

Article

Sulfate (SO_4^{2-}) Decline Supported Lake Kinneret (Israel) Invasion of N_2 -Fixing Cyanobacterium *Aphanizomenon ovalisporum*

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Abstract: Since 1990, the Lake Kinneret trophic status has shifted from phosphorus to nitrogen limitation. In the summer of 1994, an outbreak of N_2 fixing cyanobacterium *Aphanizomenon ovalisporum* invaded the epilimnion of Lake Kinneret. Since then, sporadic densities of harmful cyanobacteria (HFCB) reappeared in the lake together with other toxic non- N_2 fixing cyanobacteria. This predicted ecological modification developed because of a worldwide well-known background condition of descent N/P mass ratio. Reevaluation of the lake and its watershed ecosystems data exposed additional potential support of the process reduction of the epilimnetic sulfate (SO_4^{2-}) concentration. Climate condition changes resulted in sulfate input reduction and its potential competitive interaction with molybdenum (MoO_4^{2-}) enhanced the HFCB growth rate. The working hypothesis was the reevaluated incorporation of long-term records including rainfall, river discharge, depth of ground water table in the Hula valley peat soil, total moisture capabilities, and Kinneret epilimnion sulfate concentration. Results justify conclusive inference in Lake Kinneret of the following: sufficient phosphorus, insufficient nitrogen, and sulfate decline availabilities induced the HFCB outbreak in the summer of 1994.

Keywords: sulfate; molybdenum; Cyanophyta; nitrogen fixing; Kinneret



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1. Introduction

Lake Kinneret, the only natural freshwater lake in Israel, is a warm monomictic lake which is stratified from May through mid-December (anoxic hypolimnion) and totally mixed from mid-December through April. Due to its high temperature of seasonal and bathymetrical mean range of 15–33 °C, the thermal stratification is stable and separates the lake into two thermal compartments of epilimnetic 0–20 m depth and hypolimnetic thickness at 24 m (20 m-bottom). The epilimnion is rich in oxygen and poor in other nutrients. Oxygen is completely absent in the hypolimnion, which is rich in ammonia, sulfides, and CO_2 . Due to the stability of the thermal structure, there is a steep gradient of substances in the metalimnion, indicating a slow rate of nutrient exchange between the epilimnetic and hypolimnetic layers. The maximum and mean depth of Lake Kinneret when the water level is maximally legislated (208.8 m below sea level) is 43 and 26 m, respectively. The water surface area is 168 km² and total volume is 4.301 km³. Lake utilization is multipurposed for water supply, recreation, tourism, and fishery. About 150 active fishers harvest 1000–1200 tons of commercially marketed lake fish. During the spring and summer months, more than two million recreation days (personal time days) were recently documented. The major lake function is as a water supply for domestic demands, therefore safety of water quality for drinking, sailing, sailors, and swimmers is a national concern. Very low biomass density of HFCB was recorded in Lake Kinneret before 1990. Later, domination of algal community was due to cyanobacteria (nitrogen fixers and non-fixers). The enhancement

of toxic HFCB in Lake Kinneret initiated a national concern because of deteriorated water supply as well as human health. The Hula Valley and Lake Kinneret are located in the Syrian African Rift Valley in northern Israel (Figure A1). Lake Kinneret is the only natural freshwater lake in Israel. Until 2010, an average of 336 mcm (336 million cubic meters) of water was pumped annually (34% in winter and 66% in summer) from the lake, mostly for domestic usage and partly for agricultural irrigation south of the Kinneret. Since 2010, desalinization plants have supplied most of the demand for domestic consumption, and supply is therefore directed to other regions. The total national water supply is 2.11 bcm (billion cubic meters), of which 0.55 bcm comes from the Kinneret–Jordan water system, and 0.7 bcm comes from desalinization. The area of the Kinneret drainage basin Figure A1 is 2730 km², of which approximately 200 km² is the Hula Valley. Three major headwater rivers (Hatzbani, Banyas, and Dan) flow from the Hermon Mountain region (Figure A1) in the northern part of the Kinneret drainage basin. These three headwaters and more other rivers join the Jordan River and flow downstream into Lake Kinneret. The Jordan River contributes approximately 63% of the Kinneret water budget and more than 50% of the total external nutrient input originate from the Hula Valley.

The background of the outbreak of cyanobacteria has been widely studied. Most of the studies focus either on the mass ratio between available nitrogen and phosphorus or on limitation thresholds of those nutrients. Vast efforts were invested into studies regarding the impact of physical conditions such as temperature and stratification consequences, as well as turbulence and internal mass water motions. In other words, the impact of changes of climatic conditions. Not much was attributed to the study of the impact of trace elements such as heavy metals (molybdenum, vanadium, etc.). Intensive studies were carried out about the impact of the trace element of selenium on the bloom dynamics of *Peridinium gatunense* in Lake Kinneret. The similarity of the trace elements' influence on cyanobacteria growth was not widely implemented. Nevertheless, these studies did not include the optional existence of competitive interrelationships between *Peridinium* and cyanobacteria. The driving force of phosphorus or nitrogen on the cyanobacteria growth rate was documented [1–6]. Moreover, the positive impact of the N/P ratio on the enhancement of cyanobacteria domination in freshwater lakes and reservoirs has been intensively documented [3,4,7–10]. Nevertheless, in N-limited ecosystems the competitive capability of N₂-fixing cyanobacterium created by the nitrogenase enzyme requires sufficient Mo supply to enhance their production. This is because sufficient supply of the supplemented micro-element of molybdenum (Mo, as MoO₄²⁻), which is an enzyme cofactor of nitrogenase, is essentially required [11]. Although Mo is occasionally described as a “heavy metal”, its properties are very different from the typical agents of this elemental category. MoO₄²⁻ is much less toxic than the typical heavy metals such as lead, thallium, mercury, or cadmium. Molybdenum is a common trace element in toxic waters as MoO₄²⁻. The cytological–biochemical process of MoO₄²⁻ incorporation by N₂-fixer cyanobacterium has been well documented [12,13]. Availability of Mo has also been documented [12]. The competitive properties of SO₄²⁻ with Molybdenum have been documented [11,12]. Consequently, it has been suggested that in an ecosystem like Lake Kinneret where long periods of heavy bloom form *P. gatunense*, domination was replaced by cyanobacteria, including N₂-fixers and non-fixers, a catchment very rich in SO₄²⁻ outsources such as the peat soil in the Hula valley is relevant. The peat soil in the Hula valley contains huge loads of Gypsum which are an effective supplier of SO₄²⁻ accompanied by deep borehole-artesian flows containing SO₄²⁻ into Lake Kinneret. The purpose of this survey is to evaluate optional capabilities of ecological opportunities such as supplemental SO₄²⁻ aimed at strengthening competition with MoO₄²⁻ to suppress N₂-fixer cyanobacterium. The negative impact of cyanobacteria on water quality and human safety has been internationally and widely studied. Significant parts of the studies have been attributed to the availabilities of nitrogen and phosphorus and the consequences to lake eutrophication [3–6,8–10]. In Israel, after the 1950s when Lake Kinneret became the principal water supply qualified to be drinking water, optional eutrophication was a concern and removal of the *Peridinium* biomass was

efficiently achieved. Therefore, the appearance of the unpredicted outbreak of toxic N_2 -fixer cyanobacterium became a major topic in the master plan of Lake Kinneret research. The present paper confirms that this research continues.

2. Material and Methods

The GWT in the Hula Valley (2000–2020) were provided by the Hula Project Data Base in Migal's Scientific Research Institute. Information about the Jordan River discharge (1970–2018) ($m^3/year$; $10^6 m^3/year$) and sulfate concentration were provided by Israel Hydrological Service of the National Water Authority; Mekorot, Water Supply Company, Kinneret and River Jordan monitoring Unit., and Kinneret Limnological Laboratory, IOLR (LKDB 1970–2021). All data for Sulfate and Mo concentrations were given in ppm and mM, and ppb and μM , respectively. Rainfall data (1940–2020) were provided by the Israeli Meteorological Service–Meteorological Station, Dafna (M. Peres responsibility).

2.1. Statistical Methods

Three regression methods were performed (StataSE 17): (1) fractional polynomial regression of continuous covariates, a form of parsimonious parametric modeling (published in *Applied Statistics* 43: 429–467), (2) linear regression with confidence interval percentage (95%) (StataSE17), and (3) LOWESS Smoother (0.8 Bandwidth), which provides weighted scatterplot smoothing. All mass loadings are given in metric tons.

2.2. Ground Water Table Mapping

Distributional mapping of subterranean waters was carried out by incorporation of Ground Water Table (GWT) records and Inverse Distance Weighting (IDW), which is a deterministic method for multivariate interpolation with a known scattered set of recorded GWT depth. The assigned values to unknown points of GWT depths were calculated with a weighted average of the values available at the known points.

3. Results

3.1. Sulfate (SO_4^{2-}) Resources

What is the size and seasonality of the sulfate load in Lake Kinneret? The answer was given in 52 annual reports (1969–2021) published by the Kinneret Limnological Laboratory [14] and numerous documented papers and books published during long-term studies [2,14–16]. Due to the seasonality of the thermal structure in Lake Kinneret, concentration of SO_4^{2-} slightly varies between epilimnion and hypolimnion layers in summer (stratification) and winter (fully mixed) months. Moreover, the SO_4^{2-} supply to Lake Kinneret originates mostly from outsourcing. Water input into Lake Kinneret is contributed through the headwater river discharges of Hazbani, Banias, and Dan Rivers combining into the Jordan River (65% of total input). Nevertheless, SO_4^{2-} concentration in the headwater, including the northern flow to the joint formation of the River Jordan in the Hula Valley and several other runoff springs, is below 30 ppm. Southern to the Hula Valley, the SO_4^{2-} concentration in the Jordan River is above 100 ppm. Another significant contributor of SO_4^{2-} is sub-lacustrine salty-hot springs, where SO_4^{2-} concentrations varies between 200–780 ppm [17]. A recent new outsource was formed as a consequence of deep borehole drilling (Shamir) [18] where SO_4^{2-} concentration varies between 600–650 ppm. The SO_4^{2-} source within the Hula Valley is peat soil which contains a 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 downstream. The hydrological structure directs these drifted matters towards the Jordan River, continuing downstream into Lake Kinneret.

3.2. Sulfate (SO_4^{2-}) Outsources in the Hula Valley

The hydrological input compartments in the Hula Valley which supply SO_4^{2-} into Lake Agmon include the following: the principal drainage canal, "Canal 101" or "Canal Z"

several other branches of drainage canals; Hula East conveyor and the reconstructed River Jordan “Hula Branch”. The output of SO_4^{2-} towards River is in Table 1.

Table 1. Lake Agmon outlet: mass balance of annual SO_4^{2-} (metric tons/year) dynamics (2008–2018) [19–22].

	Source	SO_4 (ton/year)
Input	Reconstructed Jordan	40
Input	“Canal Z”	1564
Input	Hula East	105
Total Input		1709
Output	Agmon Outlet	1302
Output	Irrigation	135
Total Output		1437

The results shown in Table 1 indicate that 273 (1709–1437) tons of SO_4^{2-} are retained in Lake Agmon annually and 1437 tons are conveyed downstream. Moreover, concentrations of input SO_4^{2-} are high and low in winter and summer, respectively.

High concentrations of SO_4^{2-} of 600–650 ppm and a yield of 20 mcm/year (10^6 m^3) are measured in Shamir boreholes and contained approximately 12,000–13,000 tons of SO_4^{2-} .

Distribution of SO_4^{2-} concentrations (ppm) in Lake Kinneret (Figures 1–3) and in the Hula Valley are shown (Figures 4 and 5).

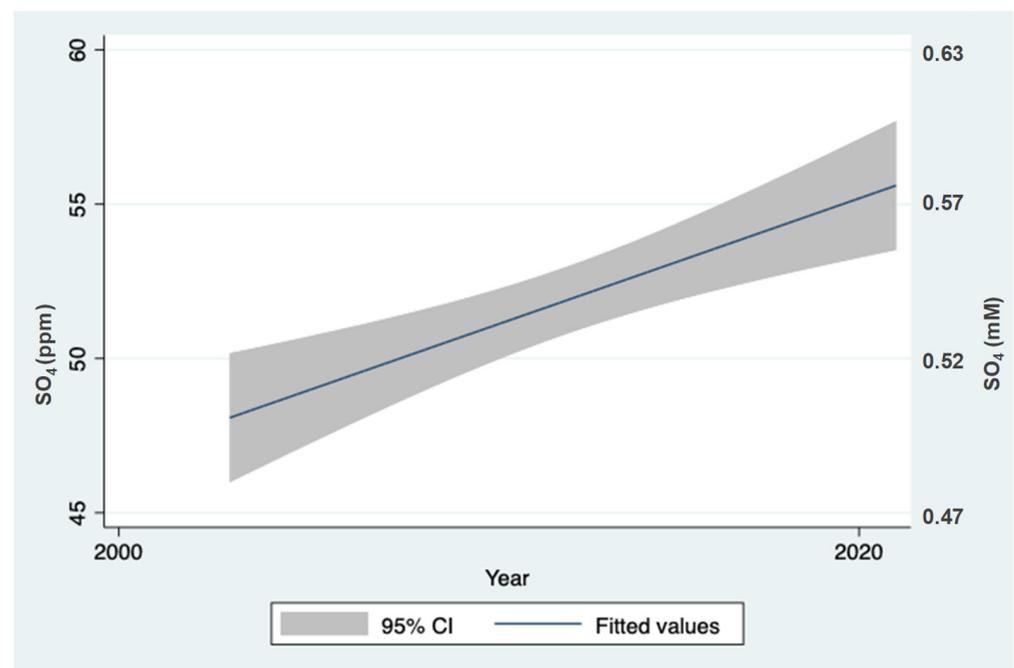


Figure 1. Temporal distribution of SO_4^{2-} concentrations (ppm) in Lake Kinneret: Linear regression (95% CI) between annual concentrations of SO_4^{2-} and years (2003–2020).

The results given in Figure 1 indicate an increase of SO_4^{2-} concentration in Lake Kinneret from 2000–2020.

Data given in Figure 2 indicate that prior to the 2010, SO_4^{2-} concentrations in Lake Kinneret significantly ($r^2 = 0.3758$; $p = 0.0002$) declined.

The trend of changes (LOWESS; 0.8 plot) of long-term SO_4^{2-} concentration (ppm; mM) fluctuations in Lake Kinneret represent the 1970–1998-decline and 1987–2004 elevation.

The seasonal changes of SO_4^{2-} concentrations in the Hula Valley are given in Figure 4, indicating significant seasonal decline.

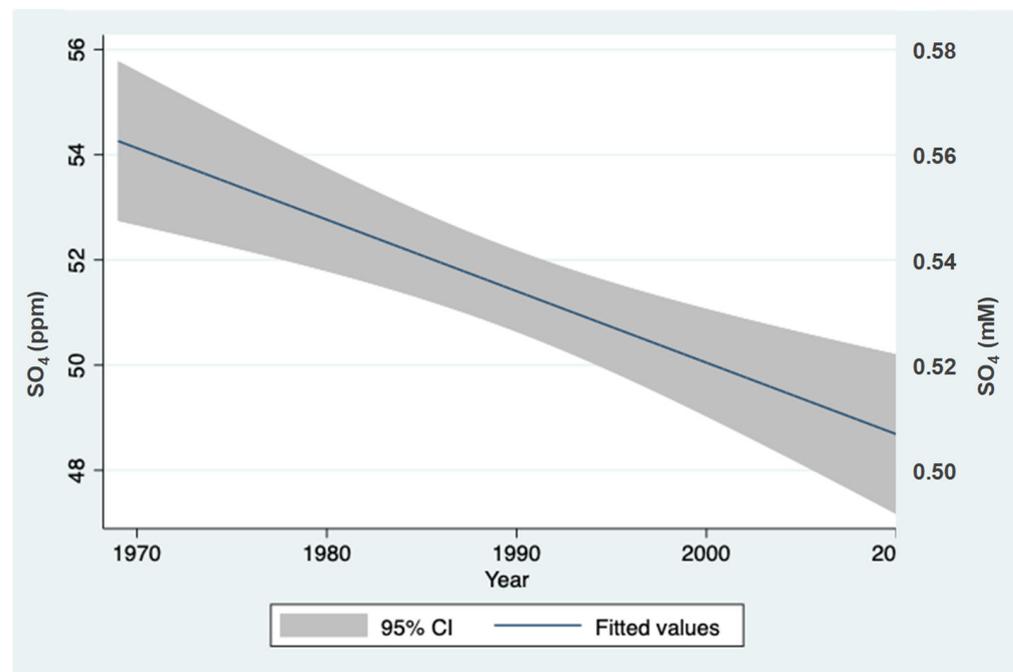


Figure 2. Temporal distribution of SO_4^{2-} concentrations (ppm; mM) in Lake Kinneret: Linear regression (95% CI) between annual concentrations of SO_4^{2-} and years (1970–2010).

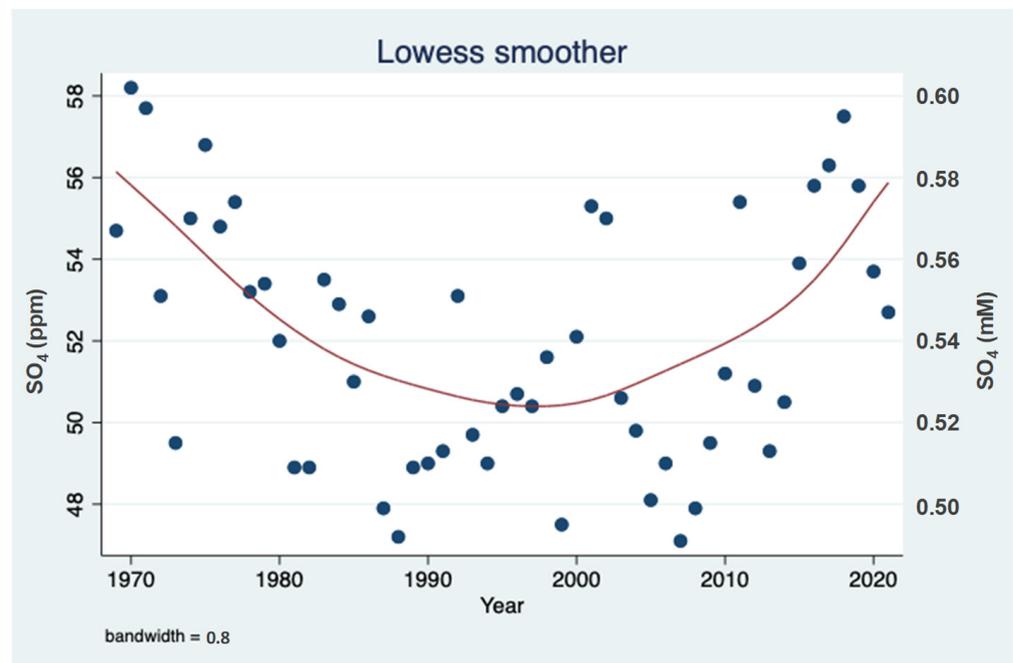


Figure 3. Temporal fluctuations of SO_4^{2-} concentrations (ppm; mM) in Lake Kinneret during 1970–2020: Annual averages are plotted vs. years as LOWESS Smoother (0.8 bandwidth).

Quantitative and seasonal relations between the River Jordan discharge and sulfate concentrations (ppm) and mass loads (ton) ranges are presented in Figures 5–11.

The long-term (1970–2010) decline of the River Jordan discharge presented in Figure 5 confirms the regional Climate Condition Changes (CCC).

The annual and monthly fluctuations of SO_4^{2-} input into Lake Kinneret through the discharge River Jordan are shown in Figures 6–12.

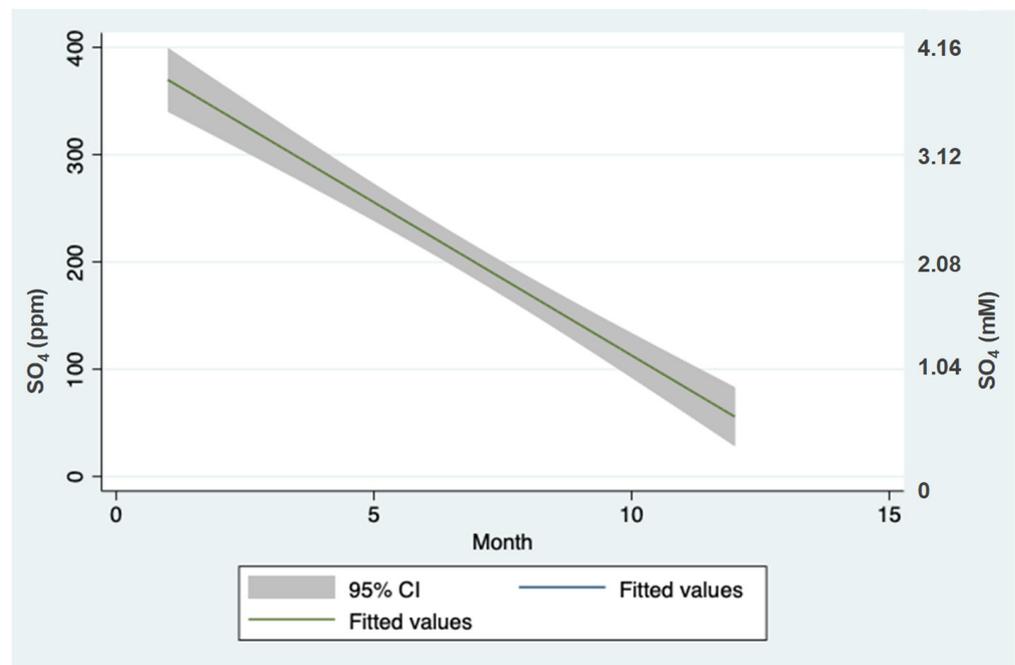


Figure 4. Grand total average of monthly mean concentrations of SO_4^{2-} (ppm; mM) of all sampling stations within the Hula Project zone in the Hula Valley during 1994–2010.

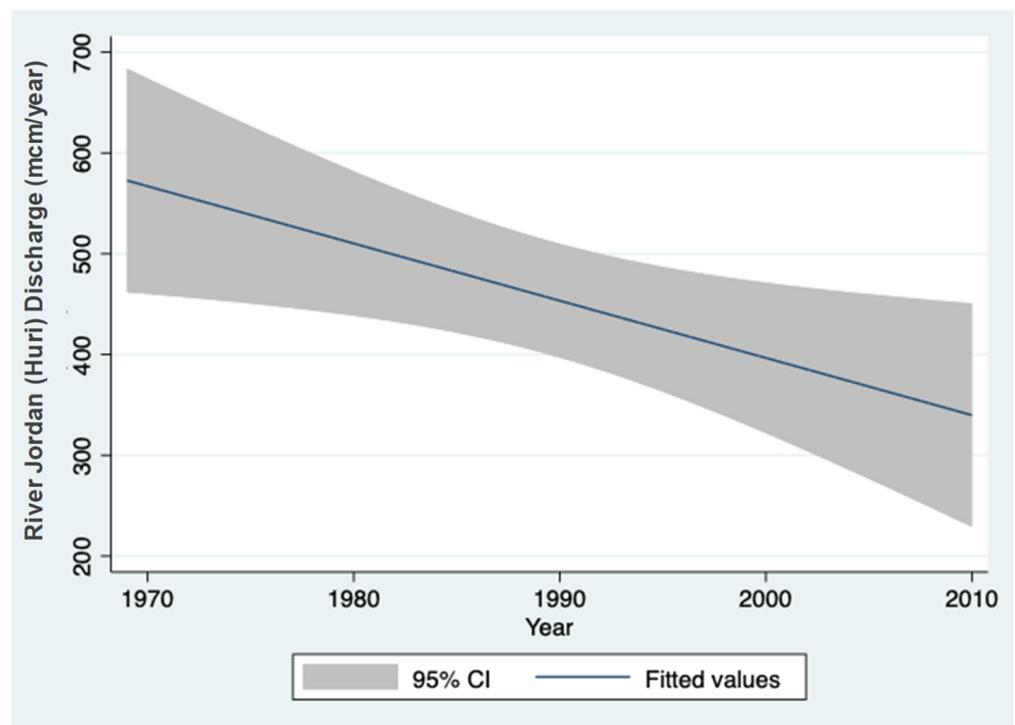


Figure 5. River Jordan (Huri Station) annual discharge (mcm/year) during 1970–2010.

The dependent SO_4^{2-} capacity within the River Jordan discharge indicates the seasonality of the CCC realities: 1970–1978, sharp decline, 1978–1998, moderate decline; early 2000s, sharp decline. The long-term decline of Jordan discharge and consequently SO_4^{2-} input was confirmed.

The dependence relation between SO_4^{2-} input and discharge is confirmed in Figure 7. The higher the discharge, the higher the SO_4^{2-} input.

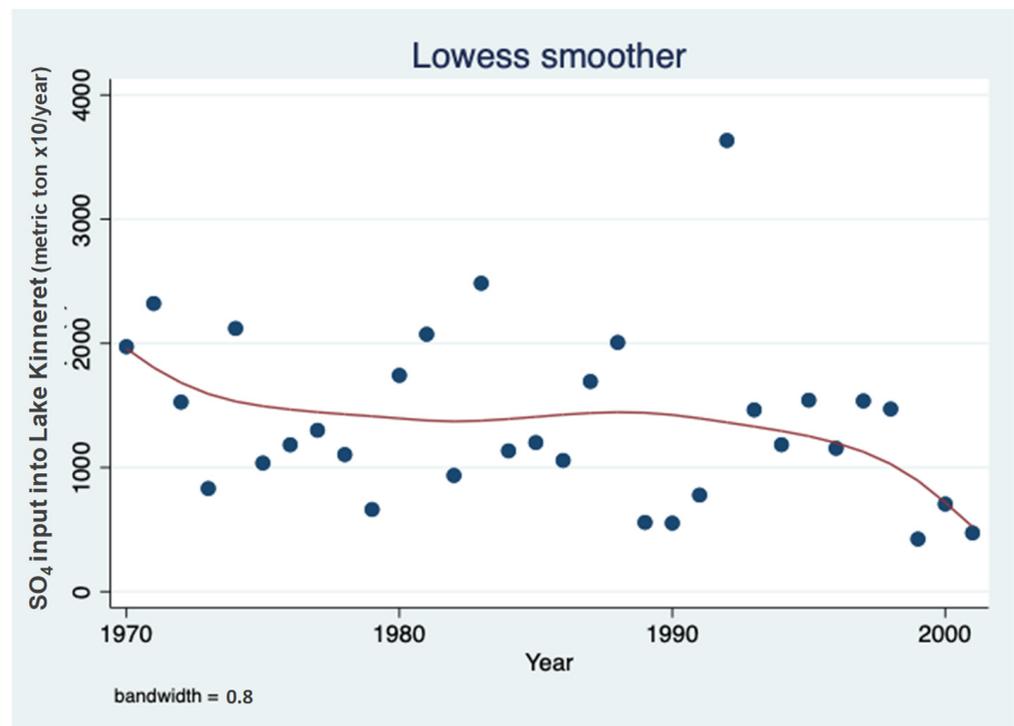


Figure 6. Trend of changes (LOWEESS Smoother 0.8 bandwidth) of annual SO_4^{2-} input into Lake Kinneret (metric ton \times 10/year) during 1970–2004.

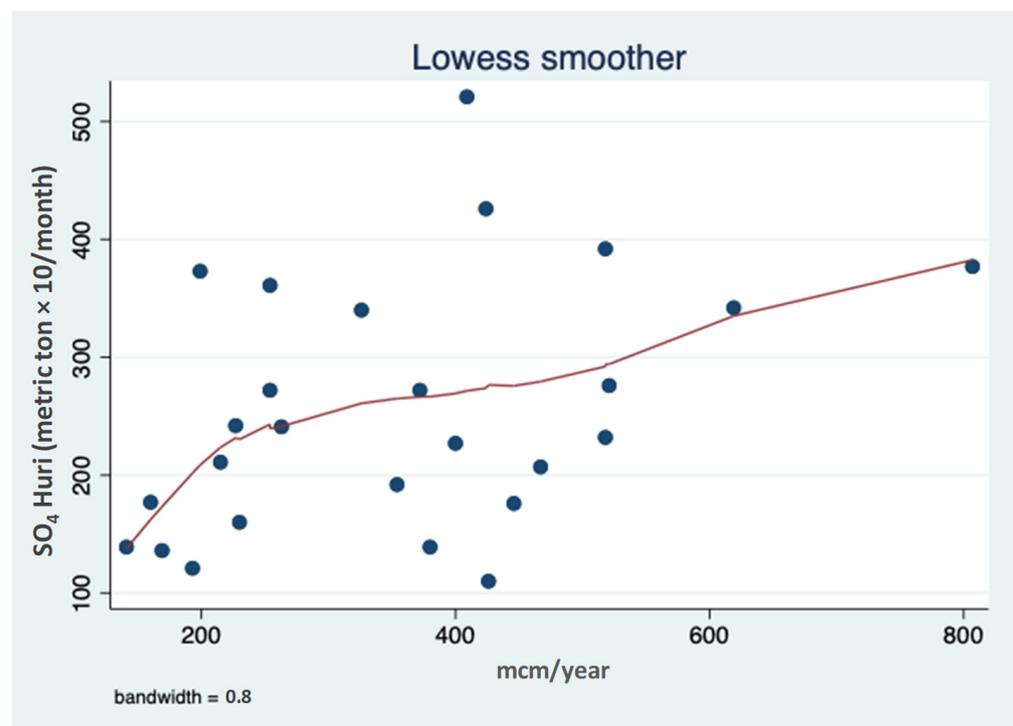


Figure 7. LOWESS Smoother (bandwidth 0.8) plot of monthly inputs of SO_4^{2-} (metric ton \times 10/month) through River Jordan discharge into Lake Kinneret during 1970–2004 in relation to the discharge capacities.

The significant linear regression between monthly values of SO_4^{2-} input and River Jordan discharge is confirmed in Figure 8.

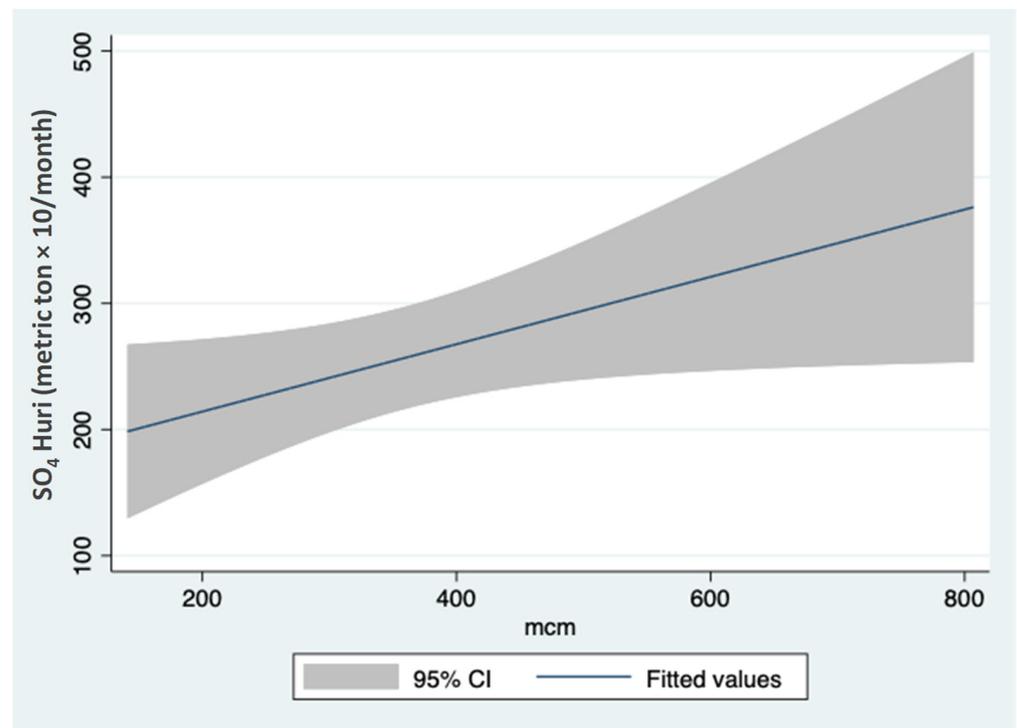


Figure 8. Linear regression (95% CI) plot of monthly inputs of SO_4^{2-} (metric ton \times 10/month) through River Jordan discharge into Lake Kinneret during 1970–2004 in relation to the discharge capacities.

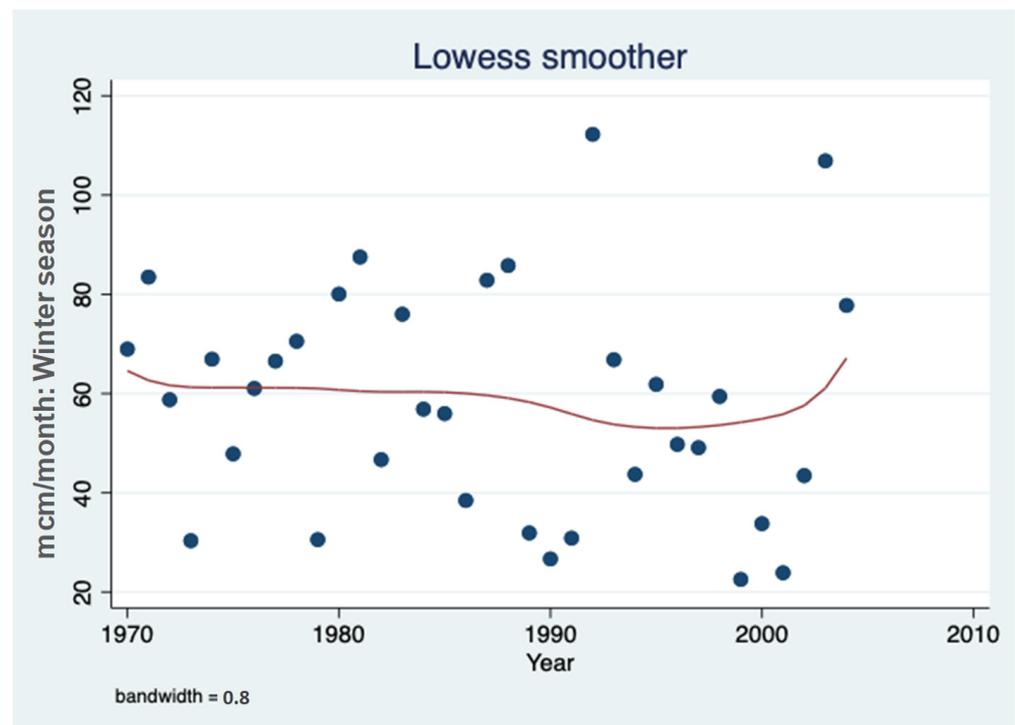


Figure 9. Annual mean of monthly winter months (1–5) discharges (mcm/m) of the River Jordan during 1970–2004, LOWESS Smoother (0.8) plot.

Results given in Figure 9 indicate that even in winter months (1–5), a long-term slight decline of River Jordan discharge was documented during 1970–1997, which then slightly elevated afterwards during early 2000s.

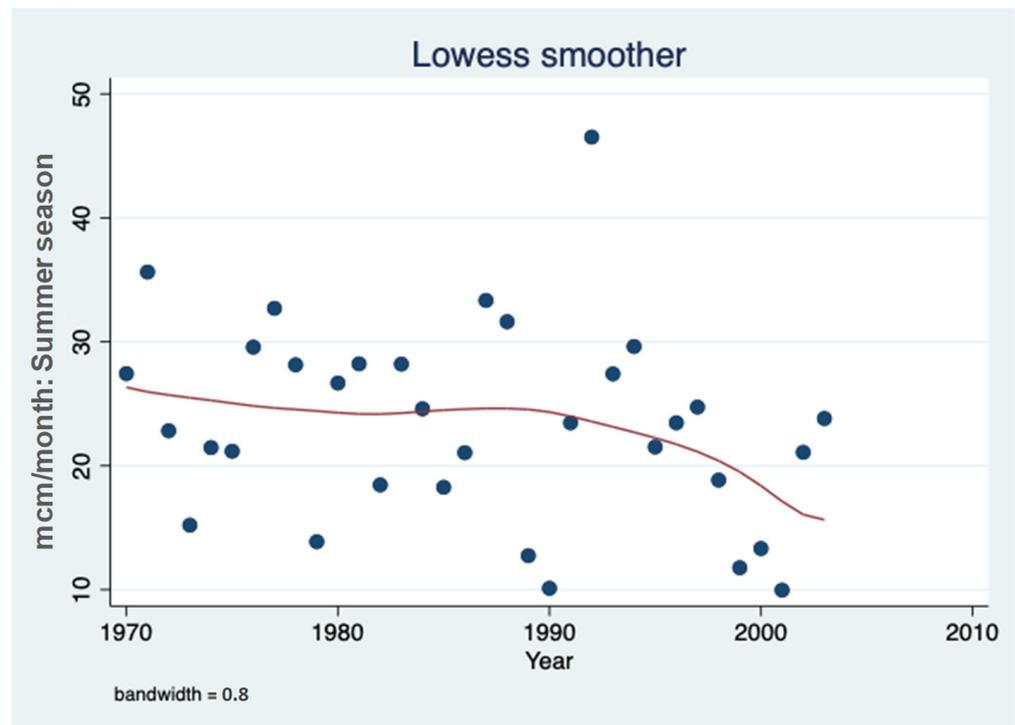


Figure 10. Annual mean of monthly summer–fall (6–12) discharges (mcm/month) of the River Jordan during 1970–2004 LOWESS Smoother (0.8) plot.

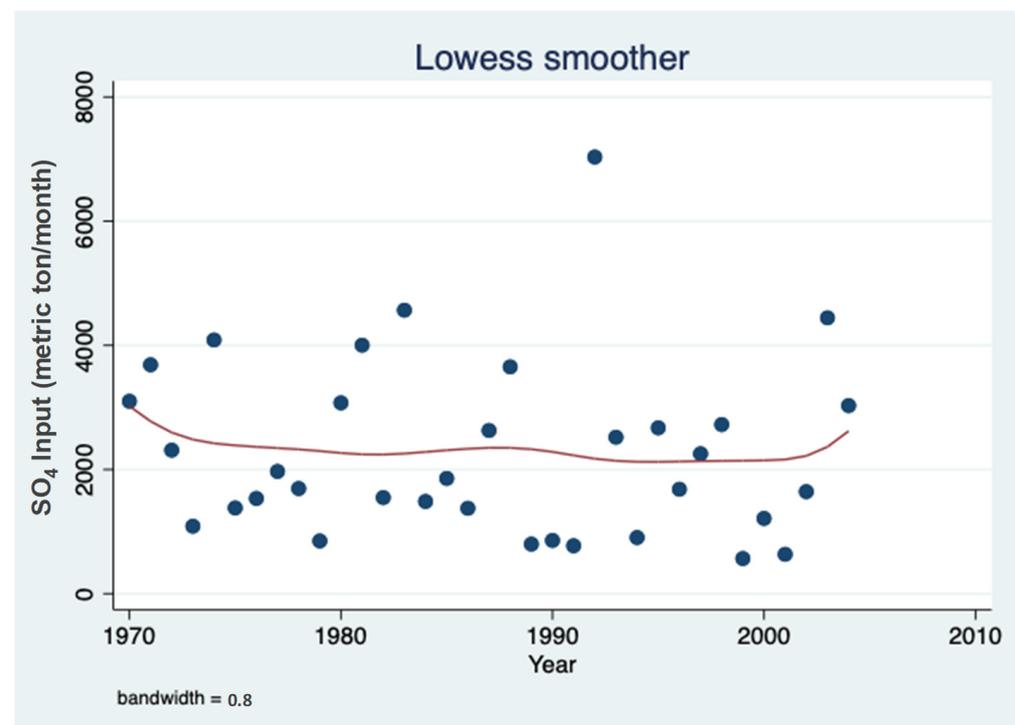


Figure 11. Annual mean of monthly winter months (1–5) SO_4^{2-} input (metric ton/month) through the River Jordan flow during 1970–2004, LOWESS Smoother (0.8) plot.

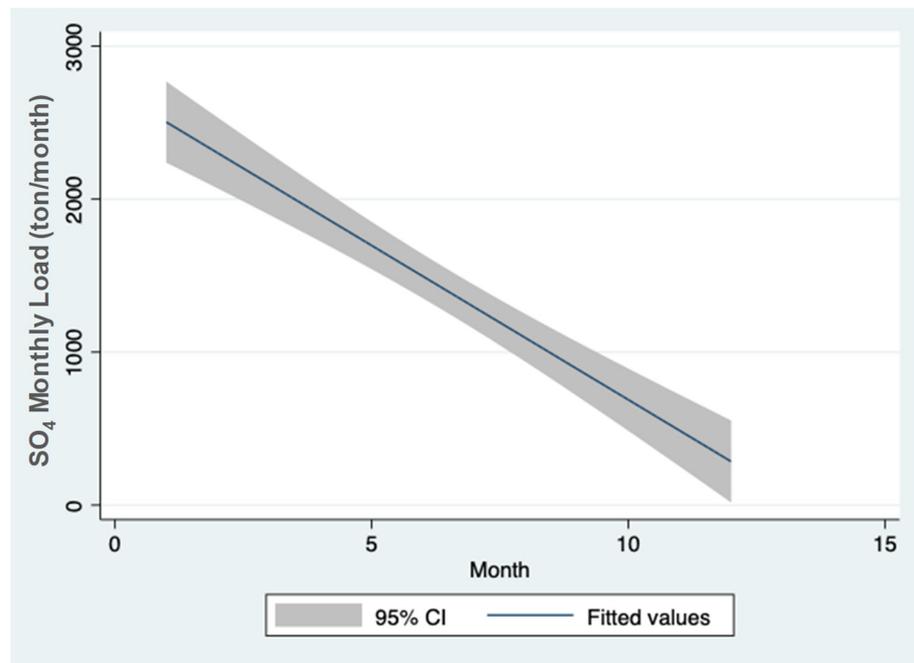


Figure 12. Linear regression (CI 95%) plot of monthly SO_4^{2-} input (ton/month) into Lake Kinneret through the River Jordan discharge during 1970–2004.

In continuity to Figure 9, the summer–fall (6–12) Jordan discharges also represent significant decline.

Figure 9 confirmed a slight decline of Jordan discharges in winter. Nevertheless, SO_4^{2-} inputs through Jordan winter discharge very slightly fluctuated (1970–2004).

SO_4^{2-} input capacities through the Jordan River discharge during summer–fall months (6–12) are shown in Figures 12–14.

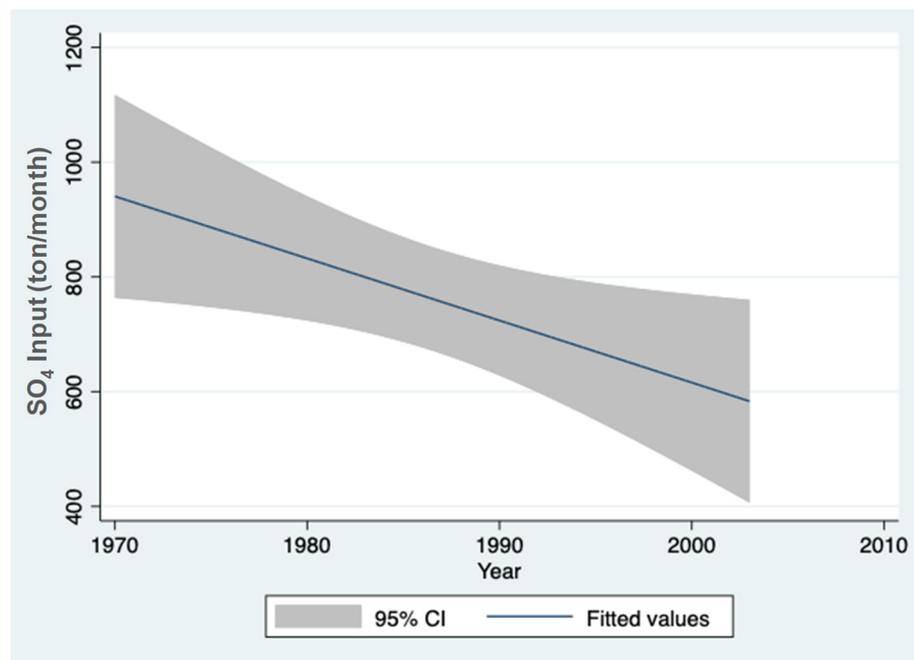


Figure 13. Linear regression (CI 95%) plot between annual (1970–2004) means of monthly values of SO_4^{2-} input (ton/month) into Lake Kinneret during summer–fall (months 6–12).

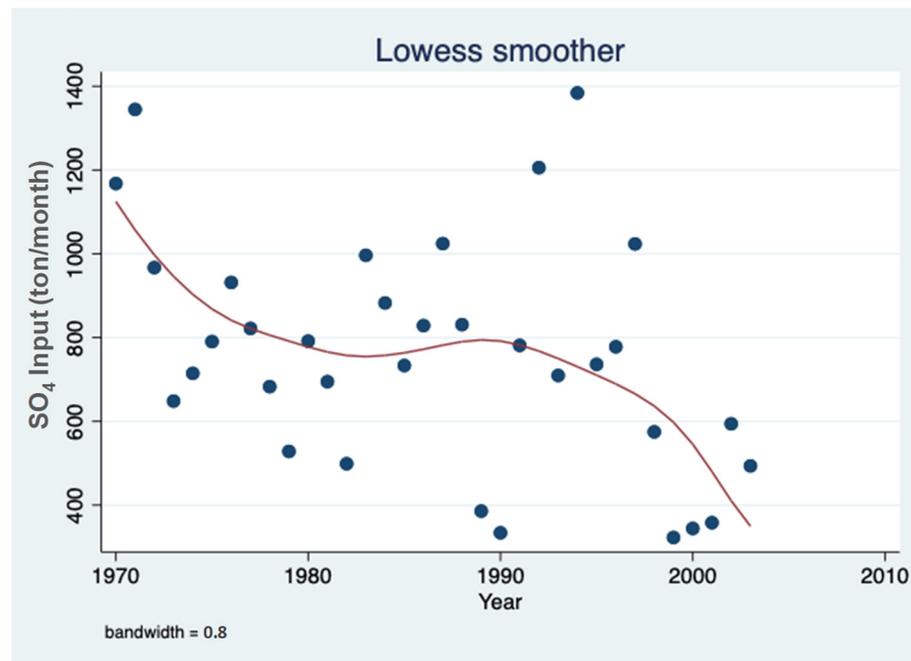


Figure 14. LOWESS (0.8) Smoother plot of annual (1970–2004) means of monthly values of SO_4^{2-} input (ton/month) into Lake Kinneret during summer–fall (months 6–12).

Lake Kinneret and its watershed are included within the tropical geographical global climate zone. Therefore, the winter is short, wet, and cold whilst the summer is long, dry, and hot. The results shown in Figure 12 support the geographical determination of significant ($r^2 = 0.7841$; $p < 0.0001$) decline of the discharges of River Jordan during second half of the year. Conclusively, the summer inputs of SO_4^{2-} through River Jordan into Lake Kinneret were reduced.

Figure 13 reinforces previous Figures showing the long-term (1970–2004) summer decline of SO_4^{2-} input capacities into Lake Kinneret. Similar conclusions are also seen in Figure 14, as outlined by the LOWESS Smoother (0.8) plot.

4. Discussion

4.1. Sulfur Cycle in Lake Kinneret

Sulfur in lake waters exists mostly as an aerobic form of sulfate and un-aerobic form of Sulfide. Major outsourcing of sulfur to Lake Kinneret is through bedrock erosion and peat soil gypsum dissolution. Internal sourcing includes organic matter protein (amino acids) microbial degradation. Cycling conversion of sulfuric compounds is carried out by bacteria and highly correlated with the seasonal changes of thermal structure and external input [2,15]. External input rate is dependent on climate seasonality; it is heavier when river discharge is enhanced during the rainy season and sharply declines in the summer months. The chemical substance oxidation commonly starts during initiation of stratification when Dissolved Oxygen (DO) is utilized and continues through reduction of nitrate through de-nitrification to nitrite and further to ammonium as a DO source. Further chemical supply of DO originates from a reduction of SO_4^{2-} to S^{2-} . Consequently, S^{2-} and SO_4^{2-} exist in anaerobic and aerobic conditions, respectively. The SO_4^{2-} reduction enriches the hypolimnion with S^{2-} , and during the de-stratification process S^{2-} is oxidized to SO_4^{2-} . It must be considered that these chemical conversions are microbially operated, which is required to dissolve organic matter supply. The summer composition of the epilimnetic waters in Lake Kinneret was defined by nutrient (nitrogen, phosphorus) limitation resulting in both bacterial activity and sharp reduction of external nutrient import. Moreover, during the summer months the temperature was high and consequently, metabolic demands were elevated as well. Moreover, long-term records of the Kinneret Phytoplankton assemblage

composition indicate a domination shift from the bloom-forming nitrogen consumer, *Peridinium gatunense*, to N₂-fixer cyanobacterium, *Aphanizomenon ovalisporum*. Apparently, the outbreak of *A. ovalisporum* in the summer of 1994 was predicted due to prolonged processing of nutrient regime modification indicated clearly in the early 1990s: The Kinneret ecosystem was modified from phosphorus to nitrogen limitation [1,7].

4.2. Molybdenum (MoO₄²⁻) in Lake Kinneret

Mo is sometimes described as a “heavy metal”, but its chemo-physical properties are very different from those of the typical heavy metals such as mercury, thallium, or lead. Mo is much less toxic than typical heavy metals. MoO₄²⁻ is found in nature as an oxidation state in minerals. Most of MoO₄²⁻ compounds have low solubility in water, but Mo minerals in contact with oxygen form soluble MoO₄²⁻ [14,23–27]. The relevance of MoO₄²⁻ to the present issue is due to the nitrogenase enzyme activity enabling N₂-fixation by species of cyanobacteria. The catalytic property of nitrogenase of breaking the chemical bond of atmospheric nitrogen molecule enables its fixation into biological substances [11,13,28–32]. Very little is known about the distribution of MoO₄²⁻ in Lake Kinneret and its drainage basin [17]. Results of an experimental study that was carried out with heavy metals (Zn, Cd, Pb, and Cu) indicated that the annual thermal structure changes, which also implies that oxic-anoxic cycling of heavy metals are fixed into the sediments during summer stagnation and might be released during winter turnover period [28–30]. A thorough survey of 24 metal (including MoO₄²⁻) concentrations (dissolved and particulate) was conducted in Lake Kinneret and Jordan and Meshushim (Golan Height) Rivers. The existence of MoO₄²⁻ was documented in the epilimnion and the hypolimnion of Lake Kinneret and Jordan and Meshushim Rivers in all samples collected. Concentration ranges of Mo in Lake Kinneret varied between 0.5–1.5 µg/L (0.00521–0.0156 µM). The inventory of Mo was partly documented [14,23]. It was indicated in those reports that during stratification MoO₄²⁻ concentrations in the hypolimnion were lower than those in the epilimnion, and temporal fluctuations were negligible. Common concentrations of Mo in Lake Kinneret varied between 0.5–1.5 µg/L (0.00521–0.0156 µM) [23]. Evaluation of the long-term fluctuation of the SO₄²⁻:Mo molecular (M) ratio was computed (Table 2).

Table 2. Periodical (1969–1978, 1985–1995) averages of mass (ppm, ppb) and molar (mM, µM) concentrations of Mo and SO₄²⁻ and molar ratio in between.

	1969–1978	1985–1995
SO ₄ ²⁻ (ppm)	56	46
Mo (ppb)	0.5–1.5	0.5–1.5
SO ₄ ²⁻ (mM)	0.583	0.479
Mo (µM)	0.00521–0.0156	0.00521–0.0156
SO ₄ ²⁻ (mM)/Mo (µM) ratio	1.11–0.37 × 10 ⁵	0.91–0.31 × 10 ⁵

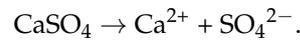
Marino and Haworth [31]; Howarth et al. [27] reported 2.6 × 10⁵ for Sea Water, and 0.22 × 10⁵ for Freshwater.

The averaged periodical (1969–1978; 1985–1995) measured concentrations of Mo (µM), which is the dissolved form of MoO₄²⁻ predominantly, the anion in the Kinneret epilimnetic oxic high pH [15,23] conditions, and the anion of SO₄²⁻, and the ratio between them is given in Table 2. Prominent differences of Mo concentrations between this oxic epilimnion and the anoxic hypolimnion were indicated, while no significant periodical differences were documented [23].

Results given in Table 2 indicate the SO₄²⁻:Mo (M Ratio) status in Lake Kinneret is of an intermediate position of salinity, probably brackish waters [11–13,15,27]. Nevertheless, prominent periodical decline of this ratio was seen during 1985–1995, as well as the outbreak of the N₂-Fixer cyanobacterium, *Aphanizomenon ovalisporum* [1,7].

4.3. SO_4^{2-} Flushing from the Peat Soil

The high content of gypsum (CaSO_4) is widely documented [19–22]. The gypsum is significantly dissolved in water releasing free Ca^{2+} and SO_4^{2-} :



Previous given results confirmed decline of rainfall, and consequently lower river discharge and suppression of SO_4^{2-} concentrations and loads in the Hula valley runoffs, River Jordan, and Lake Kinneret waters. Consequently, the potential impact of peat–soil moisture (GWT depth) and SO_4^{2-} drifting was evaluated. It has been suggested that the more wet peat–soil volume there is (higher GWT), the higher the SO_4^{2-} flushing. The last summer–fall month shortly before rain starts, October, was documented during 2013–2021 when the foremost five years were drought, and then in the period of 2019–2020 heavy rainfall was documented. Results shown in Table 3 indicate that lower rain capacity during 2014 and 2016–2018 and to a lesser extent in 2021 induced lower GWT, causing higher volume of dry peat soil and probably initiating lower levels of SO_4^{2-} drifting (Figure A1; Tables 3 and 4). On the contrary, during 2019–2020, heavy rainfall enhanced GWT elevation as greater water covered the area, which increased the volume of highly wetted peat soil and possibly enhanced SO_4^{2-} drifting (Tables 3 and 4).

Table 3. Water covered area (ha) of peat soil in relation to discrete depths of Ground Water Table (GWT) in October during 2013–2021; annual rainfall data are given (mm/year).

GWT (m)	2013	2014	2015	2016	2017	2018	2019	2020	2021
0.5	0	0	0	0	0	0	0	3	0
1	2	6	8	13	6	34	9	12	1
1.5	393	266	528	507	495	494	461	319	154
2	1303	1596	1555	826	1488	1118	1409	1098	979
2.5	682	450	321	639	369	660	526	919	765
3	27	77	5	363	55	99	13	61	481
3.5	7	12	0	61	5	11	0	6	35
4	4	6	0	8	0	3	0	0	3
4.5	0	4	0	0	0	0	0	0	0
5	0	1	0	0	0	0	0	0	0
Total	2418	2418	2417	2417	2418	2419	2418	2418	2418
Rain	671	352	607	467	477	474	848	798	535

Table 4. Volume of dry and wet layers (total $120.9 \times 10^6 \text{ m}^3$) in October during 2013–2021, and percentage of wet layer from the total.

Year	Dry Layer (10^6 m^3)	Wet Layer (10^6 m^3) (%)
2013	50.2	70.7 (58.5)
2014	70.5	50.4 (41.7)
2015	47.3	73.6 (60.9)
2016	67.3	53.6 (44.3)
2017	72.6	48.3 (40.0)
2018	70.9	50.0 (41.4)
2019	48.7	72.2 (59.7)
2020	51.9	69.0 (57.1)
2021	56.8	64.1 (53.0)

Considering 2418 ha (Table 3) as the total area of peat land (soil) and 5 m below surface as the lowest depth of GWT, a total volume of a block is formed by $120.9 \times 10^6 \text{ m}^3$. Based on GWT depth and areal stretch mapping (total area $2418 \times 10^3 \text{ ha}$), the peat soil area was divided into two layers: (1) Wet—from the top of GWT to 5 m depth, and (2) Dry—from

the top of GWT to surface. The volume of each layer in October during 2013–2021 was computed, and the results (10^6 m^3) are given in Table 4.

The higher volume of dry layer during low rainfall capacity (see Table 2) and vice versa is prominent. With the flushing of gypsum (CaSO_4) derivate, the SO_4^{2-} is moisture dependent and the soil moisture is higher, therefore the SO_4^{2-} flushing capacity is higher and vice versa. Dryness conditions therefore initiate a decline of SO_4^{2-} flushing from the Hula Valley.

Linear correlation between annual rainfall (Figure 3) and the volume of wet layer in the gypsum rich peat soil (total area $2418 \times 10^3 \text{ ha}$) was found to be significant at $r^2 = 0.6837$ and probability (p) = 0.0060, indicating prominent decline of gypsum dissolution and SO_4^{2-} flush towards Lake Kinneret during the summer droughts.

The role of trace metals, particularly molybdenum, in aquatic and terrestrial ecosystems has been widely documented [31–35]. It was suggested [36] that the expansion of N_2 -fixing cyanobacteria (NFC) was delayed while the availability of bio-essential metals such as Molybdenum in the oceans was limited. An indication was made (Parnell et al. [36]) that the evolution of NFC during the Proteromesozoic Era may have been promoted also in lakes. Molybdenum availability is critical to life in lakes and oceans [11,13,31–37]. The presence of MoO_4^{2-} in rainwater has also been documented [38]. The ecosystem implication of MoO_4^{2-} is mostly bound to the nitrogen fixation process and general primary productivity, and particularly to the nitrogen fixation process [10,11,27,31,33–40]. The potential of limited control of N_2 fixation and NO_3 uptake in lakes was documented by Romero et al. [37]. Conclusively, the nitrogen cycle and primary productivity in aquatic (freshwater and marine) ecosystems are dependents of N_2 fixation which is in turn controlled by the activity of the MoO_4^{2-} -dependent nitrogenase enzyme. A reconciliation of the complexity of interaction was initiated through the SO_4^{2-} factor. The sulfate (SO_4^{2-}) ability to compete with molybdenum (MoO_4^{2-}) on uptake sites resulted in the ions sharing similar charge-to-mass ratio and stereochemistry [13]. Suppression of cyanobacteria growth by low availability of MoO_4^{2-} in coastal ecosystems has been documented [12]. Nevertheless, precise quantification of SO_4^{2-} -Mo competition was confirmed, but not precisely indicated. The SO_4^{2-} availability parameter within such a complex of interactions in Lake Kinneret might be a factor that accelerated the domination replacement of the bloom-forming *Peridinium gatunense* by cyanobacteria. Evaluation of the long-term (1970–2020) Lake Kinneret data records confirm the following: Decline of nitrogen availability, slight increase of phosphorus concentrations, consequent decline of N/P mass ratio, nitrogen preferred *P. gatunense* suppression, the biomass of nitrogen-fixing cyanobacteria enhancing, SO_4^{2-} inputs diminishing and being accompanied by a decline of concentration and load in the lake. The Lake Kinneret ecosystem shifted from Phosphorus to Nitrogen limitation status.

The geo-chemical features of Lake Kinneret have been widely discussed [2,15], including the distinct separation between winter and summer climate conditions, the seasonal changes of the thermal structure, and the geochemical status of brackish water with a high level of salinity (including calcium), and pH and oxic epilimnion throughout full year cycle. Consequently, the availability of MnO_4^{2-} was suggested [24]. Moreover, following the classification of bodies of water on the basis of $\text{SO}_4^{2-}/\text{Mo}$ ratio [31], Lake Kinneret ranked above freshwater and below seawater (Table 2). It is likely that Lake Kinneret ranked close to the lakes of Alberta [31]. The $\text{SO}_4^{2-}/\text{Mo}$ ratio in the oceanic environment is known to be very constant, while in brackish and freshwater ecosystems (such as Lake Kinneret) geochemical conditions probably initiate fluctuating ranges. These geochemicals include an alternate of wet-dry conditions as occurring in the Hula Valley peatland soil with a heavy load capacity of gypsum. Under moisture elevation resulting from changes in climatic conditions, SO_4^{2-} is flushed downstream from the Hula into Lake Kinneret and controls the abundance of HFCB. That is a process impact that developed through the competitive interaction between SO_4^{2-} with MoO_4^{2-} resulting in inhibition of MoO_4^{2-} assimilation by HFCB and the biomass reduction. The contrary was probably developed during the summer of 1994: After several years of lowering the N/P ratio [7], which stimu-

lated HFCB enhancement of MoO_4^{2-} assimilation, resulted in SO_4^{2-} reduction supported HFCB growth rate. The increase of SO_4^{2-} activity by its concentration elevation has been documented [31].

Documentation of the significant impact of the ratio $\text{SO}_4^{2-}/\text{Mo}$ but not each of their concentrations has also been reported [31].

The event of HFCB invasion or developed sporadic domination is a case where climate and other environmental conditions are involved. Nitrogen and phosphorus nutrient dynamics were modified: Nitrogen became insufficient and phosphorus remained sufficient (even slightly increased), and the ecosystem trophic status shifted from phosphorus to nitrogen limitation (lowering N/P mass ratio). Later on, as a result of Climate Condition Change (CCC) suppression of SO_4^{2-} , inputs improved the assimilation capability of Mo by cyanophytes, and the eco-directions of the changes both improved the growth rate of HFCB.

The objective of the present study is aimed at evaluating the relevance of the information about MoO_4^{2-} and SO_4^{2-} impact on nitrogen fixation which were documented in Lake Kinneret and changes recorded its drainage basin.

The ecosystem structure of Lake Kinneret has undergone ecological modifications: During the 1970s–1980s, nitrogen declined and phosphorus slightly elevated. As a result of nitrogen deficiency, the dominance of the bloom-forming *Peridinium* spp. was replaced by harmful cyanobacteria (HFCB). Lake Kinneret shifted from phosphorus to nitrogen limitation. Moreover, since the mid 1980s, climate condition changes have become significant, and consequently the temperature has elevated while rainfall and river discharge diminished. The invasion of the N_2 -Fixer Cyanobacterium *Aphanizomenon ovalisporum* (HFCB) 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, it was recently suggested to consider the MoO_4^{2-} availability and its chemical relation with SO_4^{2-} concentrations in the Kinneret ecosystem. Several key studies confirmed the competitiveness relation between MoO_4^{2-} and SO_4^{2-} .

Sulfate (SO_4^{2-}) is very common in the Kinneret watershed, mostly released by dissolution of gypsum (CaSO_4): $\text{CaSO}_4 \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}$ in the peat soil in the Hula Valley. The linkage between sulfate transport into Lake Kinneret initiated the need to evaluate the potential impact of its effectivity 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 and dryness trend in the Hula peatland and lowered 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. Increase of SO_4^{2-} concentration might suppress MoO_4^{2-} uptake and consequently slow down. Nitrogen fixation by HFCB is an ecological advantage. Reversibly, SO_4^{2-} deficiency enables HFCB to maintain advantageous features of nitrogen fixation. It is suggested that these interaction complexities occurred in Lake Kinneret during the 1980s, together with nitrogen deficiency. Moreover, nitrogen deficiency, combined with the seasonal lowest availabilities of epilimnetic SO_4^{2-} and its input range, are common in summer months, which was the timing of the HFCB outbreak. The lack of nitrogen damaged the *Peridinium* growth rate and nitrogen fixation, supplemented by the MoO_4^{2-} competitor SO_4^{2-} decline, enhanced HFCB. The complexity of the ecological interactions includes nitrogen, phosphorus, MoO_4^{2-} , and sulfate availabilities, which encourage future management to design a wider consideration combined with previously considered nitrogen and phosphorus.

5. Future Perspectives

The tentative target suggestion is the renovation of *Peridinium* domination and reduction of HFCB. The concept given in this paper is aimed at the enhancement of nitrogen and SO_4^{2-} input into Lake Kinneret during summer–fall season when nutrients supply by river discharges are minimal. An optional implementation is the transport of water

rich with SO_4^{2-} from Shamir drills into Lake Kinneret. Sulfate concentrations in Shamir drills vary between 600–650 ppm and annual discharge is about 20 mcm. Another optional suggestion is to enhance the wettability of the peat soil during summer in the Hula Valley, which requires more water supply allocation (under consideration presently).

Author Contributions: M.G. and V.L.-O. cooperatively implemented data analysis, conceptual evaluation; V.L.-O. carried out the field measurements of GWT and surface mapping of the underground water migration; M.G. directed water chemistry; presentation design, computerization, and the preparation of the original draft and final version was carried out cooperatively. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

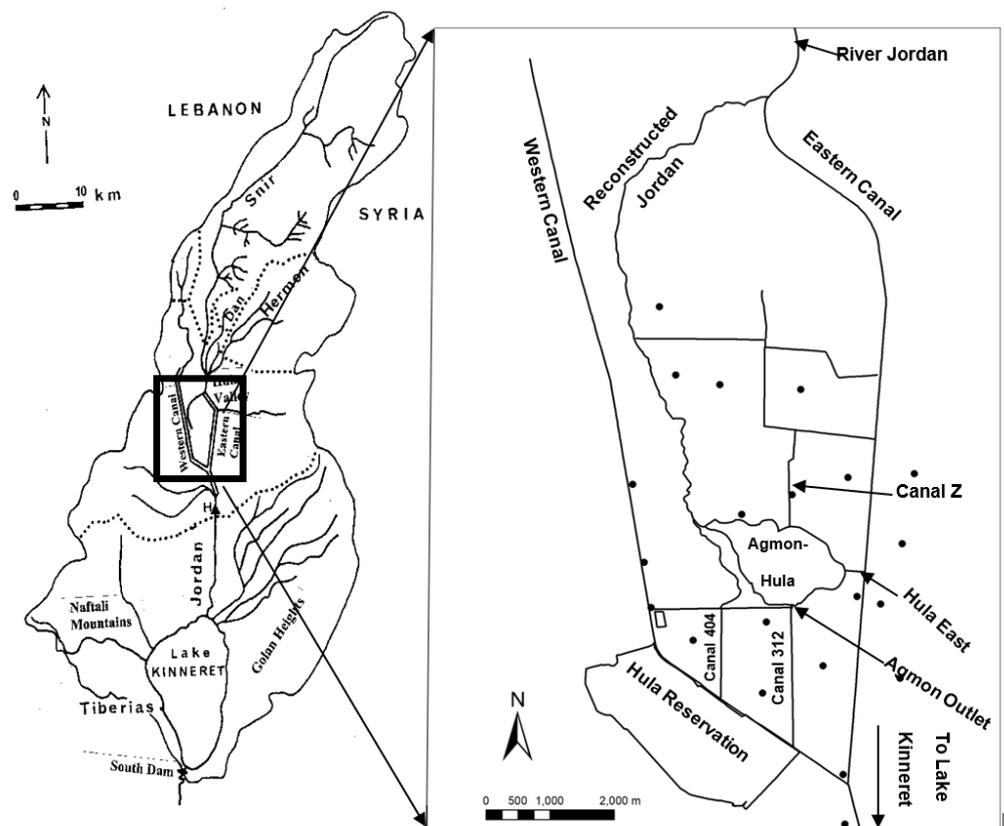


Figure A1. Geographical maps of the Kinneret watershed (left) and the Hula Valley (right); bore-hole-GWT depth monitoring (black spots) are indicated.

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