Supplementary material to article:

A Long-Term Perspective of Seasonal Shifts in Nutrient Dynamics and Eutrophication in the Romanian Black Sea Coast

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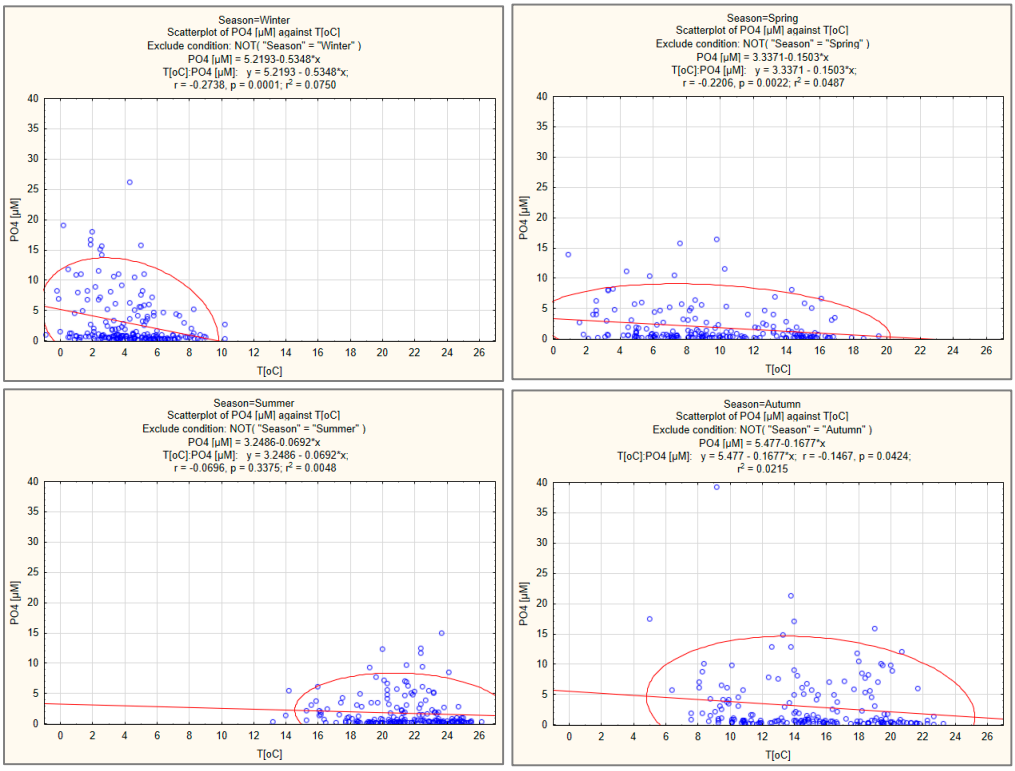


Figure S1. Seasonal Relationships Between Phosphate and Temperature monthly means in the Black Sea, 1960-2023

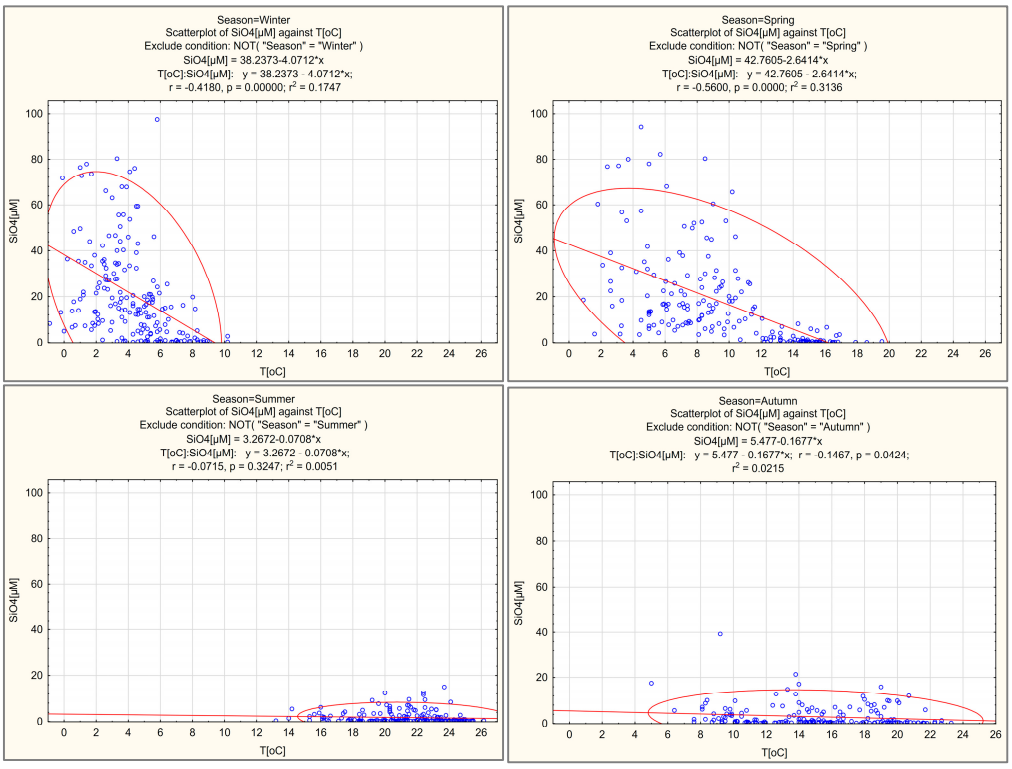


Figure S2. Seasonal Relationships Between Silicate and Temperature monthly means in the Black Sea, 1960-2023

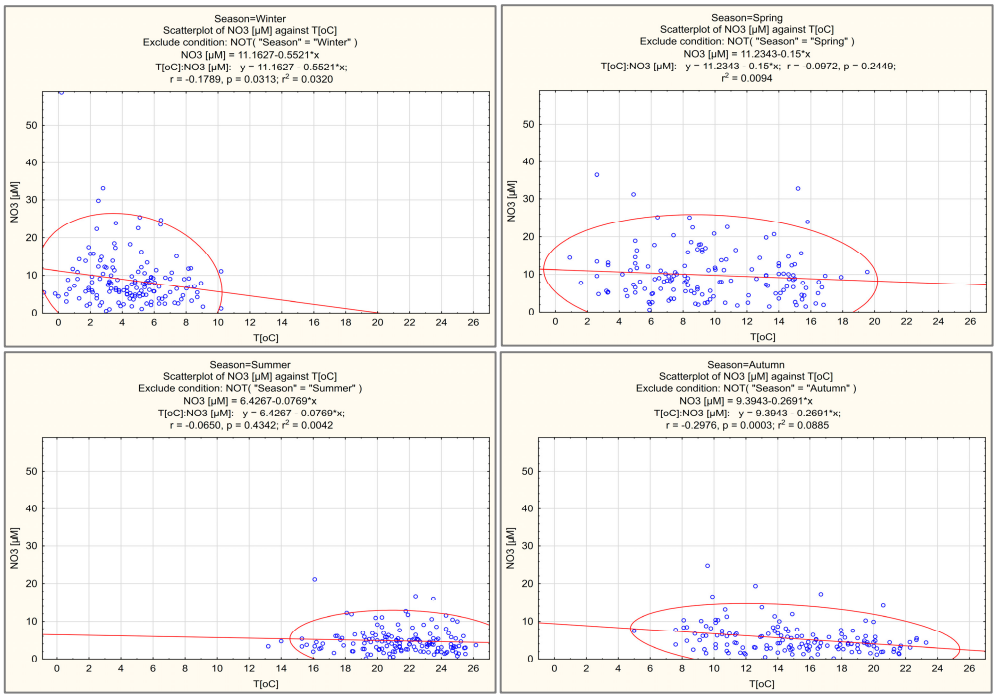


Figure S3. Seasonal Relationships Between Nitrate and Temperature monthly means in the Black Sea, 1976-2023

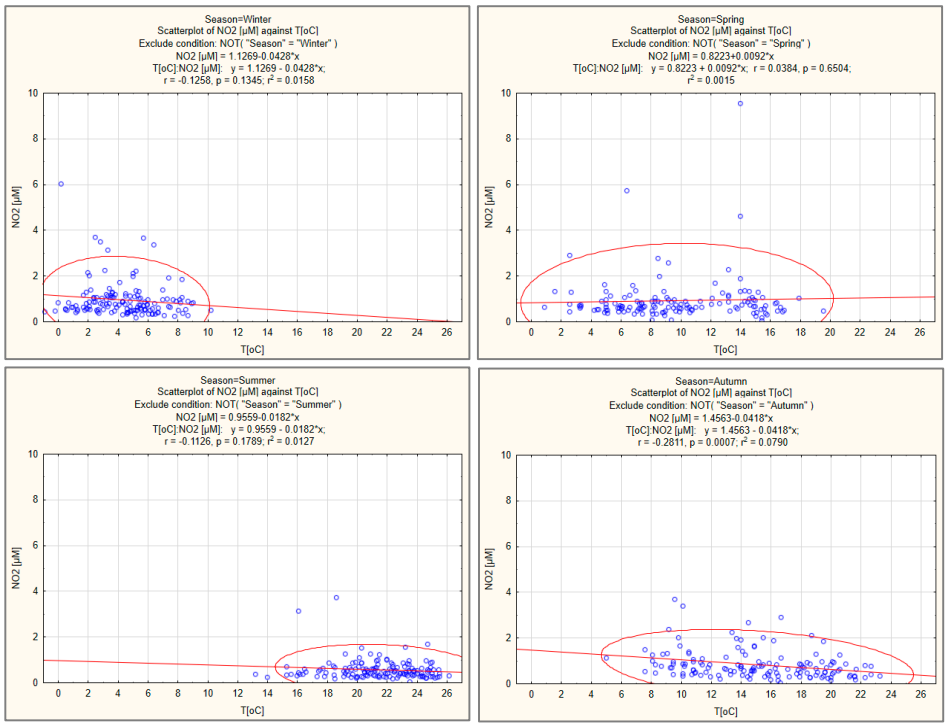


Figure S4. Seasonal Relationships Between Nitrite and Temperature monthly means in the Black Sea, 1976-2023

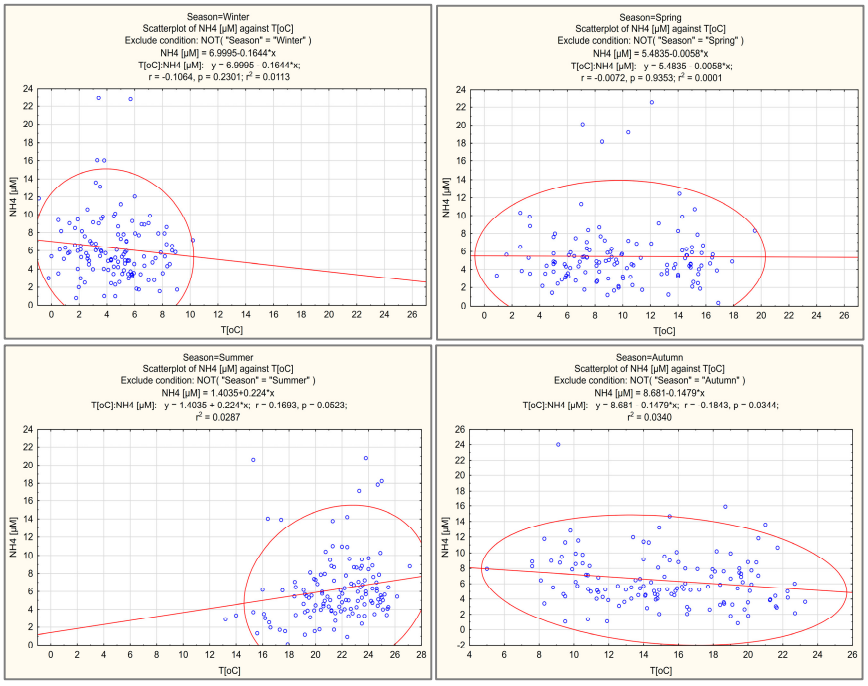


Figure S5. Seasonal Relationships Between Ammonium and Temperature monthly means in the Black Sea, 1980-2023

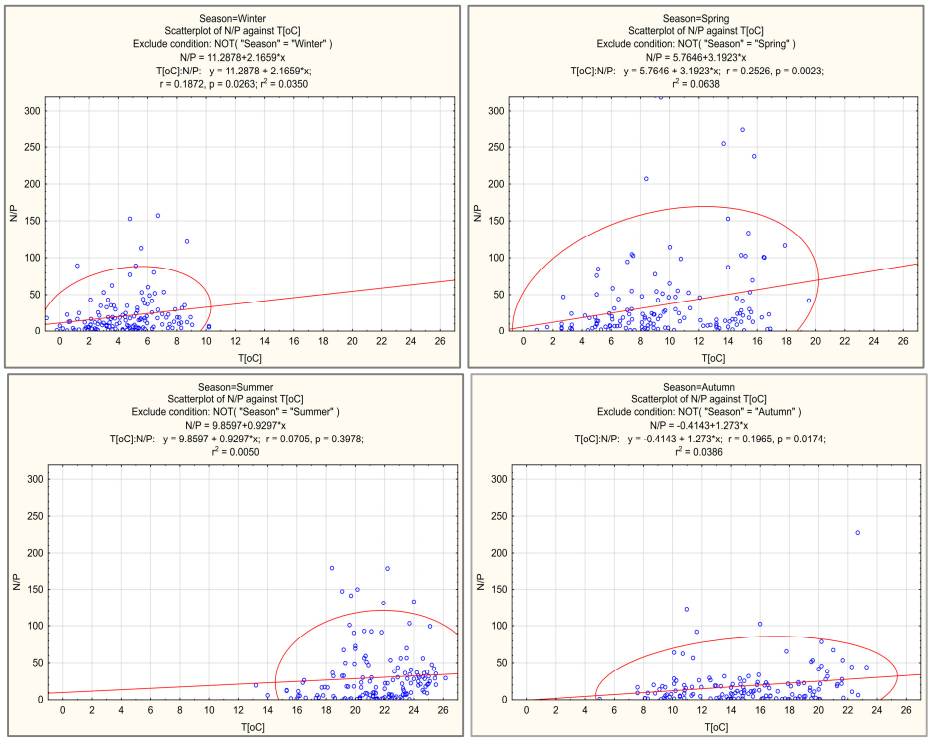


Figure S6. Seasonal Relationships Between Redfield ratio (N/P) and Temperature monthly means in the Black Sea, 1980-2023

Table S1. Overview of Environmental Parameter Collection Methods and Temporal Coverage

Parameter	Method	Time period
Sea Surface Temperature (SST)	Reversible thermometer, CastAway CTD multiparameter probe	1960-2023
Salinity	Titration	1960-2023
Dissolved Oxygen	Titration	1960-2023
Phosphate	Spectrophotometry (phosphomolybdenum complex method)	1960-2023
Silicate	Spectrophotometry (silicomolybdenum complex method)	1960-2023
Nitrate	Reduction to nitrite by hydrazine suplphate followed by Spectrophotometry (sulphanilamide-diazonium compound method)	1976-2023
Nitrite	Spectrophotometry (sulphanilamide-diazonium compound method)	1976-2023
Ammonium	Spectrophotometry (indophenol blue method)	1980-2023
Zooplankton (*Noctiluca scintillans*)	Juday net, microscopic identification, biomass calculations	1981-2023

Table S2. Correlations between environmental parameters and nutrients, monthly means, Black Sea – 1980-2023 (red-statistically significant).

Variable	All Groups Correlations Marked correlations are significant at p < .05000 N=189 (Casewise deletion of missing data) T [oC]	S [‰]	O2 [µM]	O2 [%]	pH	PO4 [µM]	SiO4 [µM]	NO3 [µM]	NO2 [µM]	NH4 [µM]	N/P
T[oC]	1.000000										
S[‰]	-0.160058	1.000000									
O2[µM]	-0.843084	-0.039520	1.000000								
O2[%]	0.088247	-0.240809	0.399139	1.000000							
pH	0.283922	-0.025862	-0.330918	-0.154791	1.000000						
PO4 [µM]	-0.191967	-0.151422	0.110901	-0.180051	0.129519	1.000000					
SiO4[µM]	-0.651605	-0.118919	0.669206	0.066213	-0.164426	0.087026	1.000000				
NO3 [µM]	-0.236435	-0.220464	0.362086	0.261608	0.021580	0.137074	0.362872	1.000000			
NO2 [µM]	-0.088387	-0.071521	0.048493	-0.070082	-0.029517	0.130464	0.040264	0.136443	1.000000		
NH4 [µM]	0.208247	-0.312740	-0.105904	0.067087	-0.022134	0.254659	-0.196672	0.110485	0.050311	1.000000	
N/P	0.072982	-0.029916	-0.010118	0.136026	-0.058804	-0.189188	-0.074239	0.166679	0.635925	0.155135	1.000000

Table S3. Correlations between environmental parameters and nutrients, monthly means, Black Sea – winter - 1980-2023 (red-statistically significant).

Variable	Season=Winter Correlations Marked correlations are significant at p < .05000 N=47 (Casewise deletion of missing data)										
	T [oC]	S [‰]	O2 [µM]	O2 [%]	pH	PO4 [µM]	SiO4 [µM]	NO3 [µM]	NO2 [µM]	NH4 [µM]	N/P
T[oC]	1.000000										
S[‰]	0.238453	1.000000									
O2[µM]	-0.669567	-0.456440	1.000000								
O2[%]	-0.196132	-0.479164	0.805843	1.000000							
pH	0.136990	0.279251	-0.395164	-0.457654	1.000000						
PO4 [µM]	0.143643	-0.249100	-0.086239	-0.055378	0.188178	1.000000					
SiO4[µM]	-0.427671	-0.420279	0.474212	0.300476	-0.075794	-0.089577	1.000000				
NO3 [µM]	0.133738	-0.449265	0.250399	0.319564	-0.029278	0.084362	0.356817	1.000000			
NO2 [µM]	0.104120	-0.166224	-0.139171	-0.099439	-0.000223	0.210604	0.111449	0.148869	1.000000		
NH4 [µM]	-0.087160	-0.396088	0.309472	0.289637	-0.378616	0.410335	-0.107467	0.172585	-0.022841	1.000000	
N/P	0.031434	-0.098435	0.141615	0.168519	0.019011	-0.428279	0.145880	0.561480	-0.140572	0.021107	1.000000

Table S4. Correlations between environmental parameters and nutrients, monthly means, Black Sea – spring - 1980-2023 (red-statistically significant).

Variable	Season=Spring Correlations Marked correlations are significant at p < .05000 N=46 (Casewise deletion of missing data)										
	T [oC]	S [‰]	O2 [µM]	O2 [%]	pH	PO4 [µM]	SiO4 [µM]	NO3 [µM]	NO2 [µM]	NH4 [µM]	N/P
T[oC]	1.000000										
S[‰]	-0.144536	1.000000									
O2[µM]	-0.655121	-0.107560	1.000000								
O2[%]	0.210579	-0.155893	0.538049	1.000000							
pH	0.231567	-0.169775	-0.301104	-0.207890	1.000000						
PO4 [µM]	-0.310483	-0.271053	0.228081	-0.124825	0.014205	1.000000					
SiO4[µM]	-0.709944	-0.101238	0.513693	-0.069951	-0.124404	0.081444	1.000000				
NO3 [µM]	0.053283	-0.140159	0.143197	0.270152	0.145495	0.033810	0.158935	1.000000			
NO2 [µM]	0.118716	-0.036850	-0.147361	-0.103037	-0.086270	-0.084777	-0.149303	0.073041	1.000000		
NH4 [µM]	-0.046864	-0.111463	0.081615	0.003245	0.138239	0.054764	-0.145328	0.161735	-0.034163	1.000000	
N/P	0.161590	0.026143	-0.165552	-0.049783	-0.102799	-0.217982	-0.187594	0.165499	0.970129	-0.001601	1.000000

Table S5. Correlations between environmental parameters and nutrients, monthly means, Black Sea – summer - 1980-2023 (red-statistically significant).

Variable	Season=Summer Correlations Marked correlations are significant at p < .05000 N=48 (Casewise deletion of missing data)										
	T [oC]	S [‰]	O2 [µM]	O2 [%]	pH	PO4 [µM]	SiO4 [µM]	NO3 [µM]	NO2 [µM]	NH4 [µM]	N/P
T[oC]	1.000000										
S[‰]	-0.247795	1.000000									
O2[µM]	-0.362348	-0.011013	1.000000								
O2[%]	-0.113769	-0.028487	0.928911	1.000000							
pH	0.222865	-0.036942	-0.130365	-0.036571	1.000000						
PO4 [µM]	0.252858	-0.306376	-0.179566	-0.143625	0.460126	1.000000					
SiO4[µM]	0.253752	-0.306423	-0.180645	-0.144578	0.460158	0.999993	1.000000				
NO3 [µM]	-0.042549	-0.175784	0.470735	0.430191	0.056521	0.271242	0.270230	1.000000			
NO2 [µM]	0.008884	-0.198834	-0.102392	-0.157493	0.225301	0.761916	0.761089	0.192116	1.000000		
NH4 [µM]	0.117603	-0.436677	-0.037912	-0.065998	-0.018741	0.527139	0.525725	0.324642	0.586308	1.000000	
N/P	-0.158260	0.003269	0.288459	0.248344	-0.186684	-0.160230	-0.163531	0.265679	0.109041	0.325106	1.000000

Table S6. Correlations between environmental parameters and nutrients, monthly means, Black Sea – autumn - 1980-2023 (red-statistically significant).

Variable	Season=Autumn Correlations Marked correlations are significant at p < .05000 N=48 (Casewise deletion of missing data)										
	T [oC]	S [‰]	O2 [µM]	O2 [%]	pH	PO4 [µM]	SiO4 [µM]	NO3 [µM]	NO2 [µM]	NH4 [µM]	N/P
T[oC]	1.000000										
S[‰]	0.063488	1.000000									
O2[µM]	-0.726505	-0.221457	1.000000								
O2[%]	0.265658	-0.174714	0.314302	1.000000							
pH	0.369547	-0.038932	-0.301758	-0.025564	1.000000						
PO4 [µM]	-0.360971	-0.017501	0.136106	-0.346330	-0.107715	1.000000					
SiO4[µM]	-0.360945	-0.016566	0.136225	-0.346358	-0.108127	0.999995	1.000000				
NO3 [µM]	-0.235047	-0.257689	0.149958	-0.157817	0.231597	0.304222	0.304108	1.000000			
NO2 [µM]	-0.215380	-0.141292	0.142444	-0.184623	0.097261	0.688201	0.687901	0.272432	1.000000		
NH4 [µM]	-0.140757	-0.298420	0.333048	0.254666	-0.132100	0.130628	0.130275	0.270890	0.427730	1.000000	
N/P	0.145635	0.033766	-0.015985	0.176193	0.361504	-0.361402	-0.361434	0.250820	0.001674	0.205830	1.000000

Table S7. Factor loadings of environmental variables before 1995 based on Principal Component Analysis (PCA).

Before 1995 (included)	Factor coordinates of the variables, based on correlations	
Variable	Factor 1	Factor 2
Noctiluca scintillans [ind/m3]	0.875648	0.482950
N/P	0.875648	-0.482950
*T[oC]	0.268543	-0.155344
*S[‰]	-0.415538	0.260789
*PO4 [µM]	-0.458313	0.280927
*NO3 [µM]	0.519314	-0.290198
*NO2 [µM]	-0.550359	0.337698
*NH4 [µM]	-0.155052	0.083588

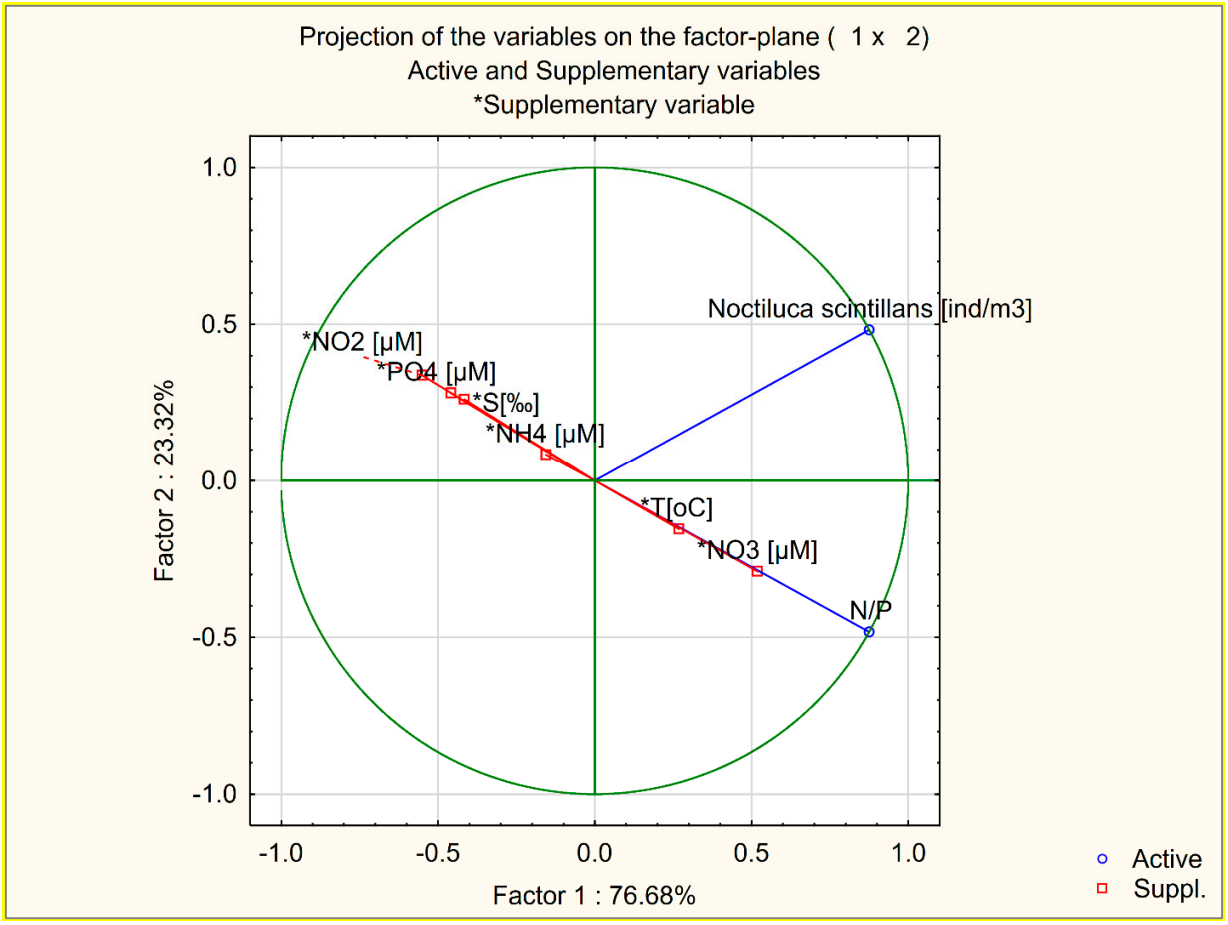


Figure S7. Projection of environmental variables on the PCA factor plane (Factor 1 × Factor 2) for the period before 1995. The plot shows the relationships between *Noctiluca scintillans*, nutrient variables, and environmental factors.

Table S8. Factor loadings of environmental variables after 1995 based on Principal Component Analysis (PCA).

After 1995	Factor coordinates of the variables, based on correlations	
Variable	Factor 1	Factor 2
Noctiluca scintillans [ind/m3]	0.765537	0.643392
N/P	0.765537	-0.643392
*T[oC]	-0.118617	0.251570
*S[‰]	-0.184419	-0.107094
*PO4 [µM]	-0.690718	0.333823
*NO3 [µM]	0.400387	-0.615169
*NO2 [µM]	-0.128715	-0.119397
*NH4 [µM]	-0.162997	0.093813

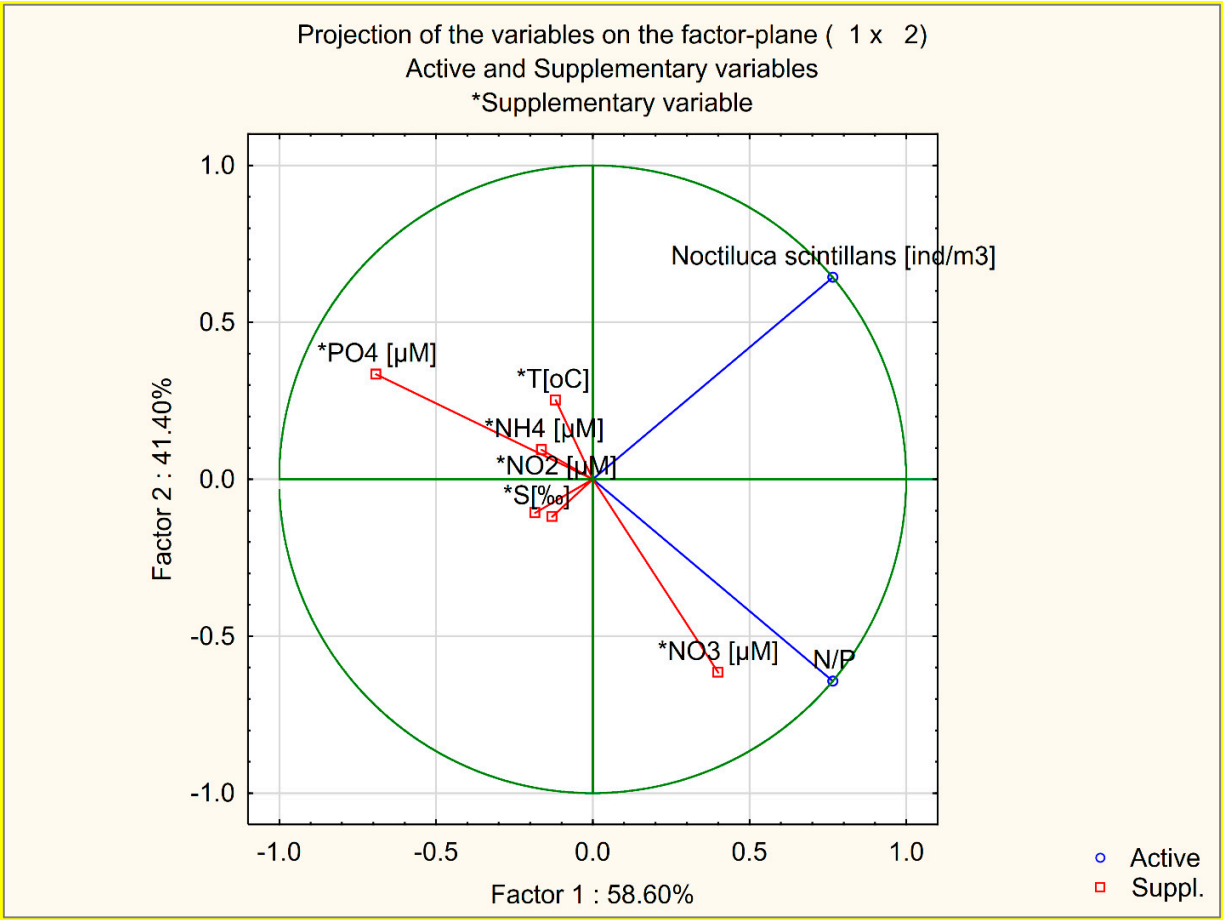


Figure S8. Projection of environmental variables on the PCA factor plane (Factor 1 × Factor 2) for the period after 1995. The plot shows the relationships between *Noctiluca scintillans*, nutrient variables, and environmental factors.