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## ORIGINAL ARTICLES

# Influence of Iron and Silicon Speciation on the Abundance of Diatoms in River Nile

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## ABSTRACT

Phytoplankton assemblage of River Nile was mainly dominated by Bacillariophyta (diatoms) followed by Chlorophyta, Cyanophyta, Euglenophyta and Dinophyta. Diatoms community was represented by 45 species and forming 30.8 - 82.7% of total phytoplankton standing crop recorded in Nile water samples. Diatoms assemblage was primarily dominated by centric forms including *Cyclotella meneghiniana*, *Melosira granulata* and *Melosira granulata v. angustissma,* and secondarily by pinnate forms where *Synedra ulna* and other *Synedra spp.* contributed with the highest share. Availability of iron and silicon for phytoplankton, particularly diatoms is considered among the major factors controlling their dominance. The bioavailability of elements in aquatic systems is not only determined by their total concentrations but also by their speciation or chemical forms that are present. In the present study, MINTEQ geochemical speciation program was used to model total iron (Fe) and silicon (Si) concentrations in River Nile to determine; whether these elements are present as a complexed species or as simple ions, possible solid phases that might control their ionic species solubilities and the influence of their dominant species on the abundance of diatoms in Nile water. According to MINTEQ model; a) predominant species of silicon in all studied samples was silicic acid ($H_4SiO_4$) b) free ions of ferric ($Fe^{3+}$) were found to be <0.01% in all water samples, c) $Fe^{3+}$-organic species predominate at low Fe concentrations d) $Fe^{3+}$-inorganic species increased with the corresponding increase in total Fe levels, with the predominance of the ion-pair $Fe(OH)_2^+$. Although silicic acid was obviously represented in all samples, diatoms growth was found to be highly affected by the availability and limitation of total Fe and its corresponding chemical forms; revealing that total Fe concentration as well as its chemical speciation influence the utilization of silicic acid by diatoms. Statistical analysis showed that at all sites, diatoms percent abundance is positively correlated with the percentages of both $Fe^{3+}$-inorganic species and $Fe(OH)_2^+$ and negatively correlated with the percentage of $Fe^{3+}$-organic species, indicating that $Fe(OH)_2^+$ is a preferable Fe form for the uptake by diatoms. MINTEQ model suggested that silicic acid and silicate ions activities were mainly controlled by tridymite, cristobalite and quartz solid phases, while $Fe^{3+}$ activities were controlled by jarosite solid phase.

***Key words:*** Iron & Silicon, Speciation, Diatoms abundance, River Nile, MINTEQ model.

## Introduction

Low availability of bioactive trace metals may directly limit physiological processes of phytoplankton. Availability of trace metals further plays a role in shaping the composition of the endemic phytoplankton assemblage. Among bioactive trace metals, iron (Fe) is required in the greatest amount. It is highly reactive in the freshwater environment, commonly used as a redox catalyst in enzymes or in proteins associated with the electron transfer pathways found in mitochondria and chloroplasts (Li, *et al.*, 2003); in addition it has been shown to have a number of significant roles in the cycling and bioavailability of other elements (Stephen, *et al.*, 2008).

Findings of many authors suggest that iron deficiency is responsible for the breakdown of cellular chlorophyll-a content in phytoplankton cells. Despite the fact that the pigment itself does not contain iron, there is both a direct and an indirect demand for iron by the enzymes involved in the chlorophyll-a biosynthetic pathway. A reduction in iron availability may simply reduce the cellular abundance and activity of these enzymes and thus reduce the rate of chlorophyll-a synthesis (Davey and Geider, 2001). In addition iron limitation was found to be responsible for a low growth rate in many marine phytoplankton species and for the release of specific iron-complexing ligands, and more so for significant biochemical changes in pigment composition (Lewandowska and Kosakowska, 2004).

Measurements of total dissolved iron concentrations alone, however, are insufficient for understanding the accessibility of iron to phytoplankton. Knowledge of the chemical speciation of iron is critical for examining the mechanisms by which phytoplankton are fulfilling their iron requirements and is important for addressing the

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question of how the lack of iron limits phytoplankton productivity in aquatic ecosystems (Rue and Bruland, 1997). Fe chemistry in oxic waters is dominated by both inorganic and organic complex formation. As a result, dissolved inorganic Fe(II) and Fe(III) species are generally present at very low concentrations in aquatic systems (Li, *et al*., 2003). Ashaked, *et al*. (2002) mentioned that in oxygenated waters Fe(III), the thermodynamically stable form of Fe, forms sparingly soluble oxides or hydroxides that are not directly available for biological uptake. Furthermore, the bioavailability of dissolved Fe is determined by the nature and stability of its complexes. Fe(II), which is more soluble than Fe(III), is thermodynamically unstable in most natural surface aquatic systems. Several studies have recently described the dynamic redox cycle of Fe in natural waters. These redox transformations have important implications for Fe availability to phytoplankton in both seawater and freshwater environments (Ashaked, *et al*., 2002).

Mosseri, *et al.* (2008) mentioned that in high-nutrient, low-chlorophyll (HNLC) aquatic systems addition of iron clearly stimulated phytoplankton growth, especially micro-phytoplankton groups such as diatoms, which typically presented the largest response to iron enrichment .Diatoms are a major group of algae, and are one of the most common types of phytoplankton. Over ninety percent of the biosphere is plant life, of which diatoms make up about a quarter by weight and supplying the atmosphere with around a quarter of its oxygen. Diatoms are important contributors to the primary production in aquatic ecosystems, sitting at the bottom of the food chain. They are eukaryotic algae, commonly unicellular, although they do exist as filamentous colonies and are good indicators of the environmental integrity (Padhi, *et al*., 2010).

A characteristic feature of diatom cells is that they are encased within a unique cell wall made of silica (hydrated silicon dioxide) called a frustule. The biogenic silica that the cell wall is composed of is synthesized intracellularly by the polymerization of silicic acid monomers. This material is then extruded to the cell exterior and added to the wall. Synthesis of DNA, synthesis of DNA polymerase and thymidylate kinase, and chlorophyll synthesis are some of the processes that have been shown to be dependent on silicon. In view of the intimate involvement of silicon in diatom metabolism it is likely that it plays a central role in diatom ecology (Azam and Chisholm, 1976). Egge and Aksnes (1992) found that diatom dominance of mesocosm communities was directly related to the availability of silicic acid, when its concentration was greater than 2 mmol/m$^3$, they found that diatoms typically represented more than 70% of the phytoplankton community. Depletion of silicic acid relative to inorganic nitrogen and phosphate has been observed to select for non-siliceous algae, as conceptually discussed in Officer and Ryther (1980), this shift is exacerbated in coastal waters receiving anthropogenic inputs of nitrogen and phosphorus and can end with the dominance of often hardly edible non-siliceous algae, which can result in harmful consequences.

Iron is considered to be one of the major factors controlling the utilization of silicon by diatoms (Mosseri, *et al*., 2008). In this connection Brzezinski, *et al.* (2005) found that iron fertilization stimulated biogenic silica production and silicic acid depletion in Antarctic and Sub-Antarctic regions during austral summer. Leynaert, *et al.* (2004) studied the silicic acid uptake kinetics of the pinnate diatom *Cylindrotheca fusiformis* grown under a wide range of iron concentrations, results showed that as the iron stress increased, the growth rate of the diatom slowed, cell size decreased, and silicification increased.

Many studies have demonstrated that River Nile phytoplankton assemblage is dominated by diatoms all the year round, among these studies; Kobbia, *et al.* (1991), Abou-Waly, *et al.* (2000), Shehata, *et al.* (2009), El-Sheekh, *et al.* (2010), Shehata and Badr (2010) and Hammad-Doaa and Radi (2010), this dominance might be attributed to the recognized occurrence of iron and silicon in Nile water, therefore; the main objectives of the present work are: 1- To model total iron and silicon concentrations recorded in Nile water samples by using MINTEQ geochemical speciation program in order to determine: a) whether these elements are present as complexed species or as simple ions b) principle solid phases that might control the solubilities of Fe and Si ionic species in water samples c) The effect of Fe and Si dominant species on the abundance of diatoms in River Nile. 2- To determine dominant species of diatoms and their relation to River Nile water quality.

## Materials and Methods

Water sampling was carried out according to standard methods for examination of water and wastewater (APHA, 2005). Surface water samples were collected in duplicates at 12 sites along the main channel of the River Nile, representing six major cities namely Edfu, Esna, Souhag, Assiut, Helwan and Cairo. Sampling sites and distances from Aswan High Dam (AHD) are presented in Table (1) and illustrated by Figure (1).

### *Physico-Chemical Parameters Measured in Water Samples:*

Physico-chemical analyses were carried out according to standard methods for examination of water and wastewater (APHA, 2005). Temperature and pH were measured in field, while major anions; chloride ($Cl^-$), fluoride ($F^-$), nitrate ($NO_3^-$), phosphate ($PO_4^{3-}$) and sulfate ($SO_4^{2-}$) were measured using Ion Chromatography (IC) (model: DX-500 Chromatography System). Carbonates ($CO_3^{2}$-) and bicarbonates ($HCO_3^-$) were measured by using Titralab 80 titration system, Radiometer Analytical, France. Major cations; calcium (Ca), potassium (K), magnesium (Mg) and sodium (Na) were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) Perkin-Elmer product, model Optima 5300 DV. Trace elements [aluminium (Al), barium (Ba), manganese (Mn), iron (Fe), silicon (Si), strontium (Sr) and zinc (Zn)] were also measured by ICP-OES. The samples were filtered by filtration system through membrane filter of pore size 0.45 µm before analyses according to standard methods (APHA, 2005). Dissolved organic carbon (DOC) was measured using DC-190 TOC analyzer, Tekmar Dohrmann with non-dispersive infrared detector (NDIR).

**Table 1:** Sampling Sites Description and their Distances from Aswan High Dam (AHD).

| Sampling Sites | Code | Description |
|---|---|---|
| Edfu | Ed-R & Ed-L | Water samples collected from right (R) and left (L) banks of River Nile at Edfu (Ed) city about 116 Km from Aswan High Dam (AHD). |
| Esna | Es-R & Es-L | Water samples collected from right (R) and left (L) banks of River Nile at Esna (Es) city about 168 Km from Aswan High Dam (AHD). |
| Souhag | So-R & So-L | Water samples collected from right (R) and left (L) banks of River Nile at Souhag (So) city about 448 Km from Aswan High Dam (AHD). |
| Assiut | As-R & As-L | Water samples were collected from right (R) and left (L) banks of River Nile at Assiut (As) city about 545 Km from Aswan High Dam (AHD). |
| Helwan | H-R & H-L | Water samples were collected from right (R) and left (L) banks of River Nile at Helwan (H) city about 883 Km from Aswan High Dam (AHD). |
| Cairo | C-R & C-L | Water samples were collected from right (R) and left (L) banks of River Nile at Cairo (C) city about 933 Km from Aswan High Dam (AHD). |

**Fig. 1:** Map Showing Sampling Sites along River Nile.

The results of water samples including temperature, pH, DOC, cations, anions and trace elements were inserted in the database of the geochemical equilibrium modeling program Visual MINTEQ version 3, beta [includes Stockholm Humic Model (SHM)] in order to form input files (Gutafsson, 2010). Activities of Fe and Si and their ionic complexes were obtained from the Visual MINTEQ output files. The activities of these elements are then represented on lines drawn by Lindsay (1979).

*Water Samples for Phytoplankton Analysis:*

Water samples for species identification and cell count were collected from each site and fixed immediately with buffered formalin (final concentration 1%). Phytoplankton was identified to species level where possible after settling in Lugol's iodine solution (Utermohl, 1958). The samples were examined by using binocular research microscope at 16X eyepiece and 40X objective, 100X objective with oil immersion was used if needed. The drop method was applied for identification and counting of different algal species (APHA, 2005). Identification followed Taft and Taft (1971), Dodage (1985), Mizumo (1990) and Dillard (1991).

*Statistical Analysis:*

The SPSS 16.0 software package was used for statistical analysis. Differences among means were determined using a two-tailed t-test. Differences were considered significant at r<0.05 and highly significant at r <0.01. The relationships between diatoms percent abundance and percentages of ferric-inorganic species, ferric-organic species, $Fe(OH)_2^+$, $Fe(OH)_3$ and $Fe(OH)_4^-$ were described using correlation bivariate statistics.

## Resluts and Discussion

*Phytoplankton Assemblage of River Nile:*

Phytoplankton assemblage of River Nile was represented by five algal groups; Bacillariophyta (diatoms), Chlorophyta, Cyanophyta, Euglenophyta and Dinophyta. Minimum Phytoplankton standing crop of 539.0 Cells/L was existed at Es-R while the maximum standing crop of 113600.0 Cells/L was observed at So-L. The increase in total phytoplankton count in River Nile was mainly attributed to diatoms which were represented by 45 species (Table 3) and forming 30.8 - 82.7% of total phytoplankton standing crop recorded at River Nile sampling stations. Diatoms population density was primarily dominated by centric forms including *Cyclotella meneghiniana*, *Melosira granulata* & *Melosira granulata v. angustissma,* and secondarily by pinnate forms where *Synedra ulna* and other *Synedra spp.* contributed with the highest share. Among all diatoms, *Cyclotella meneghiniana* was the most dominant species at all the investigated sites, where it accounted for 17.98 to 67.44% of total diatoms standing crop, while *Synedra ulna*, the dominant pinnate species in all samples, participating with 6.9 – 29.0% of total diatoms standing crop. Total phytoplankton, diatoms, *Cyclotella meneghiniana* and *Synedra ulna* counts were shown in Table (2) and illustrated by Figure (2).

**Table 2:** Total Phytoplankton, Diatoms, *Cyclotella meneghiniana* & *Synedra ulna* Counts (Cells/L) Recorded at River Nile Sampling Stations

| Location | Total phytoplankton | Diatoms | *Cyclotella meneghiniana* | *Synedra ulna* |
|---|---|---|---|---|
| Ed-R | 6222.0 | 2400.0 | 445.0 | 356.0 |
| Ed-L | 27378.0 | 15822.0 | 2845.0 | 1778.0 |
| Es-R | 539.0 | 166.0 | 71.0 | 48.0 |
| Es-L | 948.0 | 365.0 | 197.0 | 52.0 |
| So-R | 58667.0 | 36445.0 | 17778.0 | 8889.0 |
| So-L | 113600.0 | 89778.0 | 50133.0 | 13334.0 |
| As-R | 58133.0 | 35378.0 | 16000.0 | 2667.0 |
| As-L | 34133.0 | 17200.0 | 11600.0 | 1867.0 |
| H-R | 970.0 | 702.0 | 286.0 | 152.0 |
| H-L | 1896.0 | 1568.0 | 1024.0 | 108.0 |
| C-R | 916.0 | 596.0 | 168.0 | 80.0 |
| C-L | 900.0 | 572.0 | 248.0 | 72.0 |

Several studies elucidated that the seasonal succession of phytoplankton in River Nile is dominated by Bacillariophyceae (diatoms); Kobbia, *et al.* (1991) found that Bacillariophyta contributed the highest percentage composition in River Nile with average seasonal percentage ranged from 42.86% to 59.36%. Abou-Waly, *et al.* (2000) studied the influence of nitrogen/phosphorus ratios on the productivity of River Nile phytoplankton and concluded that Bacillariophyta was the dominant group followed by Chlorophyta and Cyanophyta. Shehata, *et al.* (2009) recorded that River Nile water contains algal species belonging to three major phytoplankton groups, namely; Chlorophyta, Cyanophyta and Bacillariophyta (diatoms); they mainly attributed the increase in total phytoplankton number in Nile water to diatoms which represent 75% - 97.8% of total algal counts with the dominance of centric forms. El-Sheekh, *et al.* (2010) determined that Bacillariophyta was the predominant group of phytoplankton in River Nile followed by Cyanophyta, Chlorophyta, Euglenophyta and Dinophyta and they illustrated that *Cyclotella meneghiniana* and *Melosira spp.* were the most frequent species of diatoms. Shehata and Badr (2010) monitored water quality changes in River Nile, and found that diatoms are the major group of phytoplankton assemblage.

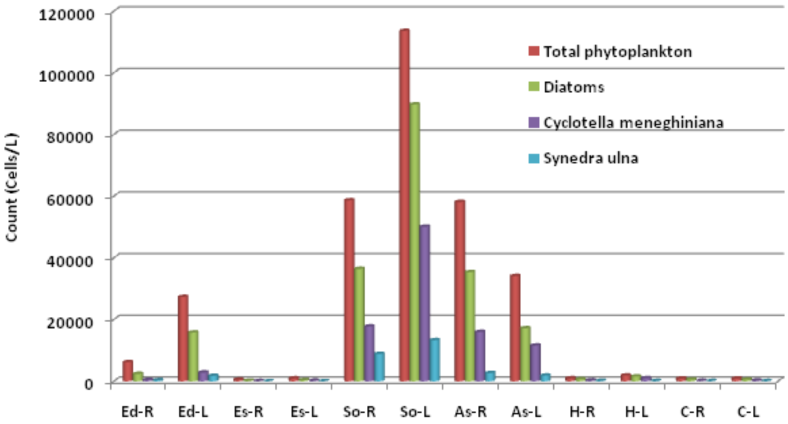

**Fig. 2:** Total Phytoplankton, Diatoms, *Cyclotella meneghiniana* & *Synedra ulna* Counts (Cells/L) in River Nile Samples.

**Table 3:** Diatoms Species Encountered in the Phytoplankton of River Nile.

| | |
|---|---|
| *Achnanthes minutissima* | *Navicula cryptocephala* |
| *Amphora ovalis* | *Navicula dubium* |
| *Bacillaria paradoxa* | *Navicula humerosa* |
| *Brachysira vitrea* | *Navicula tuscula* |
| *Cocconeis placentula* | *Nitzschia acicularis* |
| *Cyclotella glomerata* | *Nitzschia amphibia* |
| *Cyclotella meneghiniana* | *Nitzschia capitellata* |
| *Cyclotella ocellata* | *Nitzschia dissipata* |
| *Cymbella cistula* | *Nitzschia filiformis* |
| *Cymbella cymbiformis* | *Nitzschia fonticola* |
| *Cymbella minuta v. silesiaca* | *Nitzschia frustulum* |
| *Cymbella turgida* | *Nitzschia gracilis* |
| *Fragillaria construens* | *Nitzschia obtusa* |
| *Fragillaria construens (girdle view)* | *Nitzschia obtusa v. scalpelliformis* |
| *Gomphonema olivaceum* | *Nitzschia palea* |
| *Gomphonema parvulum* | *Nitzschia paleacea* |
| *Gyrosigma acuminatum* | *Nitzschia sublinearis* |
| *Melosira granulata* | *Nitzschia thermalis* |
| *Melosira granulata v. angustissma* | *Sellaphora pupula* |
| *Melosira varians* | *Synedra acus v. radians* |
| *Navicula anglica* | *Synedra delactisma* |
| *Navicula cincta* | *Synedra rempens v. familiaris* |
| | *Synedra ulna* |

Hutchinson (1957) demonstrated that *Cyclotella spp.* are representatives of oligotrophic lakes, while *Asterionella* and *Melosira granulata* may be observed in oligotrophic lakes as well as eutrophic lakes. Hecky and Kilham (1988) mentioned that centric diatoms have been classed as the most desirable phytoplankton in coastal waters because they are important in marine food chains, they do not form noxious surface blooms, and they are not toxic. In general dominance of diatoms in Nile water with the abundance of centric species could be a good indicator of River Nile water quality.

### *Physico-chemical analysis:*

Temperature is an important factor which regulated the biogeochemical activities in the aquatic environment. It is one of the most important ecological parameters affecting phytoplankton growth and biological activity (Ye, *et al.*, 2011). In the present study water temperatures varied from 24.2$^{o}$C (minimum temperature recorded at Es-L) to 30.0$^{o}$C (maximum temperature recorded at As-R) with a mean value 26.88$^{o}$C. Abdalla, *et al.* (1995) mentioned that temperature in relation to eutrophication seems to have pronounced effect on the rate of phytoplankton photosynthesis as well as periodicity and abundance of phytoplankton species.

pH values in all collected samples was shifted towards the alkaline side (above 7). Values of pH varied between 7.07 and 8.0 with a mean value 7.6. In the studied samples, the increase in total phytoplankton count was accompanied by an increase in pH values ($r<0.05$), this could be explained by Lai and Lam (1997) who mentioned that phytoplankton photosynthetic activity at surface water consumes acidic carbon dioxide in the water, resulting in increasing pH values.

Dissolved organic carbon (DOC) in the studied samples ranged from 0.2 to 8.9 mg/l, with a median value 8.25 mg/l. Although concentrations as high as 80 mg/l have been found in eutrophic lakes (Weber, 1963), values reported for rivers have not exceeded 50 mg/l (Nelson and Scott, 1962 and Wilson, 1963). In the present study, a low correlation was found between DOC and total phytoplankton standing crop, which could be related to the low contribution of cyanophyta (5.9 – 30.2%) in the phytoplankton of River Nile. The lowest DOC concentrations of 0.2 – 2.9 mg/l were recorded at Helwan and Cairo sampling sites, this was coinciding with the lowest cyanophyta percent abundance (5.9 – 9.9%). On the same line, Ye, *et al.* (2011) found no significant correlation between DOC concentration and Chlorophyll-a in the entirety of Lake Taihu, China, except in Gonghu Bay, where the cyanobacterial bloom was the direct source of DOC. Additionally Meon and Kirchman (2001) mentioned that the contribution of cyanobacterial blooms to dissolved organic matter (DOM) formation and accumulation is substantial.

Nitrate concentrations in River Nile ranged between 0.28 mg/l as a minimum value recorded at Es-L and 1.32 mg/l as a maximum value recorded at So-R, while phosphate was below the detection limit (<0.2 mg/l) at all the investigated sites. Similarly El-Sheekh, *et al.* (2010) recorded nitrate concentration of 0.28 mg/l and low phosphate value of 0.01 mg/l in River Nile. In addition Abdelsatar-Amaal (2005) determined concentrations of 0.012 – 0.6 mg/l for nitrate and 0.024 – 0.117 mg/l for orthophosphate in Nile water.

Silicon (Si) concentrations ranged from 2.50 to 5.60 mg/l with a median value 5.21 mg/l. Silicon concentrations decreased from upstream to downstream, where the lowest values were recorded in Helwan and Cairo samples. Similar findings determined by Abdelsatar-Amaal (2005) who found that silicate fluctuated between 0.77 and 6.66 mg/l in River Nile without defined seasonal trends, she also added that silicate showed higher values in the upstream sites than the downstream ones. Treguer, *et al.* (1995) recorded that average world-wide concentrations of dissolved Si ranged from 2.0 mg/l in the oceans and 4.0 mg/l in rivers (Conley, 1997) to 6.0 mg/l in freshwaters (Aston, 1983 and Willén, 1991). El-Sheekh, *et al.* (2010) mentioned that the minimum silicate level at which diatoms growth can occur is between 0.03 and 0.04 mg/l. Hecky and Kilham (1988) reported that some freshwater diatoms have been shown to out-compete other algal groups for both N and P when adequate Si is available. Therefore, the availability of Si can channel N and P into diatoms and away from less desirable species; this could explain the high abundance of diatoms in River Nile where Si levels were obviously exceeding those of nitrate and phosphate.

Total iron concentrations ranged from 0.049 to 4.914 mg/l with a median value 0.341 mg/l (Table 4). Iron levels increased in Nile water from upstream to downstream, recording maximum values of 2.10 - 4.91 mg/l at Helwan and Cairo sampling stations. On the other side, least iron concentrations were detected in Ed-R, Es-R and Es-L samples, ranging between 0.049 and 0.06 mg/l. While an intermediate total iron concentrations were determined in Ed-L, As-R, As-L, So-R and So-L samples, fluctuating between 0.162 and 0.616 mg/l. Similar results were recorded by Abdelsatar-Amaal (2005) during monitoring water quality of River Nile from Edfo to Cairo, she observed progressive increase in Fe levels from up to down stream sites where Fe values fluctuated between 0.17 and 2.03 mg/l. Abdel-Aal (1988) found that Fe, Mn and Zn concentrations in River Nile water at Helwan segment were found to be 4 times their normal concentrations. Reynolds (1984) mentioned that iron has long been considered to be the most important trace metal for phytoplankton. Sunda and Huntsman (1995) noted diminishing growth rates with decreasing iron concentrations not only in the large oceanic diatoms *Thalassiosira pseudonana* and *Thalassiosira oceanica* but also in other oceanic and coastal phytoplankton species they examined. A similar effect on the growth of the diatom *Phaeodactylum tricornutum* was recorded by Hayward (1968) and Kudo, *et al.* (2000).

### *Speciation of Iron and Silicon in River Nile:*

#### *Iron:*

As calculated from Visual MINTEQ model, $Fe^{3+}$-organic species in River Nile accounted for 0.39 - 86.01% with median value 56.83% of total dissolved iron; it was the predominant species at Ed-R, Es-R and Es-L recording 79.64, 86.01 and 82.57% respectively. On the other hand, $Fe^{3+}$-inorganic species accounted for 13.98 - 99.61% with a median value 43.17%. In all water samples, the ion-pair $Fe(OH)_2^+$ was the most dominant inorganic species where it formed 13.47 - 98.71% with a median value 38.99% of total dissolved iron. Other inorganic species were $FeOH^{2+}$, $Fe(OH)_3$ and $Fe(OH)_4^-$, they accounted for <0.01 - 0.06%, 0.28 - 2.26% and 0.19 - 5.20% respectively, while the free ions of $Fe^{3+}$ were <0.01% in all water samples (Table 4 & Figure 3). The percentage of $Fe(OH)_2^+$ and $FeOH^{2+}$ were negatively correlated with water pH values, while the percentage of $Fe(OH)_4^-$ was positively correlated with pH values. In accordance with our results Tawfic and Abdel-Tawab (2001) modeled metal content of industrial effluents discharged to River Nile by using MINTEQA2 geochemical speciation model, they found that; $Fe^{3+}$ solubility decreased considerably with the increase in pH, complexed-Fe ions were the predominant soluble species over pH > 4, metal-complexes with $PO_4^{3-}$, $SO_4^{2-}$, $HCO_3^-$, $CO_3^{2-}$ and $OH^-$ accounted for > 90% of total soluble Fe concentrations through the formation of neutral, negative and positive ion-pairs. Elkorashy-Reham (2002) used MINTEQ speciation model to determine ion activity of some metals in polluted water areas of Helwan, she found that the most available species of $Fe^{3+}$ in water was attributed to $Fe(OH)_2^+$ ranging between 65.3 and 76.9%.

### *Silicon:*

In the present study and as calculated from Visual MINTEQ model, the predominant species of silicon in the studied water samples is silicic acid ($H_4SiO_4$). The silicic acid accounted for 98.43 – 99.80% with a mean value 99.14% of total soluble silicon while silicate ions ($H_3SiO_4^-$) accounted for 0.20 – 1.50% with a mean value 0.86% of total soluble silicon (Figure 4). Our findings coincide with Golterman (1975), who mentioned that in the pH and temperature range of 6 - 9 and 0 - 30 ºC respectively, and at silicon concentrations normally found in natural water ecosystems (< 65 mg/l), all dissolved Si occurs as silicic acid and its dissociation products were mainly silicate (Tan, 1994).

**Table 4:** Fe Total Concentrations, $Fe^{3+}$ Activities, Diatoms Percent Abundance and Percentages of $Fe^{3+}$-Organic Species, $Fe^{3+}$-Inorganic Species, $FeOH^{2+}$, $Fe(OH)_2^+$, $Fe(OH)_3$ & $Fe(OH)_4^-$ in River Nile Samples.

| Sampling Site | Fe (mg/l) | $Fe^{3+}$ activity (mol/l) | Diatoms | $Fe^{3+}$ Organic species | $Fe^{3+}$ Inorganic species | $FeOH^{2+}$ | $Fe(OH)_2^+$ | $Fe(OH)_3$ (aq) | $Fe(OH)_4^-$ |
|---|---|---|---|---|---|---|---|---|---|
| Ed-R | 0.054 | -16.505 | 38.57 | 79.64 | 20.36 | ----- | 18.79 | 0.60 | 0.96 |
| Ed-L | 0.162 | -15.370 | 57.79 | 54.35 | 45.64 | ----- | 43.52 | 0.96 | 1.11 |
| Es-R | 0.060 | -16.317 | 30.8 | 86.01 | 13.98 | ----- | 13.48 | 0.28 | 0.23 |
| Es-L | 0.049 | -17.140 | 38.5 | 82.57 | 17.43 | ----- | 15.15 | 0.76 | 1.50 |
| So-R | 0.350 | -15.665 | 62.12 | 61.41 | 38.60 | ----- | 34.94 | 1.36 | 2.30 |
| So-L | 0.616 | -15.588 | 79.03 | 49.54 | 50.45 | ----- | 43.02 | 2.26 | 5.16 |
| As-R | 0.332 | -15.891 | 60.86 | 59.30 | 40.69 | ----- | 33.68 | 1.79 | 5.20 |
| As-L | 0.271 | -15.783 | 50.39 | 64.50 | 35.50 | ----- | 31.62 | 1.26 | 2.60 |
| H-R | 4.12 | -12.596 | 72.37 | 0.39 | 99.61 | 0.06 | 98.71 | 0.65 | 0.19 |
| H-L | 2.100 | -13.596 | 82.7 | 9.32 | 90.68 | 0.02 | 88.61 | 1.24 | 0.80 |
| C-R | 4.910 | -12.618 | 65.07 | 0.39 | 99.61 | 0.05 | 98.70 | 0.66 | 0.20 |
| C-L | 2.860 | -13.237 | 63.56 | 6.92 | 93.08 | 0.03 | 91.57 | 0.99 | 0.48 |

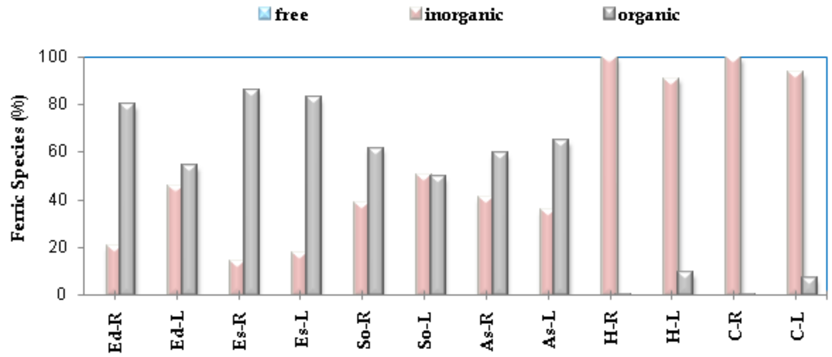

**Fig. 3:** Distribution of Free, Inorganic and Organic Ferric Species in Water Samples.

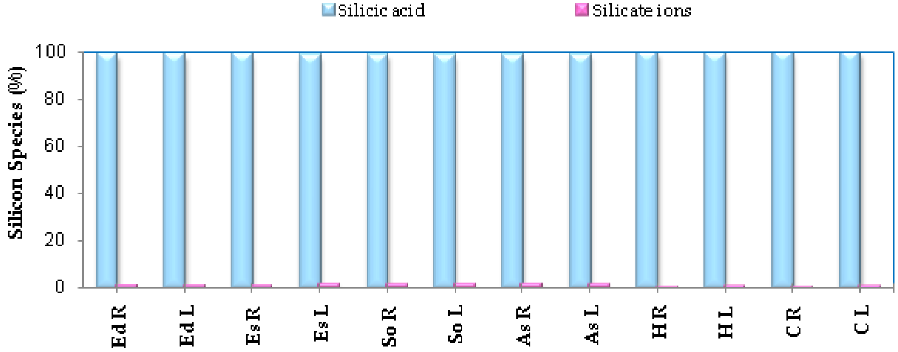

**Fig. 4:** Distribution of Silicon Species in Water Samples.

### *Influence of Iron and Silicon Dominant Species on Diatoms Abundance in River Nile:*

Data represented in Table (4) and illustrated by Figure (5) showed that the least percent abundance of diatoms (30.8 – 38.57%) was recorded at Ed-R, Es-R and Es-L sampling sites; these sites were characterized by high occurrence of silicic acid (99.387 – 98.525%), low concentrations of total iron (0.049 – 0.06 mg/l) associated with the predominance of $Fe^{3+}$-organic species (79.64 – 86.01%) and declined percentages of $Fe^{3+}$-inorganic species (13.98 - 20.36%), indicating that organic iron might be a non preferable iron form for the uptake by diatoms and that the amount of inorganic iron present could be insufficient to satisfy the growth requirements of diatoms, which by turn might limit the utilization of silicic acid by diatoms population.

In agreement with our findings; Li, *et al.* (2003) studied the effect of organic Fe complexes formed by the reaction between iron and desferal (Fe chelator) on the growth and physiology of two freshwater diatoms, *Fragilaria sp.* UTCC 294 and *Cyclotella sp.* UTCC 432; they observed that growth rates of both diatoms were adversely affected by desferal addition, even when the chelator was supplied at levels equimolar to total Fe. Of the two diatoms assessed, desferal had a greater negative impact on growth of *Fragilaria sp.* compared to *Cyclotella sp.*; this could explain the higher occurrence of *Cyclotella meneghiniana* in Ed-R, Es-R and Es-L samples compared to other diatoms.

Naito, *et al.* (2005) studied the influence of iron chelation with organic ligands on the growth of red tide phytoplankton; they found that the dissolved iron species are predominantly the hydrolysis products $Fe(OH)_2^+$, $Fe(OH)_3$ and $Fe(OH)_4^-$ in the inorganic $FeCl_3$ medium. The diatom *Ditylum brightwellii* and other phytoplankton species showed good growth in $FeCl_3$ medium, while they grew better at higher concentrations of iron hydroxides in different organic Fe media (iron salicylate chelates, iron citrate chelates & Fe-EDTA chelates). They observed that the growth of *Ditylum brightwellii* and the other phytoplankton species were inhibited by the presence of an excess of organic ligands in each medium, indicating that these species prefer inorganic Fe to organic Fe for iron uptake, even when organic Fe is also available.

Lewandowska and Kosakowska (2004) found that the response of depressing iron concentration on *Cyclotella meneghiniana* was a decrease in chlorophyll-a and soluble protein content, as well as reduced cell number of *C. meneghiniana* in relation to control cultures grown under optimal iron conditions and they observed that not only the form of iron but also its concentration affect the population of *C. meneghiniana* by retarding its growth.

Rue and Bruland (1997) recorded in initial studies in the central North Pacific gyre low concentrations of dissolved iron, coupled with an excess of strong $Fe^{3+}$-binding ligands, resulted in calculated equilibrium inorganic iron concentrations as low as 0.01 pM (10 - 14 M) and that more than 99.9% of the dissolved Fe was estimated to be chelated with natural organic ligands. Naito, *et al.* (2005) mentioned that the uptake of major nutrients (nitrate, phosphate and silicate) seems to be directly related to Fe availability. Mosseri, *et al.* (2008) reported that in high nitrate low silicate low chlorophyll (HNLSLC) regions, bottle incubation experiments have often shown that phytoplankton growth was stimulated in treatments with Fe addition only and in most cases to a much greater degree in treatments with both Fe and silicic acid added together, whereas growth was not stimulated in treatments with only silicic acid addition.

On the other side when total iron levels increased (0.162 - 0.616 mg/l) in Ed-L, As-R, As-L, So-R and So-L samples, $Fe^{3+}$-organic species decreased (49.54 - 64.50%) while $Fe^{3+}$-inorganic species increased (35.50 - 50.45%), this was accompanied with the maximum increase in diatoms cell numbers (15822.0 - 89778.0 Cells/L), revealing that, inorganic $Fe^{3+}$-species (which was mainly dominated by the ion-pair $Fe(OH)_2^+$) are more preferable and utilizable by diatoms. In this connection Morel, *et al.* (1991) reported that oceanic culture studies revealed that only the dissolved inorganic forms of iron, chiefly the dominant hydrolysis species $Fe(OH)_2^+$, are taken up by marine phytoplankton. Kosakowska, *et al.* (2004) found that the optimum iron level at which the highest cellular chlorophyll-a content of the diatom *P. tricornutum* occurred was 0.56 mg/l, which supported our findings in River Nile, where the highest diatoms population density of 89778.0 Cells/L was observed at So-L sampling station where iron concentration recorded 0.616 mg/l.

In Helwan and Cairo samples, the highest concentrations of total iron (2.10 - 4.91 mg/l) were recorded, this was coupled with an obvious decrease in $Fe^{3+}$-organic species (0.39 – 9.32%) and the dominance of $Fe^{3+}$-inorganic species (90.68 - 99.61%), in addition to a noticeable decrease in diatoms count (572.0 - 1568.0 Cells/l) while their percent abundance (63.56 - 82.7%) was high, this could be related from one side to the elevated iron concentrations in these samples which by turn might stress diatoms growth due to possible toxicity, and by turn decreasing diatoms cell number, In this aspect El-Sayed, *et al.* (1998) mentioned that Fe is likely to show toxic effects when organisms are exposed to levels higher than normally required. The United Nation Environmental Program (UNEP) stated that the threshold toxicity value of Fe in aquatic environments is 0.3 mg/l (Hammad-Doaa and Radi, 2010). From the other side the decrease in diatoms count in Helwan and Cairo samples might be related to the low occurrence of organic iron in these samples to a level that might affect diatoms growth; this was clear in H-L sample where the highest contribution of $Fe^{3+}$-organic species (9.32%) was associated with maximum diatoms count and abundance. In this connection Benderliev and Ivanova (1997) mentioned that the presence of organic Fe chelators could enhance Fe solubility and by turn its availability. However, rates of Fe uptake from these complexes are generally low and their presence usually results in physiological deficit for the strains tested (Hutchins, *et al.*, 1999).

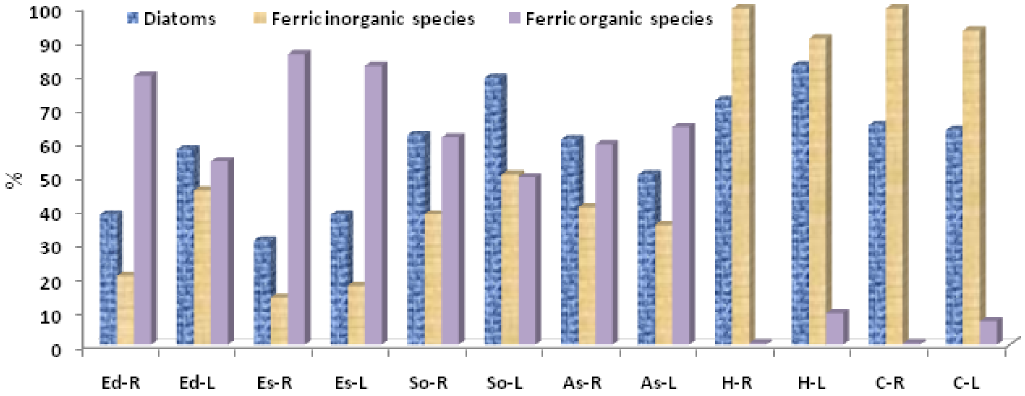

**Fig. 5:** Diatoms Abundance in Relation to Ferric Inorganic & Organic Species in River Nile Samples.

At all the investigated sites, diatoms percentages are positively correlated with ferric inorganic species, $Fe(OH)_2^+$ and $Fe(OH)_3$ but negatively correlated with the percentage of organic species (Table 5).

**Table 5:** Correlation Coefficient Matrix between Diatoms Percent Abundance and Percentages of Ferric Inorganic Species, Ferric Organic Species, $Fe(OH)_2^+$, $Fe(OH)_3$ & $Fe(OH)_4^-$

| | Diatoms % Abundance | $Fe^{3+}$ Inorganic Species % | $Fe^{3+}$ Organic Species % | $Fe(OH)_2^+$% | $Fe(OH)_3$% | $Fe(OH)_4^-$% |
|---|---|---|---|---|---|---|
| $Fe^{3+}$ Inorganic Species % | 0.773** | . | . | . | | |
| Sig. | 0.003 | . | . | . | | |
| $Fe^{3+}$ Organic Species % | -0.773** | -1.000** | . | . | | |
| Sig. | 0.003 | 0.000 | . | . | | |
| $Fe(OH)_2^+$ % | 0.737** | 0.998** | -0.998** | . | | |
| Sig. | 0.006 | 0.000 | 0.000 | . | | |
| $Fe(OH)_3$ % | 0.582* | 0.016 | -0.016 | -0.049 | | |
| Sig. | 0.047 | 0.962 | 0.967 | 0.880 | | |
| $Fe(OH)_4^-$ % | 0.231 | -0.318 | 0.318 | -0.380 | 0.897** | |
| Sig. | 0.469 | 0.313 | 0.313 | 0.223 | 0.000 | |

**Correlation is highly significant at the 0.01 level *Correlation is significant at the 0.05 level

## *Solid Phases Controlling $Fe^{3+}$, $H_4SiO_4$ and $H_3SiO_4^-$ Activities in River Nile:*

### *Ferric ions ($Fe^{3+}$):*

The activities of the $Fe^{3+}$ ions in water samples were plotted on stability diagrams along with the solid phases that had log solubility indices close to zero (indicating equilibrium) assuming that the solids are in their standard states. In all cases, these lines represent the most insoluble minerals, which are the most stable form. The stability lines in this study were drawn from the data calculated by Lindsay (1979).
The solubilities of iron hydroxide and jarosite are shown in reactions (1-2):

$$Fe^{3+} + 3\,H_2O \leftrightarrow Fe(OH)_3\ (\text{amorp}) + 3\,H^+ \qquad \log K^o = -3.54 \qquad (1)$$

From equation (1) we can conclude that:

$$\therefore \log Fe^{3+} = -3.54 - 3\,pH$$

$$3\,Fe^{3+} + K^+ + 2\,SO_4^{2-} + 6\,H_2O \leftrightarrow KFe_3(SO_4)_2(OH)_6\ (\text{jarosite}) + 6\,H^+ \qquad \log K^o = -12.51 \qquad (2)$$

From equation (2) we can conclude that:

$$\therefore \log Fe^{3+} = -2.51 - 2\,pH \qquad \text{At } \log(K^+) \text{ and } \log(SO_4^{2-}) = -2$$

$\therefore \log Fe^{3+} = -1.17 - 2\ pH$ At $\log(K^{+})$ and $\log(SO_4^{2-}) = -3$

$\therefore \log Fe^{3+} = -0.17 - 2\ pH$ At $\log(K^{+})$ and $\log(SO_4^{2-}) = -4$

The activities of $Fe^{3+}$ increased as the pH values of water samples decreased, (Figure 6). The resulting activities were regressed against pH to give the empirical model:

$$\therefore \log Fe^{3+} = 17.8\ (5.2) - 4.32\ (0.7)\ pH \qquad R^2 = 0.78\ (0.74)$$

Where, the values between brackets are standard error.

The resulting activities were regressed against pH and total dissolved iron concentration (mg/l) to give the empirical model:

$$\therefore \log Fe^{3+} = -5.30\ (7.9) - 1.39\ (1.0)\ pH + 0.63\ (0.19)\ Fe_{total} \qquad R^2 = 0.89\ (0.52)$$

The data points of samples Ed-R, Ed-L, As-R, As-L, Es-R, Es-L, So-R and So-L are grouped around the jarosite, which means that jarosite may be the solid phase that control $Fe^{3+}$ activities. For samples C-R, C-L, H-R and H-L, $Fe^{3+}$ activities are supersaturated with respect to jarosite.

The non-agreement between solubility products and metal activity products for samples C-R, C-L, H-R and H-L, can be attributed to one or more of the following reasons.

- The hypothetical solid phase is not present in the soil;
- The minerals in soils were not pure;
- The presence of dissolved ligands, which their thermodynamic data is not available, alters the trace element solubility.

The percentage of diatoms growth increased as the activity of iron increased in the studied samples (R= 0.68 the coefficient is significant at 0.015, r<0.05).

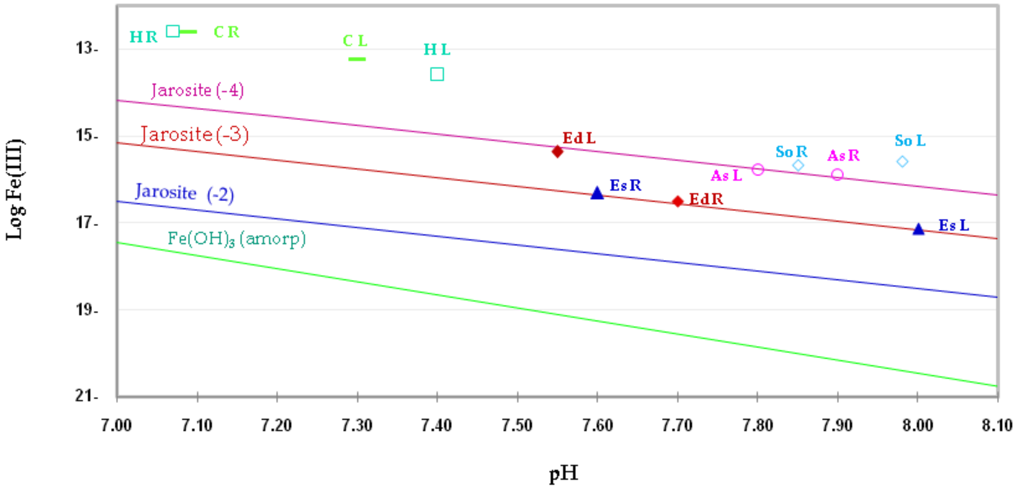

**Fig. 6:** Activity of $Fe^{3+}$ as Calculated from Visual MINTEQ Program for Water Samples.

*Silicic Acid ($H_4SiO_4$):*

The solubilities of tridymite, cristobalite and soil-silica are shown in reactions (3-6) and are plotted on Figure (7). The activities of silicic acid in water samples were plotted on stability diagrams and the stability lines in this study were drawn from the data calculated by Lindsay (1979).

$$\alpha - SiO_2(\text{tridymite}) + 2H_2O \leftrightarrow H_4SiO_4^o \qquad \log K^o = -3.76 \qquad (3)$$

$$\therefore \log H_4SO_4^o = -3.76 + pH$$

$$\alpha - SiO_2(\text{cristobalite}) + 2H_2O \leftrightarrow H_4SiO_4^o \qquad \log K^o = -3.94 \qquad (4)$$

$$\therefore \log H_4SO_4^o = -3.94 + pH$$

$$\alpha - SiO_2(\text{soil}) + 2H_2O \leftrightarrow H_4SiO_4^o \qquad \log K^o = -3.94 \qquad (5)$$

$$\therefore \log H_4SO_4^o = -3.94 + pH$$

$$\alpha - \mathrm{SiO_2(quartz)} + 2\mathrm{H_2O} \leftrightarrow \mathrm{H_4SiO_4^o} \qquad \log K^o = -4.00 \qquad (6)$$
$$\therefore \log \mathrm{H_4SO_4^o} = -4.00 + \mathrm{pH}$$

The data points of samples Ed-R, Ed-L, Es-R, Es-L, So-R, So-L, As-R and As-L are grouped around the tridymite line, which suggest that tridymite was the solid phase controlling $H_4SiO_4$ activities in these samples. The data of sample C-R is in line with the equilibrium line of quartz which indicates that quartz was the solid phase controlling silicic acid activity in that sample. The data points of samples H-R, H-L and C-L are grouped around the equilibrium line of quartz, which indicate that quartz may be the solid phase that control silicic acid activities.

The growth of total phytoplankton and diatoms increased as the activity of silicic acid increased, without a clear relationship. The activity of silicic acid increased as the pH of water samples and total dissolved silicon increased. The resulting activities were regressed against pH and $Si_{\text{total dissolved}}$ to give the empirical model:

$$\therefore \log \mathrm{H_4SiO_4^o} = -4.7\ (0.43) + 0.048\ (0.07)\ \mathrm{pH} + 0.11\ (0.18)\ \mathrm{Si_{total\ dissolved}} \qquad R^2 = 0.92\ (0.04)$$

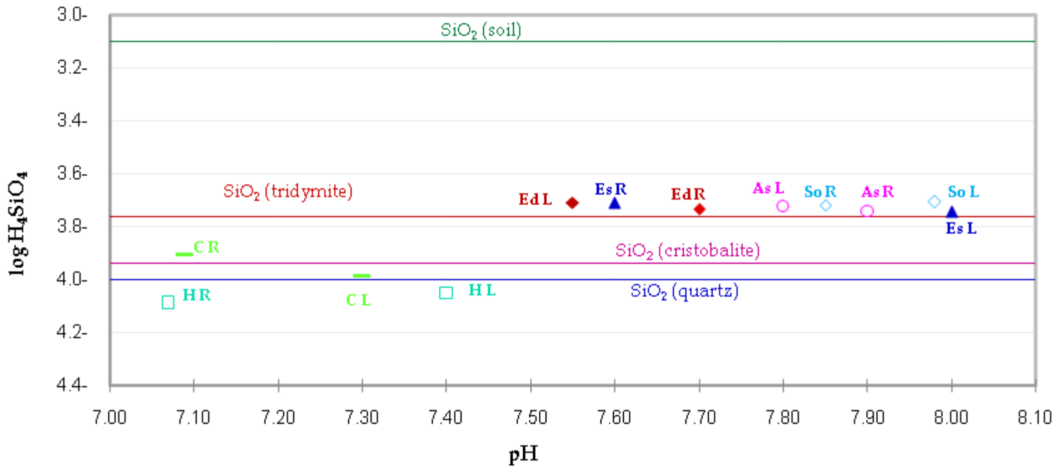

**Fig. 7:** Activity of $H_4SiO_4$ as Calculated from Visual MINTEQ Program for Water Samples.

*Silicate Ions ($H_3SiO_4^-$):*

The solubilities of silicate ions were developed and plotted on Figure (8), under the condition that $H_4SiO_4^o$ are controlled by tridymite (reactions 7 and 3), cristobalite (reactions 7 and 4) and quartz (reactions 7 and 6).

$$\mathrm{H_4SiO_4^o} \leftrightarrow \mathrm{H_3SiO_4^-} + \mathrm{H^+} \qquad \log K^o = -9.71 \qquad (7)$$

$$\alpha - \mathrm{SiO_2(tridymite)} + 2\mathrm{H_2O} \leftrightarrow \mathrm{H_4SiO_4^o} \qquad \log K^o = -3.76 \qquad (3)$$
$$\therefore \log \mathrm{H_3SO_4^-} = -13.47 + \mathrm{pH}$$

$$\alpha - \mathrm{SiO_2(cristobalite)} + 2\mathrm{H_2O} \leftrightarrow \mathrm{H_4SiO_4^o} \qquad \log K^o = -3.94 \qquad (4)$$
$$\therefore \log \mathrm{H_3SO_4^-} = -13.65 + \mathrm{pH}$$

$$\alpha - \mathrm{SiO_2(quartz)} + 2\mathrm{H_2O} \leftrightarrow \mathrm{H_4SiO_4^o} \qquad \log K^o = -4.00 \qquad (6)$$
$$\therefore \log \mathrm{H_4SO_4^o} = -13.71 + \mathrm{pH}$$

The activities of silicate ions increased as water pH and silicon concentration increased. The resulting activities were regressed against pH and $Si_{\text{total dissolved}}$ to give the empirical model:

$$\therefore \log \mathrm{H_3SiO_4^-} = -14.4\ (0.6) + 1.03\ (0.09)\ \mathrm{pH} + 0.124\ (0.024)\ \mathrm{Si_{total\ dissolved}} \qquad R^2 = 0.99(0.05)$$

The data points of samples Ed-R, Ed-L, So-R, So-L, As-R, and As-L are grouped around the equilibrium line of silicate-tridymite which suggest that silicate-tridymite was the solid phase controlling $H_3SiO_4^-$ in these water samples. The data points of samples Es-R and Es-L are grouped around the equilibrium line of silicate-cristobalite which suggests that silicate-cristobalite was the solid phase controlling $H_3SiO_4^-$ in these two samples. The data point of sample C-R is in line with the equilibrium line of silicate-quartz which indicates that silicate-quartz was the solid phase controlling $H_3SiO_4^-$ in this sample. The data points of samples C-L, H-R and H-L are undersaturated with respect to silicate-quartz line.

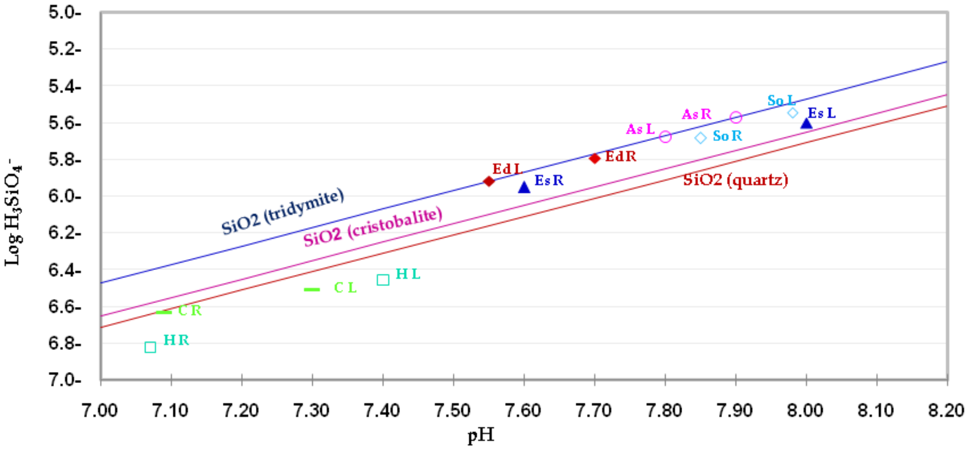

**Fig. 8:** Activity of $H_3SiO_4^-$ as Calculated from Visual MINTEQ Program for Water Samples.

*Conclusion:*

- Phytoplankton assemblage of River Nile was mainly dominated by Bacillariophyta (diatoms) followed by Chlorophyta, Cyanophyta, Euglenophyta and Dinophyta.
- Diatoms population density was primarily dominated by centric forms including *Cyclotella meneghiniana*, *Melosira granulata* and *Melosira granulata v. angustissma,* and secondarily by pinnate forms where *Synedra ulna* and other *Synedra spp.* contributed with the highest share.
- Dominance of diatoms in Nile water with the abundance of centric species could be a good indicator of River Nile water quality.

*According to MINTEQ model:*

- The predominant species of silicon in the studied water samples was silicic acid ($H_4SiO_4$), accounting for 98.43 - 99.80%.
- The activities of silicic acid and silicate ions increased as the pH of water samples and total dissolved silicon increased.
- The activities of $Fe^{3+}$ increased as the pH values of water samples decreased
- The free ions of $Fe^{3+}$ were found to be <0.01% in all water samples.
- Ferric-organic species predominate (79.64 – 86.01%) at low Fe concentrations.
- Ferric inorganic-species increased (13.98 - 99.61%) with the corresponding increase in total iron concentrations, and were mainly represented by the ion-pair $Fe(OH)^+$.
- $H_4SiO_4$ and $H_3SiO_4^-$ activities are mainly controlled by tridymite, cristobalite and quartz solid phases, while $Fe^{3+}$ activities are found to be controlled by jarosite solid phase.

- The percentage of diatoms growth increased as the activity of iron increased in the studied samples (R= 0.68 the coefficient is significant at 0.015, r<0.05).
- The growth of total phytoplankton and diatoms increased as the activity of silicic acid increased, without a clear relationship.
- In-spite of the high percentages of silicic acid in all samples, diatoms growth was found to be highly affected by the availability and limitation of total iron and the corresponding percentages of ferric organic and inorganic species; indicating that iron concentrations as well as its chemical speciation influenced the utilization of silicic acid by diatoms.
- Maximum growth of diatoms (89778.0 Cells/L) was observed at 0.616 mg/l total Fe concentration, 49.54% $Fe^{3+}$-organic species and 50.45% $Fe^{3+}$-inorganic species.
- At all sites, diatoms percentage are positively correlated with ferric-inorganic species and $Fe(OH)_2^+$ and negatively correlated with the percentage of ferric-organic species, which means that the dominant hydrolysis species $Fe(OH)_2^+$ is a preferable Fe form for the uptake by diatoms.

- Results suggest that iron availability in the presence of silicon is an important factor determining the success of diatoms in being the major group of phytoplankton assemblage of River Nile.

*Recommendations:*

- According to the nature of diatoms of being readily dispersed, can invade a variety of habitats, easy to sample and sensitive to very subtle changes in environmental conditions; it is therefore recommended that a biological index for diatoms could be used as a simple biological method for monitoring water quality that avoids the need for complicated chemical analysis.
- The succeed of the centric diatom *Cyclotella meneghiniana* in dominating diatoms assemblage of River Nile under different iron concentrations, recommends this species to be employed as a test organism in studying the influence of Fe availability and limitation on phytoplankton production in freshwater systems.
- Role of iron in seawater and freshwater productivity, biogeochemical cycles and global climate should gain more attention and specific investigation.
- The use of mathematical models as Visual MINTEQ can give hand for predicting the chemical behavior of elements in different environments where it uses a huge thermodynamic database in-order to examine a wide variety of chemical equilibrium relationships. Results could be very useful to decision makers, especially in risk assessment and environmental impact analysis.

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