic conditions (Wongsin, 2015). Also, Berner (1984) stated that surface sediments, which contain large amounts of the freshly deposited planktic organic compounds, are very important in the production of H_2S by sulfate reducing bacteria.

H_2S is an extremely potent metabolic poison, lethal at low concentrations (<1 ppm) to most vertebrates alike (Evans, 1967, Smith *et al.,* 1976; Oscid and Smith 1974 a, b).

The toxicity of hydrogen sulphide for some fauna (*Tilapia gallilae*; Nauplii larvae of *Artemia salina* (*Ocenebra erinacea*) and *Idotea baltica* have been recorded by Tayel and Shriadah (1991). The aim of this research is to

Comment [114]: Should read “research” study the interrelationship between selected hydrochemical variables and H_2S level in the sediments of Lake Burullus, Egypt.

2. Material and Methods

2.1. Study area

Lake Burullus is one of the five Mediterranean Lakes in Egypt and is used for fishing, recreation and contains many organisms. It is bordered in the north by Mediterranean Sea and in south by agricultural land and fish farms between 30^{o} 30\` $31^{o}$ 10\`E and 31^{o} 20\` $31^{o}$ 35\`N (citation needed). It extends for a distance 41.8km within area of about 460 km^2. Lake Burullus is connected to the Mediterranean Sea through El-Burullus outlet (Boughaz El-Burullus) which is about 250 m wide and 5 m deep (citation needed)... The depth of the Lake varies between 40 cm in its middle sector and near the shores and 200 cm near the outlet to the sea (El-Bayomi, 1999; Zahran and Willis, 2009).

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The lake receives (4 milliard m^3/y^{-1}) drainage water from several drains which were considered the main source of pollution in the lake (citation needed). -The maximum amount of drainage water discharge from drain 9 at the middle sector of the lake. The lake receives drainage water from several drains which were considered the main source of pollution in the lake. The maximum amount of drainage water discharge from drain 9 at the middle sector of the lake (EMI, 2012). The estuarine water of Rosetta mouth of the River Nile is mixed with the lake water through Brimbal canal. Sea water may also flow into the lake at Burullus outlet (Al-Sayes *et al*., 2007).

Surficial sediment samples were collected from nine stations covering Lake Burullus; (Figure 1). The description of these locations is as shown in Table (1).

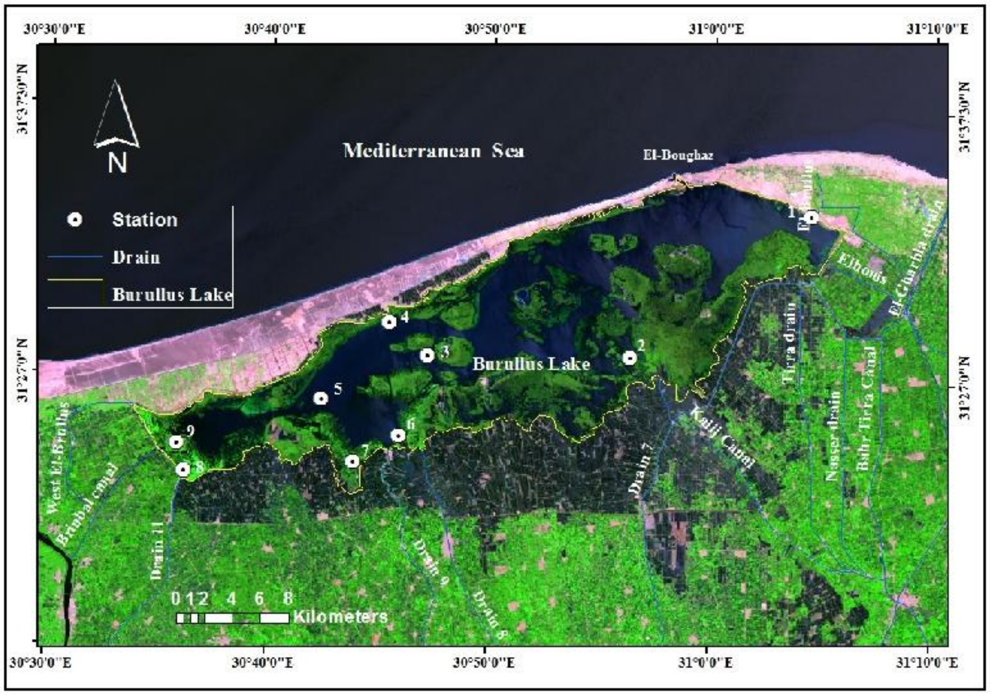


Fig.1. Sampling stations at Lake Burullus, Egypt

Table (1): Latitudes and longitudes of the sampling stations at Lake Burullus

St. NO	Station name	Latitude N	Longitude E
1	El-Burullus (east)	31^{o} 33` 29.9``	31^{o} 04` 25.3``
2	inf. of drain 7	31^{o} 27` 56.1``	30^{o} 56` 17.5``
3	El-Zankah	31^{o} 27` 53.3``	30^{o} 47` 10.0``
4	Mastarouh	31^{o} 29` 09.0``	30^{o} 45` 24.4``
5	Abo-Amer	31^{o} 26` 07.0``	30^{o} 42` 23.3``
6	El-Tawelah	31^{o} 23` 43.8``	30^{o} 43` 52.8``
7	inf. of drain 8 & 9 (Shakhlobah)	31^{o} 24` 46.9``	30^{o} 45` 54.9``
8	inf. of drain 11 (El-Hoksa)	31^{o} 23` 15.5``	30^{o} 36` 15.3``
9	inf. of Brimbal Canal	31^{o} 24` 06.0``	30^{o} 35` 00.4``

St= station inf= infront

2.2. Analytical methods

Nine geo-referenced water samples were collected within Lake Burullus. In the field, water temperature and dissolved oxygen (DO) were measured using the DO meter (Lutron YK-22 DO meter). pH is measured using pH-meter (Model Lutron YK-2001, pH meter). EC was determined using EC-meter (Thermo, Orion 150 A+ advanced conductivity). The biological oxygen demand (BOD) determination was carried out using the conventional Winkler method (APHA, 1998). Organic matter (OM) is determined by Permanganate oxidation method (FAO, 1975).

Hydrogen sulfide is a colorless, flammable and toxic gases smell like rotten eggs, even at low concentrations (Tuntoolavest and Tuntoolavest, 2004).

Oxidation of hydrogen sulphide in natural waters either produces or consumes hydrogen ions, depending on products and other conditions (Tayel and Shriadah 1991).

Thus

$$2HS^{-}+O_2 \rightarrow 2H_2O + 2S$$

$$2HS^{-} + 2O_2 \rightarrow H_2O + (S_2O_3)^{-2}$$

$$2HS^{-} + 4O_2 \rightarrow 2(SO_4)^{-2}+2H^{+}$$

In absence of biological activity, sulphide can be slowly oxidized to sulpher which then combines with remaining sulphide to form polysulphide.

Estimation of hydrogen sulphide in sediment samples occurred as follow: 0.1 –0.8gm wet acidified samples with nearly 5ml Conc H_2SO_4 in closed system, (Figure 2). The involved hydrogen sulphide gas was displaced with oxygen free nitrogen gas into zinc acetate traps. The recovery of sulphide in this manner is 99% efficient. Sulphide collected in the traps was measured calorimetrically using methylene blue method (Youssef, 1999). Results are expressed as mg/gm.

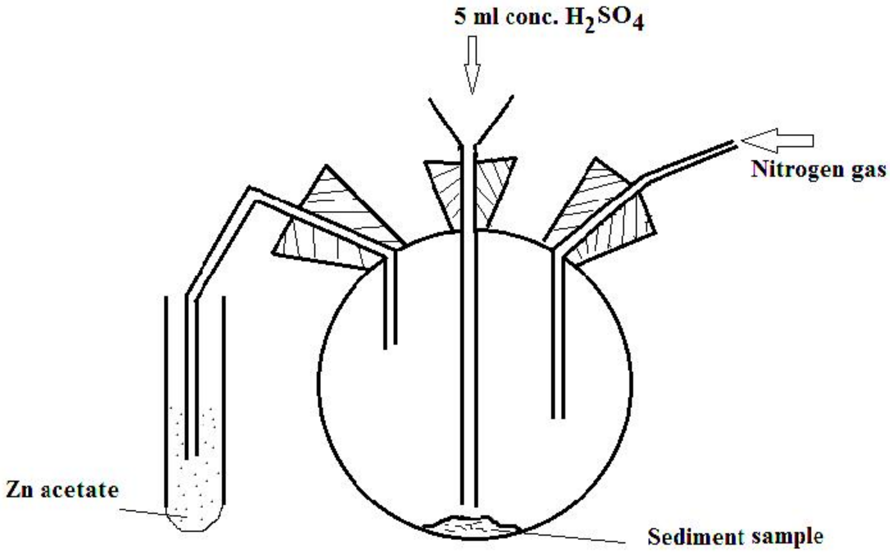


Fig. 2. The apparatus used for estimation of hydrogen sulphide

2.3. Statistical analysis:

The statistical analysis for the data were carried out to determine the correlation coefficient (r) using the formula

$$r = \frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{\left[n\sum x^2 - (\sum x)^2\right]\left[n\sum y^2 - (\sum y)^2\right]}}$$

Where X the concentration of H_2S and Y is the corresponding concentration of variant and n is the number of data.

2.4. Geo-statistical Analysis

Inverse distance weight (IDW) is a deterministic interpolation procedure that estimates values at prediction points (V) using the following equation

$$V = \frac{\sum_{i=1}^{n} v_i \quad (\frac{1}{d_i^p})}{\sum_{i=1}^{n}(1/d_i^p)}$$

Where d is the distance between prediction and measurement points, Vi is the measured parameter value, and p is a power parameter (Isaaks *et al.* 1989). The main factor affecting the accuracy of inverse distance interpolator is the value of the power parameter p, as well the size of the neighborhood and the number of neighbors are also relevant to the accuracy of the results (Burrough and McDonnell, 1998).

3. Results and discussion

Results of hydrogen sulphide concentrations in sediments as well as concentrations of some related parameters in the water as organic matter, dissolved oxygen, biological oxygen demand and hydrogen ion concentration were shown in Table (2) and the spatial distribution maps of depth, pH, EC, BOD, DO, OM and H_2S within water and sediment of Lake Burullus are as shown in Figure 3 (A-G).

H_2S concentration in sediments ranged between 4.3 at Abu-Amer and 7.7 at El-Tawelah and Brinbal canal with mean value of 6.72 mg/g. The highest value was recorded at Brinbal, and may attributed to the nature of sediment characteristics of clay and high content of organic matter that aid in the release of H_2S in sediments. Radwan and Lotfy (2002) estimated that sediments of Lake Burullus have a complex nature. More specifically, the sediments change from coarse particles-sand, usually abundant in the northern coast and at the coast of islets, whereas it's muddy in the southern parts of lakes.

Organic matter also takes the same distribution of H_2S as its high percent content was found at Brinbal canal may attributed to agricultural wastes from different agricultural areas. High discharge of drained water in the southern part of the lake led to the consumption of DO due to oxidation of such OM. This is agreed with observations of El-Ghobashy (1990) in Lake Manzala.

In Lake Burullus, the highest concentrations of organic matter and organic carbon were distributed at the western, southern and eastern parts of the lake; this agrees with Masoud (2011) and El-Alfy (2015).

The southern parts are described as having clayey sediments or fine particles which contain high amount of organic carbon not as sandy soils which are very poor with organic matters at the northern parts of the lakes (Palma *et al*. 2012).

The site at Brinbal canal is distinguished by high density of vegetation especially hydrophytes i.e. *Eichhornia crassipes* and other vegetative plants. So it's an important reason for high concentration of organic matter (OM) in these areas as may attributed to sinking and decaying of dead plants on the bottom (Nafea, 2005).

These results are in agreement with Moussa *et al.* (1994) and Khalil *et al.* (2007) for Lake Edku where the content of OM in sediment was controlled by the amount of clay and silt in addition to the plant detritus from nearby vegetatative areas.

Electrical conductivity (EC) fluctuated between 3.9 at Brinbal canal (source of fresh water from Rosetta Branch /River Nile) to 30.9 ms/cm at east of El-Burulls (this sites is near from El-Boughaz area) so it may be highly affected by the sea water intrusion.

Hydrogen sulphide was produced in the anoxic part of the sediment, with reduction of sulphate. It's noticeable that, the reduction of sulphate in sediments reaches a percent of nearly 13% of total organic matter in acidic conditions and to 50% in marine sediment (Kühl and Jorgesen, 1992).

pH is very significant parameter in the metabolic and physiological processes that is important in growth of aquatic organisms (Lawson, 2011).
Values of pH changed within different sites. As it was acidic especially in the

outlets of drains, and may be attributed to release of different nutrients like ammonia that responsible for acidification and decreasing of pH. This is in agreement with Koerkamp *et al.* (1998) and Ibrahiem *et al*. (2012). Also Abbas *et al.* (2001) and Sayed (2003) stated that low pH values are attributed to liberation of H_2S during the decompositions of OM. The highest value of pH was recorded in site 5, may attributed to high density of hydrophytes as increase of pH value is accompanied by a flourishing photosynthesizing organisms (El-Sonbati *et al.* 2009).

The excess of OM produced during photosynthesis process in the euphotic zone eventually sinks down through the water to the sediments where respiration processes dominate. The depth of the Lake does not exceed 1.5 meter, thus, a significant difference often exists between the oxygen rich euphotic zone and underlying oxygen-poor aphotic zone. The presence or absence of oxygen has significant effect on the oxidation-reduction chemistry, also attributed to the anaerobic bacteria where the biological oxygen demand is an empirical test used to determine the relative oxygen requirements needed for the biochemical decomposition and oxidation of OM and inorganic material. The highest concentrations of BOD were recorded in stations close to the point of discharges as pronounced at station 7 (drains 8&9), where huge amount of OM originated from drains led to more consumption to DO by the bacterial activities which leads to oxygen depletion and rise in H_2S level in the sediment.

Sedimentary production of hydrogen sulphide can increase the oxygen demand rate of sediment leading to a reduction in dissolved oxygen in the overlying water as shown in our investigation at stations 5 and 9. Utilizing combined oxygen as sulphate, purification then occurs resulting from decomposition of OM to hydrogen sulphide as end product (Klein, 1962). From the results obtained in Table 2, its clear that, the whole water body of the lake is well oxygenated during the time of sampling with a minimum of $5.1 mg^{-1}$ at station 7 (in front of drain 8,9) a maximum of 10.6 mg^{-1} at station 5 in the middle sector.

From the statistical analysis (Table 3), it is obvious that highly inverse significant proportion was observed between hydrogen sulphide and dissolved oxygen (r= - 0.67). Meanwhile, there was a positive significant correlation with organic matter (r= 0.74). On the other hand, the relation was insignificant between hydrogen sulphide, BOD, (r= 0.32), pH (-0.24) and with water temperature (r= 0.47). The distribution maps of depth, pH, EC, BOD, DO, OM and H_2S within water and sediment of Lake Burullus as shown in figure (3) proved the relation between the presences of different parameters within the H_2S, which highly attributed to drainage waters from different waste drains. El-Amier *et al*. (2016) and El-Alfy *et al*. (2017) used geostatistical and deterministic methods for creating spatial distribution maps of different pollutants in Lake Burullus.

Conclusion

It's concluded that areas besides drainage water as waste drains recorded high levels of H_2S. Strong relation between drained water containing low concentrations of dissolved oxygen, high concentration of BOD and high levels of OM in sediments with the levels of H_2S. Areas with low pH values or characterized by acidic nature may be indication for high levels of H_2S in sediments of lake. So it's highly recommended to reduce organic load to the lake by using different methods of remediation aid in reducing of H_2S sources in sediments to keep the aquatic life. Also removal of invasive aquatic plants from Lake Burullus' water could aid to solve such problems.

Table (2): Hydrogen sulphide concentration (mg/g) in sediment and concentration of selected hydrochemicals in water of Lake Burullus.

St.	H_2S mg/gm	OM %	DO mg/l	BOD mg/l	pH	T°C	EC	Depth
1	6.9	1.8	8.5	3.8	8.67	22.7	30.8	70
2	7.2	3.1	5.8	6.5	8.78	23.0	9.11	60
3	7.2	2.4	9.1	5.7	8.55	23.0	10.1	90
4	6.8	2.9	8.1	11.4	8.78	22.8	9.29	110
5	4.3	1.6	10.6	7.3	8.83	22.1	9	120
6	7.7	3.6	5.9	13.5	8.0	25.0	8.61	100
7	6.8	2.9	5.1	18.3	7.86	24.0	4.52	70
8	5.9	2.1	7.4	10.6	6.88	25.0	4.1	80
9	7.7	4.4	6.0	21.4	6.37	25.7	3.9	90
σn	0.997	0.842	1.728	5.596	0.8518	1.1935	7.74	18.72
σn.1	1.058	0.893	1.833	5.936	0.9035	1.2658	8.21	19.61
X	6.722	2.7525	7.38	10.944	8.08	23.700	9.94	87.77

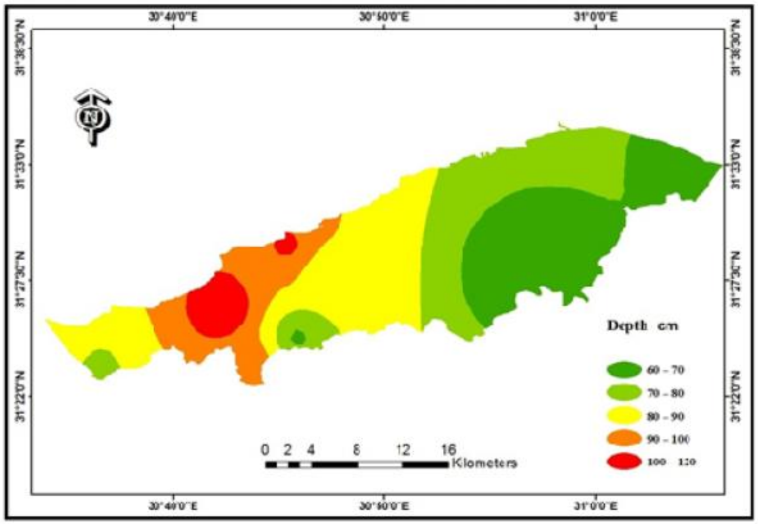
H_2S: hydrogen sulphide; OM: organic matter; DO: dissolved oxygen; BOD: biological oxygen demand ; pH: hydrogen ion concentration; T°C: temperature and EC: electrical conductivity.

Table (3): Pearson moment correlation matrix between some hydrochemical parameters and H_2S in sediments.

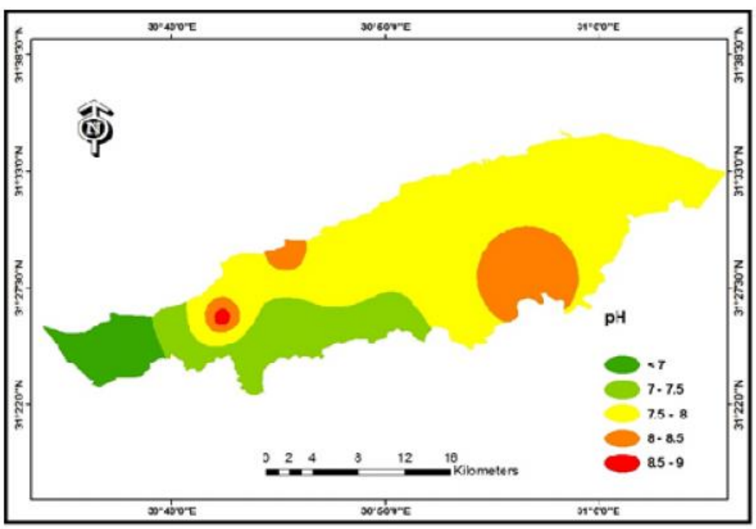
Variables	H_2S	OM	DO	BOD	pH	T°C
H_2S	1					
OM	0.743*	1				
DO	-0.675*	-0.741*	1			
BOD	0.329	0.756*	-0.648	1		
pH	-0.246	-0.524	0.471	-0.734*	1	
T°C	0.48	.692*	-0.666	0.754*	-0.917**	1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

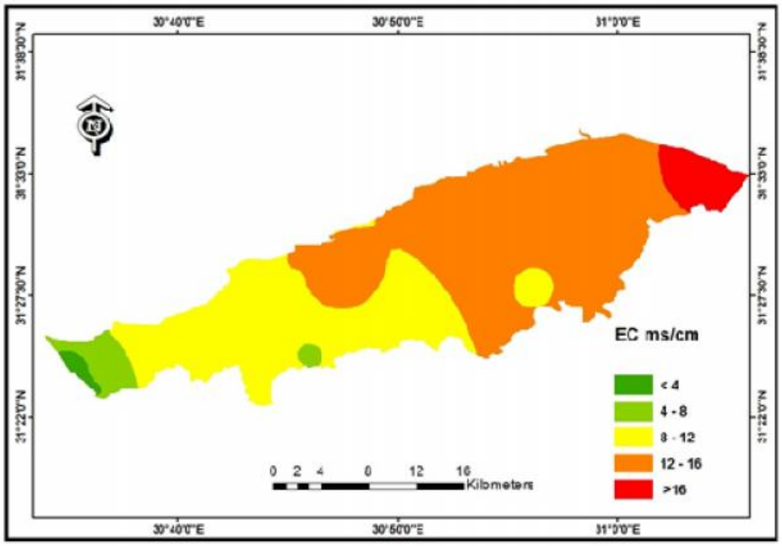
H_2S: hydrogen sulphide; OM: organic matter; DO: dissolved oxygen; BOD: biological oxygen demand ; pH: hydrogen ion concentration and T°C: temperature

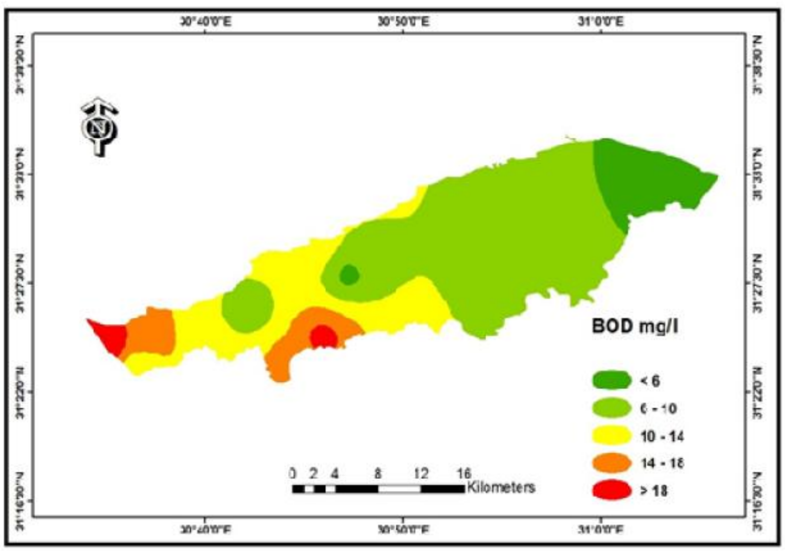

30°40'0"E
30°50'0"E
31°0'0"E
Depth cm
60 - 70
70 - 80
80 - 90
90 - 100
100 120
0 2 4 8 12 16 Kilometers

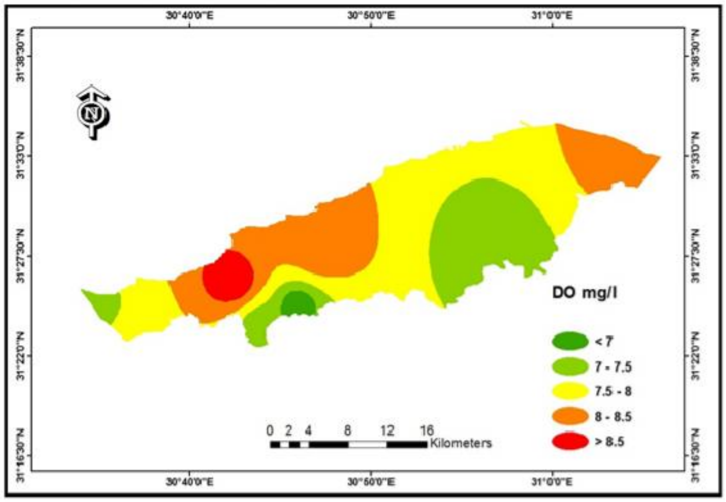
A)


pH
7 - 7.5
7.5 - 8
8 - 8.5
8.5 - 9
0 2 4 8 12 16 Kilometers

B)


EC ms/cm
< 4
4 - 8
8 - 12
12 - 16
>16
Kilometers
C)


BOD mg/l
< 6
6 - 10
10 - 14
14 - 18
> 18
Kilometers
D)



30°40'0"E
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31°33'0"N
31°27'30"N
31°22'0"N
31°16'30"N
N
DO mg/l
< 7
7 - 7.5
7.5 - 8
8 - 8.5
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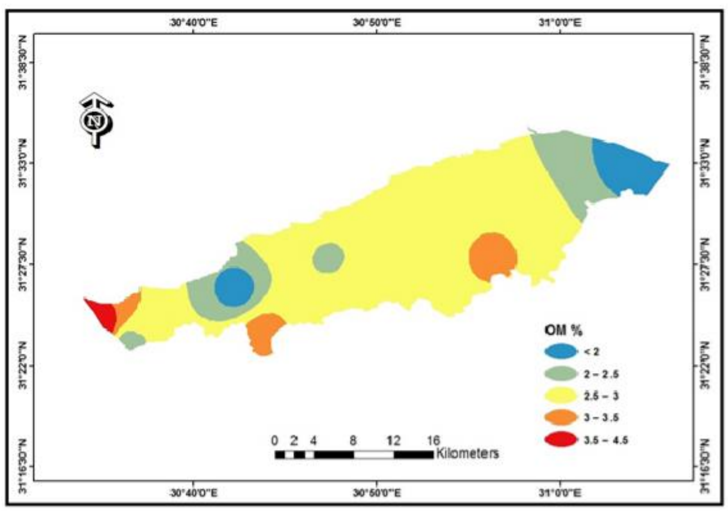
Kilometers

E)



30°40'0"E
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31°38'30"N
31°33'0"N
31°27'30"N
31°22'0"N
31°16'30"N
N
OM %
< 2
2 – 2.5
2.5 – 3
3 – 3.5
3.5 – 4.5
0 2 4 8 12 16
Kilometers

F)

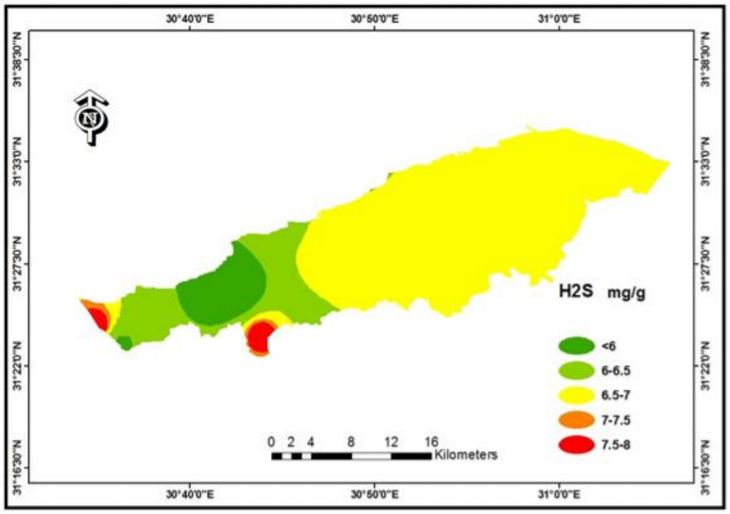
G) 

Fig. 3.(A-G) Spatial distribution of depth, pH, EC, BOD, DO, OM and H_2S within water and sediment of Lake Burullus.

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