



# Lake Kinneret (Israel) Invasion by $N_2$ -Fixer Cyanobacterium was Enhanced Simultaneously by Nitrogen Deficiency, Phosphorus Sufficiency and Sulfate Decline

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## Introduction

The Lake Kinneret Ecosystem has undergone significant modification since mid-1980's which particularly were: The previous trophic status of Phosphorus limitation was modified to Nitrogen limitation; the long-term domination of *Peridinium gatunense* (PRG) was declined and replaced by Cyanobacteria, Chlorophytes and Diatoms. The distribution enhancement of Harmful Cyanobacteria (HFCB) in Lake Kinneret initiated in summer 1994 when a bloom of *Aphanizomenon ovalisporum* was documented followed by several studies about the outbreak of HFCB were carried out [1,2]. Despite precaution signals that were publicized since 1987, no special attendances were given to it prior to the outbreak. Nevertheless, supportive background conditions which potentially might enhance similar ecological changes were indicated [3]. The significance of PRG demands for Nitrogen were documented [3-5]. Moreover, the unlimited source of Phosphorus for the PRG growth in lake Kinneret sediments through cysts dormancy was also widely documented [3]. The progressive promoted of the process of N/P mass ratio decline and its critical impact on the Kinneret invasion by  $N_2$ -fixing HFCB was studied thoroughly and documented afterwards [2,6]. Independent other studies and monitored data were published about Climate Condition Changes in the Kinneret watershed causing decline of rainfall and consequently lower headwaters discharges and diminished loads of lake nutrient inputs [4,6]. Consequently, the Nitrogen deficiency accompanied by Phosphorus sufficiency conditions which are well known and warmly accepted by the international community of limnologists as supporter of HFCB blooming, were also confirmed causation in the Kinneret 1994's case.

The close and far history of the Hula Valley and Peat-soil structure were crucial part of the Hula Project research and widely presented in scientific papers and annual reports [6]. The role of Molybdenum as cofactor within the biochemical process of the

Nitrogenase, Nitrogen fixation process and the competitive value, of the anion  $SO_4^{2-}$  on it, in marine, brackish, saline lakes and freshwaters [7-9] is well known and documented since early 1980's. Although, Nitrogen deficiency and Phosphorus sufficiency resulting outbreak of HFCB as well as the Mo (as  $MoO_4^{2-}$ ) availability [10] affected by the hinder  $SO_4^{2-}$  were all confirmed solely but were never attended simultaneously for the Kinneret case of HFCB outbreak. A renovated evaluation of the case of the  $N_2$ -Fixer HFCB invasion to Lake Kinneret where all the previously presented as confirmed parameters solely are combined.

## Methods

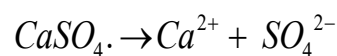
Long term(1970-2020) data records of Lake Kinneret, Hula Valley and Kinneret watershed provided from the Lake Kinneret Data Base and Hula Project Monitor Program (Migal) were re-evaluated.

## Result and Discussion

Before the HFCB outbreak (1994), sporadic low densities of non-toxic- $N_2$  fixing Cyanobacteria were recorded in lake Kinneret rarely accompanied by with other toxic species. Reevaluation of the lake and its watershed ecosystems data highlighted an additional potential supporter of the process which is, reduction of Sulfate ( $SO_4^{2-}$ ) concentration. Climate condition changes resulted in Sulfate input reduction into Lake Kinneret. An awareness to the potential competitive interaction between  $SO_4^{2-}$  and Molybdenum ( $MoO_4^{2-}$ ) predicted as an enhancement of HFCB growth rate initiated the present study. The Peat soil in the Hula valley contain vast load of Gypsum which is an effective supplier of  $SO_4^{2-}$  to Lake Kinneret. The purpose of the present survey is to evaluate optional capabilities of ecological opportunities such as supplemental  $SO_4^{2-}$  aimed at strengthening competition with  $MoO_4^{2-}$  to suppress  $N_2$ -Fixer

Cyanobacterium. Extra potential sources of  $SO_4^{2-}$  are deep boreholes (namely "Shamir drills") artesian flows and sub-lacustrine gushing out through the Lake Kinneret bottom sediments. The  $SO_4^{2-}$  concentration in the Shamir drill waters is varied between 600-650 and 9.4 - 10.2 ppm and  $\mu M$  respectively. The  $SO_4^{2-}$  source within the Hula Valley are Peat soil which contain high content of Gypsum ( $CaSO_4$ ). The anthropogenic activity of agricultural cultivation,

irrigation and drainage in the Hula Valley enhance Gypsum dissolution and  $SO_4^{2-}$  drifting down stream. The hydrological structure is directing these drifted substances towards the Jordan River continuing downstream into Lake Kinneret (Table 1).



**Table 1:** Periodical (1969-1978, 1985-1995) averages of mass (ppm, ppb), and Molar (mM,  $\mu M$ ) concentrations of Mo and  $SO_4^{2-}$  and Molar ratio between them. Comparative ratios for Freshwater and Sea water [13,14] are given.

	1969-1978	1985-1995
ppm- $SO_4^{2-}$	56	46
ppb- Mo	0.5-1.5	0.5-1.5
mM- $SO_4^{2-}$	0.583	0.479
$\mu M$ - Mo	0.00521-0.0156	0.00521-0.0156
$SO_4^{2-}$ / Mo (M) Ratio		
Kinneret	$1.11 \times 10^5 - 0.37 \times 10^5$	$0.92 \times 10^5 - 0.31 \times 10^5$
Seawater	$2.6 \times 10^5$	
Freshwater	$0.22 \times 10^5$	

Data given in Figure 1 indicates a significant ( $r^2=0.3758$ ;  $p=0.0025$ ) decline of,  $SO_4^{2-}$  concentrations in Lake Kinneret during 1970-2010. Data given in Figure 2 indicates significant seasonal decline of  $SO_4^{2-}$  concentration in runoff waters in the Hula Valley in summer when soil moisture is low. The long-term (1970-2010) decline of the River Jordan discharge presented in Figure 3 confirm the regional dryness Climate Condition enhancement. Data shown in Figure 4 confirm loads decline in the lake during summer months. Conclusively, changes in climate condition resulted a decline of rainfall and headwater discharges in the watershed, and consequently, seasonal inputs of  $SO_4^{2-}$  which are normally decline in summer when soil moisture diminish and furthermore reduced under dryness conditions. Concentrations of  $SO_4^{2-}$  during early 1990's, particularly in summer were exceptionally low probably improved  $MoO_4^{2-}$  availability and consequently HFCB growth rate. The invasion of the  $N_2$ -Fixer Cyanobacterium *Aphanizomenon ovalisporum* was attributed to the advanced simultaneous development of Nitrogen deficiency and Phosphorus sufficiency (decline of N/P mass ratio). Although reduction of N/P ratio supports a significant factor for HFCB enhancement [11,12] the present study suggests a consideration of  $MoO_4^{2-}$  availability and its chemical relation with  $SO_4^{2-}$  concentrations as a partial stressor too. Previously published studies confirmed the competitiveness relation between  $MoO_4^{2-}$  and  $SO_4^{2-}$ . The anion of  $SO_4^{2-}$  is very common in the Kinneret watershed, mostly released by dissolution of Gypsum ( $CaSO_4$ ):  $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$  in the Peat Soil

in the Hula Valley. The linkage between Sulfate transportation to Lake Kinneret initiated the need to evaluate the potential impact of its quantitative range on  $MoO_4^{2-}$  uptake by HFCB. Results given in this paper confirmed a reduction of  $SO_4^{2-}$  input into Lake Kinneret which followed the reduction of river discharge, dryness trend in the Hula Peat-Land and lowering its concentration in the lake. Several studies confirmed enhancement and diminishment of  $MoO_4^{2-}$  uptake by HFCB as correlated with  $SO_4^{2-}$  availability [8,9,13]. Increase of  $SO_4^{2-}$  concentration might suppress  $MoO_4^{2-}$  uptake and consequently slow down Nitrogen fixation by HFCB which is their ecological advantage. Reversibly,  $SO_4^{2-}$  deficiency improve the activity of HFCB's Nitrogen Fixation through improvement of Nitrogenase activity enabling growth rate maintenance improvement [14]. These interactions are probably the Lake Kinneret case of *A. ovalisporum* outbreak in summer 1994 together with earlier Nitrogen deficiency development. The seasonal lowest availabilities of  $SO_4^{2-}$  and its input range as routinely documented in past and present occur during summer months. Eventually, summer season was the time in which the HFCB outbreak was documented. Moreover, the Nitrogen diminishment damaged the *Peridinium* growth rate and Nitrogen fixation, supplemented by the  $MoO_4^{2-}$  competitor-  $SO_4^{2-}$ , enhanced HFCB. The complexity of the ecological interactions includes Nitrogen, Phosphorus,  $MoO_4^{2-}$  and Sulfate availabilities which encourages future management to design a wider consideration combined with all of them although previously were only solely attended, Nitrogen and Phosphorus.

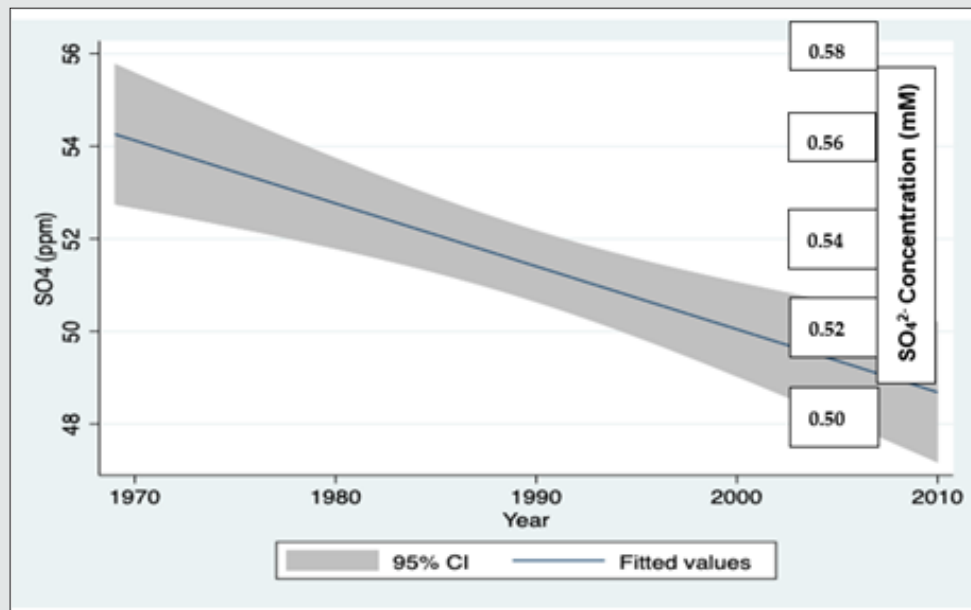


Figure 1: Linear Regression (95% CI) of Temporal (1970-2010) changes of SO<sub>4</sub><sup>2-</sup> concentrations (ppm; mM) in Lake Kinneret.

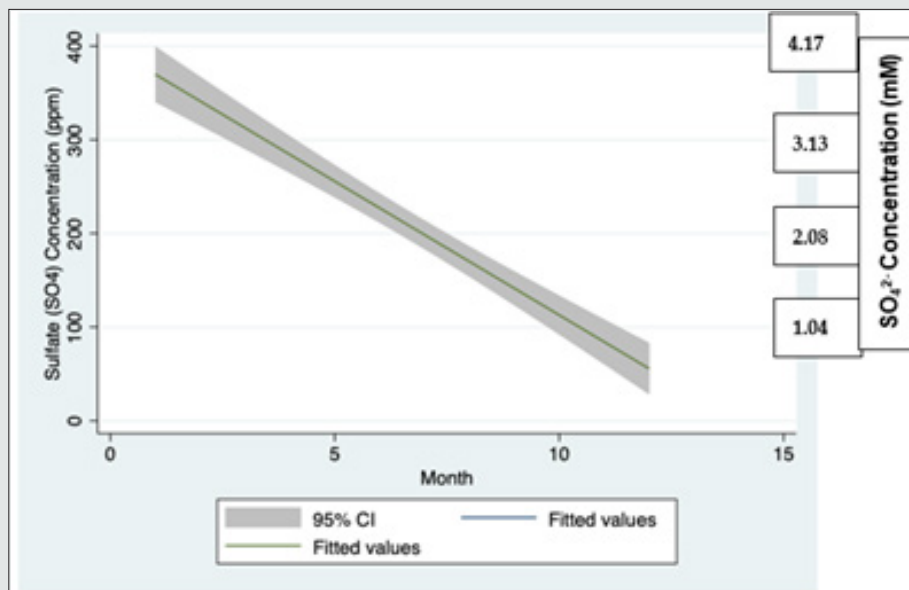


Figure 2: Seasonal (monthly) changes of averaged concentrations (ppm; mM) of SO<sub>4</sub><sup>2-</sup> of all sampling stations within the Hula Valley during 1994-2010.

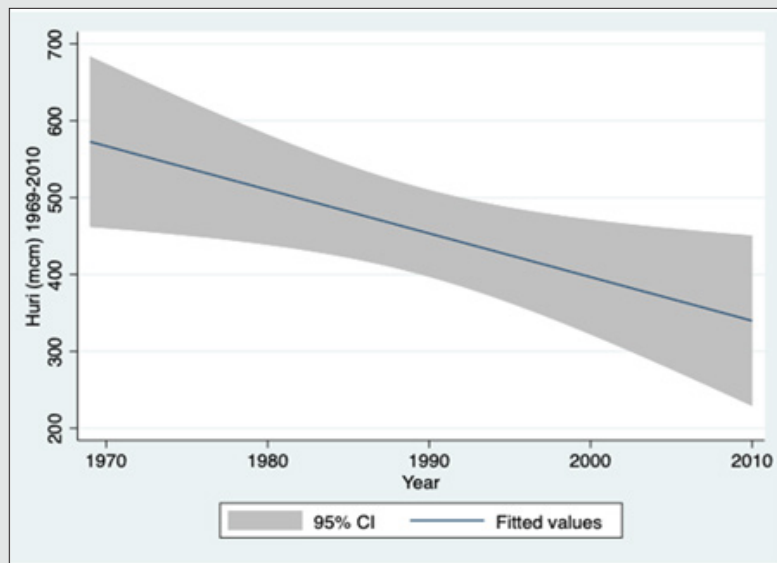


Figure 3: River Jordan Annual Discharge (mcm/y) during 1969-2010.

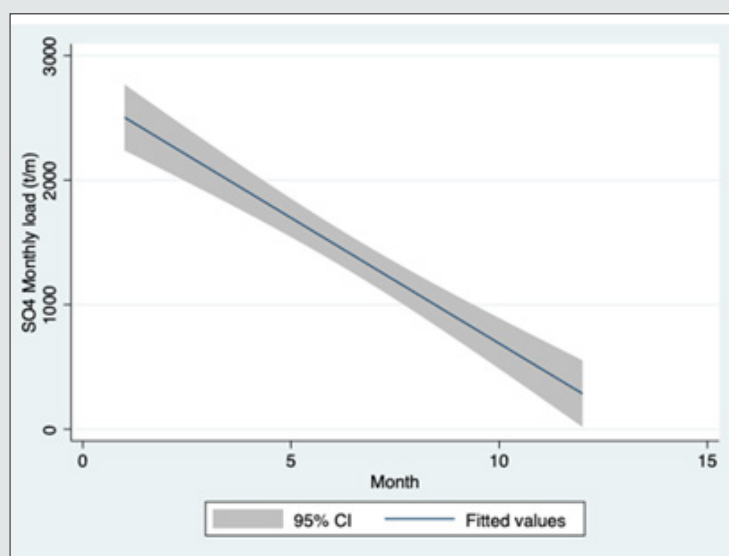


Figure 4: Linear regression (CI 95%) plot between monthly  $\text{SO}_4^{2-}$  loads input (t/m) into Lake Kinneret through the River Jordan discharge during 1970-2004.

## Conclusion

Previous studies confirmed long term progressively promoted process of Nitrogen deficiency and Phosphorus sufficiency which enhanced during the early 1990's the invasion of Lake Kinneret by the  $\text{N}_2$ -Fixer Cyanobacterium *Aphanizomenon ovalisporum*. Recent awareness suggested that simultaneous decline of  $\text{SO}_4^{2-}$  input into Lake Kinneret followed by diminishing of its concentration during early 1990's supported the outbreak of this Cyanobacteria.

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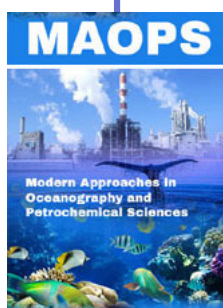
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