

## Fertilizers Effect Blue Green Algae and increasing their Toxins

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### Article History

Article ID: AR1876a

Received in 28<sup>th</sup> May, 2018

Received in revised form 01<sup>st</sup> June, 2018

Accepted in final form 07<sup>th</sup> June, 2018

### Abstract

Urban activities add pollutants to the environment, and increase Phosphorous [P], Nitrogen [N], Sulfate [S] and Iron [Fe], these pollutants in Aquatic environment can cause Eutrophication of Blue green algae (BGA), which they are an auto nutrition organisms via photosynthesis and organic materials, prokaryotic and they have not specialized organelles and produce phycocyanin pigment which it's just in cyanobacteria, which have been recognized in different environments such as Antarctica below 0 °C also in spring. Many species can produce toxic substances which they are secondary metabolic products, formed by cyanobacteria, these toxins can cause humans toxication, in different parts of the world which is an evidence of algal toxins accumulation in treated drinking fresh water, and can cause neurosystem illness and digestion system especially Hepatic also dermatitis, algal toxins represent an international problem in all water types salty, brackish and fresh water, also can be produced by terrestrial species. These types of toxins found in all types of waters fresh, brackish and salty waters. Most of these toxins are carcinogenic, many countries needs to go on to monitor this phenomenon and limitation of toxic species with fixation of routine tests for drinking water. Impact of health in more by exposure to the toxins and keep water safety imposes its presence through the permanent observer and early monitoring. Non floating algae on the surface of water let us judge on being free of algae. Sometimes one alga can produce more than one type of toxins and many species can produce one type of toxin.

**Keywords:** Fertilizers, BGA, algal toxins, hepatotoxins, neurotoxins, dermatoxins, endotoxins

### 1. Introduction

Urban activities had relies a lot of ecological pollutants as a by-products such as pesticides and fertilizers (Abbasi et al., 2014). Hence a long time ago, where the human concerned to develop productivity and increasing of his crops, via addition minerals and organic materials. This situation continued until the end of the sixteenth century, where this subject has become somewhat experimental (Kakhia, 2011). According to several factors was distributed between coincidence or error and right, animal organic wastes and additive substances to agricultural soils, led to an increase in plant growth clearly (Hossain et al., 2017). From used material at this period was bone powder, plant ash, animal manure and potassium powder ( $\text{KNO}_3$ ) (Kilmer, 1979). but the results were very different. Some treatments did not give the desired results from one field to another (Roy et al., 2006). It is worth mentioning that we refer to the attempts of Van Helmont in Belgium, as he planted a cleft of willow (*Salix fragilis*) and used only rain water in irrigation or ground water, one of the first attempts to improve plant production, but at 1660, Digby succeed in using salt gunpowder as a fertilizer for arid lands in agriculture. But Liebig at 1840 established the basis of modern fertilizer industry, in turn confirmed that these

materials are replenished soil, Liebig realized the importance and value of nitrogen N plants, but he was convinced that plants can get their nitrogen N through the air and not through the soil (Kakhia, 2011). Production of fertilizers was developed at the first quarter of 19<sup>th</sup> century (Savci, 2012), powders of animal bones were used and added to the plants, there are traces and evidences that human bones were collected from cemeteries, from battlefields and even the bones of dead animals in that period, they were crushed and added to the plantings (Kilmer, 1979), but at 1830 Sulfuric acid  $\text{H}_2\text{SO}_4$  was added to the bone with distribution on the farm by wood drums. In the same period of time, Potassium salts, Ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) or Sodium nitrate  $\text{NaNO}_3$  were sometimes added to plants, then he introduced first mixed liquid of chemical fertilizer. Fertilization is considered as one of the most important conditions for increasing efficiency of agricultural lands and one of the most important methods to increase the fertility of agricultural land and raise the productivity of agricultural crops. Chemical fertilizers mainly contain phosphates, nitrates, ammonium and potassium salts (Svaci, 2012). The fertilizer industry is a very important source of natural radionuclide's and heavy metals as potential sources of crops. It also contains most heavy metals such as



mercury, cadmium, lead, copper and nickel (Atfar et al., 2010). Moreover, it contains natural radionuclides such as uranium U238, Thorium TH232 and Polonium Po 1-2210 (Chauhan and Kumar, 2015; Savaci, 2012). However, the growth and consumption of plant fertilizers has increased dramatically worldwide, with increasing environmental problems such as accumulation of heavy metals in soils and plants (Atfar et al., 2010). It is possible that environmental pollutants reach the food chain, and because of fertilization there is deterioration in the quality of water, soil and air as a result of manufacturing processes, so there are countries that have regularized the use of chemical fertilizers such as some developing countries and Turkey where its considered as least country in using chemical fertilizers per hectare, which use  $100.4 \text{ kg ha}^{-1}$  of NPK, but the highest is Netherlands, which use  $624.8 \text{ kg ha}^{-1}$ . (Svaci, 2012). Increasing of agricultural production is considered as global phenomenon, and the increasing of crops depends to a large extent on the types of fertilizer which used as nutrient supplements to the plants due consumption of some plants in their previous growth in the fields of food needed for their growth due to the consumption of some of the plants for nutrients in their previous growth at the fields, as well as increasing, maximizing productivity and economic returns (Conforti, 2011). It is also necessary to consider the environmental impact of these additives (chemical fertilizers) on the soil, animals and insects that are necessary living in the soil, also taking into consideration the effect of climate directly on these materials and their effectiveness on both of soil and living organisms, where these organisms effect directly in formation of organic waste fertilizers of the soil (Rai et al., 2014). In addition to that waste water which reach with organic and inorganic materials which increase many problems, one of these problems is Eutrophication, quality of fresh water and impacts of public health due to due excretion alkaline toxic and carcinogenic materials, also can cause diseases such as syndromes related with neurosystem, digestive system and allergy (Bitton, 2014). Although green and blue green algae reached water with Oxygen  $O_2$  in natural growth, but they exhaust nutrients of nutrients of another organisms and oxygen. Algae have high ability to live in different aquatic environments, where they can tolerate a range of temperatures beginning from  $0^\circ\text{C}$  to high temperatures which giving them a good chance of growth and reproduction naturally (Whitton, 1992), due to availability of important plant nutrients such as Nitrogen (N) and Phosphorus (P), in addition to that salts, minerals and micro nutrients which they are necessary for growth and reproduction (DalCorso et al., 2014). Algae can grow to over-growth and their appearance on the surfaces of water bodies many times, also they can produce a massive quantities of biomass which can cause heavy losses in the production of fish and livestock's (Khan and Mohammad, 2014), in addition to the impact on public health and can be collected at the bottom of the body or water side margins and there is difficulty in dispersion at that gathering toxins in freshwater (Chorus and Bartram,

1999). These toxins can be classified in four main groups which they Hepatotoxin, Neurotoxins, Dermatotoxins and Endotoxins (Funari and Testai, 2008). The produced algal toxins by blue-green algae are alkaloid chemical compounds that accumulate in the tissues of fish and other aquatic organisms (Jung et al., 2003). Some of cyanotoxins such as Neurotoxins target the neuromuscular system, paralysing peripheral, skeletal and respiratory muscles with different mechanisms (Zaccaroni and Scaravali, 2008). Toxication with these toxins depend on intensity of consumed toxins amount (Funari and Testai, 2008). Some of blue green algae toxins due to their structure contained an amino acids (Mankiewicz et al., 2003), but others are very close to carbamate compounds, especially Organophosphorus pesticides (Patocka et al., 2011). These toxins cannot effected by increasing of temperature in aquatic ambient also aggregate in water bodies therefore they impact public health, bird's health and domestic animals which consume polluted water, also production of cyanotoxins linked with temperature (Holland and Kinnear, 2013). Efforts have been combined around the world for monitoring and determining how to minimize economical and public health impacts of algae to keep environment from deteriorating especially in the quantities of scarce water (EEA, 2011). The leaking of untreated wastewater to the waters bodies can increase massive algal growth up to the extent of environmental impacts via depleting oxygen and cause lake of enough light access to the water body and impact sustainability of biodiversity which leads to massive losses reaching massive density, less individuals of cyanobacteria in water body may occur to bloom if conditions helps for increasing Eutrophication (Smith, 2003). If cyanobacteria grew in water bodies at the case of Eutrophication it possible to spread on the surface of water bodies via winds and water streams then may cover surface in some times and threats water body and living organisms which live in (WHO, 2016).

## 2. Blue Green Algae (Cyanobacteria)

Blue green algae (BGA) considered as oldest group had been lived in wide range of temperature from  $35^\circ\text{C}$  in worm areas to below  $0^\circ\text{C}$  in Antarctica (Whitton, 1992). BGA can produce toxins as a secondary natural metabolism products, these toxins are different in toxicity from species to the others and ifferent in impacts upon health and economic (Zain, 2011), less toxicity can cause dermatitis and highly toxic to liver Hepatotoxic. Active BGA toxins are global phenomenon in fresh waters, marine's wagers and brackish waters, also it may can produces via terrestrial species of BGA. At last decades the numbers of BGA increased, there for toxicity accidents increased also. Analyses at laboratories and active methods to detect toxicity of BGA, depend on natural samples and BGA isolation in laboratory to manage waters to decrease growing of toxic BGA mass, need to understand how to produce toxins, toxins proprieties and paths of exposure which shows health impacts to prevent or reducing of BGA toxins

impacts (Dellinger, et al., 2017; Zaccaroni and Scaravali, 2008; Hitzfeld et al., 2000b). Toxins producers algae are unicellular microscopic organisms, auto nutrition via photosynthesis and organic materials. BGA have a different in general properties from another species of algae and bacteria, therefore they behave like plants in another hand behaves like bacteria because cellular contains similar to cellular contains of bacterial cell, where its cellular wall has no cellulose, reproduce asexually, prokaryotic and they have not specialized organelles and produce phycocyanin pigment which it's just in cyanobacteria, due to that BGA have blue color and called Cyanobacteria, some of these toxic types are *Microcystins*, *Anabaena*, *Nostoc* and *Planktothrix* (Dellinger et al., 2017).

Cyanobacteria are very important microorganisms to study because they are in period of blooming responsible about many risks and his animal and aquatic resources such as fish, water birds and another aquatic animals due to producing toxins which accumulate in animals and birds bodies, blooming of Cyanobacteria evidence about increasing of Cyanobacteria toxins concentrations to Dangerous levels on humans and animals alike (Chorus and Bartram, 1999). These toxins also impacts all companied organisms in aquatic environment like zooplankton which feeding on phytoplankton, invertebrate and all vertebrate, also impact fish directly and indirectly due to direct feeding on zooplankton which feeding on Cyanobacteria. And direct impact due to eutrophication where organs of animals like liver, kidney and gills by Cyanobacteria (Zaccaroni and Scaravali, 2008). Each type of toxin probably produced by more than one type of Cyanobacteria, and they can produce one type of toxin by many types of Cyanobacteria (Funari and Testai, 2008). In (Table 1). In different types have a variable genotype, some of them has responsible gene to produce toxins others have not this gene (Kurmayer et al., 2002). The toxicity combined with produce different Cyanobacteria toxins (An and Carmichael, 1994).

### 3. Health Effects of Cyanotoxins

Understanding of Cyanotoxins importance depend on basic researches at the levels of toxicology and toxins ambient. Also depend on recognition and verification of adverse health outcomes in Animals and humans alike (Dellinger et al., 2017). There were many cases of toxification had been reported at USA after destruction of cyanotoxins cells and realizing toxins to the aquatic ambient after chemical remediation at nature with Copper sulfate ( $\text{CuSO}_4$ ), where thousands of people toxified with Cyanotoxins toxins, cases varied between simple with first aid, while others were suffering from severe died (Falconer, 2005; Tisdale, 1931). At 1996 In Zimbabwe toxification with Cyanotoxins were identified after drinking contaminated water from child's, Australia after 1983 and in Brazil at 1993 (Zaccaroni and Scaravali, 2008)

Cyanotoxins can be classified in four groups, 1) Hepatotoxins impact liver. 2) Neurotoxins impact neurosystem. 3) Dermatotoxins can cause irritation of respiratory system and skin. 4) Endotoxins were reported they can cause irritation

Table 1: Types of Cyanobacteria toxins and types of algae producers

Cyanotoxin	Main producing cyanobacteria
Microcystins	Most of <i>Microcystis</i> spp. and <i>Planktothrix</i> spp, some <i>Anabaena</i> , <i>Nostoc</i> and <i>Synechocystis</i> and <i>Cyanobium bacillare</i> , <i>Arthrospira fusiformis</i> , <i>Limnothrix redekei</i> , <i>Phormidium formosum</i> , <i>Hapalosiphon hibernicus</i>
Nodularins	<i>Nodularia spumigena</i>
Cylindrospermopsin	<i>Cylindrospermopsis raciborskii</i> , <i>Umezakia natans</i> , <i>Aphanizomenon ovalisporum</i> , <i>Aphanizomenon flos-aquae</i> , <i>Raphidiopsis curvata</i> , <i>Anabaena lapponica</i> , <i>Anabaena bergii</i>
Anatoxin-a	Most of <i>Anabaena</i> spp., some <i>Aphanizomenon</i> ( <i>A. flos-aquae</i> , <i>A. issatschenkoi</i> ), <i>Cylindrospermum</i> , <i>Microcystis</i> and <i>Planktothrix</i> spp. and <i>Raphidiopsis Mediterranea</i>
Homoanatoxin-a	<i>Oscillatoria formosa</i> , <i>Raphidiopsis mediterranea</i>
Anatoxin a-(s)	<i>Anabaena flos-aquae</i> and <i>A. lemmermannii</i>
Saxitoxins (PSP)	<i>Aphanizomenon</i> , <i>Anabaena</i> , <i>Lyngbya</i> and <i>Cylindrospermopsis</i> spp.
LPS endotoxins	All Cyanobacteria
Aplysiatoxin, Lyngbyatoxin Debromoaplysiatoxin	<i>Lyngbya majuscula</i> (marine waters), <i>Oscillatoria nigro-vridis</i>
Microviridin J	<i>Microcystis</i> spp.
$\beta$ -N-methylamino-Lalanine	<i>Microcystis</i> , <i>Anabaena</i> , <i>Nostoc</i> and <i>Planktothrix</i> spp. and most of cyanobacteria symbionts tested

of stomach and intestine (Chorus, 2005). For all planktonic algae and benthic types aggregate and become near coasts there for they concentrate, due to that they need non short time to separate, in general, therefore they cause hygienic problems to human and impact negatively economic animals. Now, many of BGA communities are highly toxic (Zaccaroni and Scaravali, 2008).

### 4. Types of Cyanotoxins

#### 4.1. Neurotoxins-1

These types of toxins prevent neuronal signal via two mechanisms

##### 4.1.1. Anatoxins

Higher or lesser concentrations can effect negatively



acetylcholine and act as inhibitor of cholinesterase enzymes and cause organo phosphorous syndrome, symptoms similar to toxification with organo phosphorous pesticides (Zaccaroni and Scaravali, 2008). It's one of major groups of Cyanotoxins which produce by different types of BGA in fresh waters some times in case of Eutrophication as floating area near shores of rivers and lakes. Anatoxins are alkaline compounds have a fast and severe effect and cause death for a lot of livestock (Messineo et al., 2009). Now identified as three alkaline compounds Figure 1. Produced by *Anabaena flosaquae*, non aromatic amine, highly toxic and can cause death during 15 minutes. It was distinguished at first as Anatoxin-a impact muscular nerves and cause death via paralysis of respiratory system (Tisdale, 1931), produced from three widespread types of BGA *Aphanizomenon*, *Anabaena*, *Planktothrix* (Tatters et al., 2017)

#### 4.1.2. Anatoxin-a(s)

They are less widespread during algal BGA communities development and blooming in nature, however, they have been identified by tracking livestock mortality at USA (Patocka et al., 2011). Also they impact nerves in its stimulations also they are working to disrupt the flow of Sodium ions  $\text{Na}^+$  and works to activate the Calcium pump ions  $\text{Ca}^{++}$  (Soliakov et al., 1995). In structure are similar to organo phosphorous insecticides Figures (1 and 2). They are working as anticholinesterase, one of the symptoms of toxification, they causes excessive saliva from the victim's mouth (Falconer, 2005).

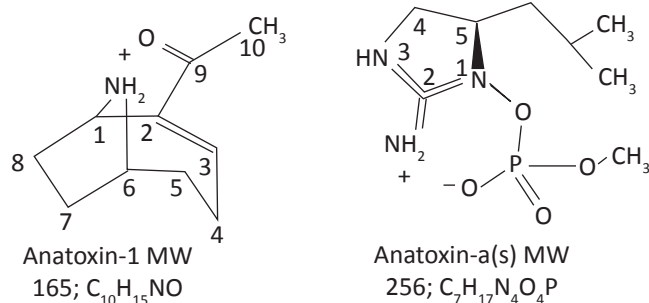


Figure 1: Structure formula of alkaline cyanotoxins from (Funari and Testai, 2008)

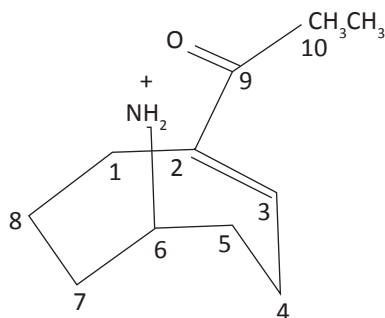


Figure 2: Homoanatoxin structural formula from (Funari and Testai, 2008)

Among all Anatoxins there are just three structures were known figures (1 and 2), Anatoxin-a Anatoxin-a(s) and Homoanatoxin-a, although of similarity of names, but they aren't connected with factors of Common chemical and Homoanatoxin-a is an isomer of Anatoxin-a, also Anatoxin-a is the first toxin of BGA toxins was identified and known well as effect and chemically when discovered. Anatoxin-a highly polar and dissolved well in water, his ionic state depend on pH. Anatoxin-a(s) is ester mono phosphate with aromatic structure formula of N-hydroxyguanidine (Zaccaroni, and Scaravali, 2008).

#### 4.2. Saxitoxin

One of known well of toxins which impact nerves and can cause Paralytic Shell Poisoning (PSP). Which directly kill a hundreds of people in different parts of world (Cirés et al., 2017). Can block Potassium  $\text{K}^+$  sodium  $\text{Na}^+$  pump which make unbalanced Na inside neurons. In some cases nerve poisoning detected via drinking of polluted water from livestock or consumption of contaminated water foam (Zaccaroni, and Scaravali, 2008). Saxitoxins not produced from BGA and marine algae only, but produces also from another BGA in fresh waters like *Anabaena*, *Aphanizomenon* and *Lyngbya* (Falconer et al., 1983; Velzeboer et al., 2000). Saxitoxins are characterized stable and fixed molecules even in the case of heating and not easy to remove from waters in classic methods unless pH is controlled and residual chlorine but can be removed efficiently by ozone or activated carbon (Falconer et al., 1989).

##### 4.2.1. Chemical structure

Saxitoxins at least consist from a group of 19 toxin from Carbamate Alkaline Neurotoxins (CAN) which is one of the endemic neurotoxins in freshwater and brackish waters, they Inhibits nervous transport by blocking sodium channels, also this group of toxins produced from Dinoflagellate in phytoplankton community (Dellinger et al., 2017) (Figure 3).

#### 4.3. Cytotoxin or cylindrospermopsin

Alkaline substance can blocking paths of producing protein

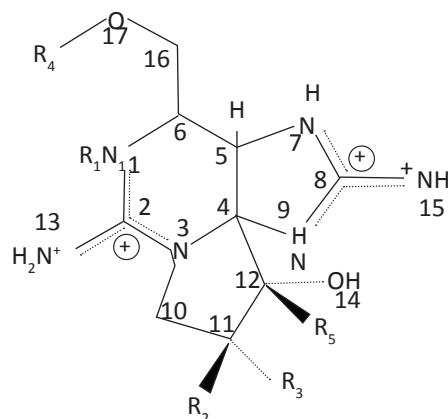


Figure 3: General structure of saxitoxins from (Funari and Testai, 2008)



due to covering DNA or RNA, and responsible of damage of Crushing the helix of genetic material DNA for all chromosomes (Asymmetry of chromosomes) and proved as a carcinogen. The toxicity of cylindrospermopsin associated with obvious losses of glutathione and glutathione depletion leading to cell death, decreasing of glutathione rates due to blockage of general pathway to build glutathione (Zaccaroni, and Scaravali, 2008).

#### 4.3.1. Chemical structure

Cytotoxin or Cylindrospermopsin is one molecule consisting from a group of aromatic Tri quandin which Includes contains Hydroxy methyl ureasil, Figure 4. Hydrophilic, easy intestinal absorption, need active transport system and has the ability to inter to the liver cells, Cylindrospermopsin can use special active transport system of bile acid, due to the size of small molecule, minor changes occur because of negative

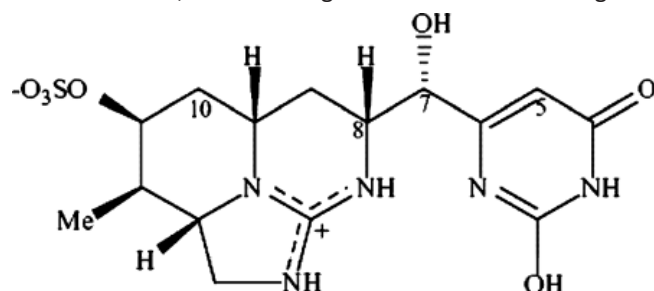


Figure 4: Chemical structure of Cylindrospermopsin from (Funari and Testai, 2008)

propagation through the bio membranes, Showing the effects of toxins inside and along the cells, not just across the channel transport system of bile acid at the liver (Chong et al., 2002). All studies in vivo (Norris et al., 2001; Norris et al., 2002), and in vitro also in primary hepatocytes cells (Runnegar et al., 1994; Runnegar et al., 1995), showed that Cylindrospermopsin was activated vitally with proteins of electronic transport P-450 (P450) (Norris et al., 2002). In addition, there are projects to prove (CYN) is one of the cause's cancer, because there are an evidence about this opinion (Falconer and Humpage, 2001).

#### 4.4. Microcystins or nodularin

Widespread more than other toxins of BGA, It works to stop the enzymes of protein phosphorylation 1 and 2 A and caused liver toxification in bile channels which used as a carrier of the bile to pass through cells membranes. The toxicity of Microcystins or Nodularins is more inside peritoneal cavity. Hepatic damage is a result of Microcystins at Australia (Cirés et al., 2017). Microcystins or Nodularins toxicity is cumulative toxicity, and considered as an important factors development of tumors and increase in liver also lead to human injury of hepatic tumors (Zaccaroni and Scaravali, 2008). After exposure to Microcystins-LR, the lab mice are affected 10 times more often than their consumption through oral exposure and are infected vascular lobe decomposition with damage to the lining of the respiratory tract (Fitzgeorge et al., 1994). Early in 1975, blood decomposition found as a result of exposure

to the BGA toxins via orally (Hindman et al., 1975). People are exposed to BGA toxins through the daily consumption of polluted water by drinking or exposure to them through recreation (Falconer and Humpage, 1996; Falconer, 1998).

#### 4.4.1. Chemical structure

Microcystins are polypeptides associate with seven amino acids, which include 80 isomers, therefor they are considered as the most widespread of other toxins in the world, in general structure formula, all Microcystins share it as shown in figure (Dellinger et al., 2017). These amino acids are distributed as shown in the attached parts such as X, Z, R<sup>1</sup>, R<sup>2</sup> (Butler et al., 2009) Figure 5.

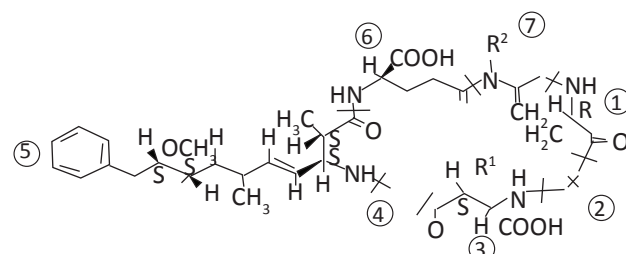


Figure 5: General structure formula from (Funari and Testai, 2008).

Numbers in the figure represent link locations of four amino acids which they distributed over seven locations, either two locations R<sup>1</sup> R<sup>2</sup> represents two locations for two groups of methyl, for other two locations Z and X, shows posts of four aminoacids Table 2.

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Table 2: Sites of amino acids in the morphological form of Microcystins

Name	X-position amino acid	Z-position amino acid	Molecular weight
910.06	Alanine (A)	Leucine (L)	Microcystin LA
1045.19	Arginine (R)	Tyrosine (Y)	Microcystin YR
1038.2	Arginine (R)	Arginine (R)	Microcystin RR
995.17	Arginine (R)	Leucine (L)	Microcystin LR

1999 and reported variability of Microcystins (Falconer, 1998). As shown in Table 3. which refer to these Microcystins and there 60 isomers .

In order to what reported in Table 3. Some formulas of Microcystins have been partially described (Butler et al., 2009; Sivonen and Jones, 1999; Boland et al., 1993; Craig et al., 1993). From many scientific projects found most of Microcystins even if they vary, they are very toxic and 50-300 µg highly toxic to mice (Jones et al., 1995; Harada et al., 1990a). But few of Microcystins isomers are found non-toxic (Harada et al., 1990b). Recently, and more obvious there are 80 isomers of Microcystins where fixed from (Codd et al., 2005), and producers of them, as shown in Table 4.

Table 3: Mycosestines and blue-green algae producers

Molecular Weight	Organisms	Micro-cystin	Molecular Weight	Organisms	Micro-cystin
MCYST-LA	<i>Microcystis aeruginosa</i> <i>M. viridiss</i>	909	[D-Asp3, ADMAdda5, Dhb7] MCYST-LR	<i>Nostoc sp.</i>	1,009
MCYST-LAba	<i>M. aeruginosas</i>	923	[L-MeSer7]MCYST-LR	<i>Microcystis spp.</i>	1,012
MCYST-LL	<i>M. aeruginosab</i>	951	[Dha7]MCYST-FR	<i>Microcystis sp.</i>	1,014
MCYST-AR	<i>Microcystis spp.</i>	952	[L-Ser7]MCYSTE(OMe)E(OMe)	<i>Anabaena sp.</i>	1,015
MCYST-YA	<i>M. aeruginosas</i>	959	[ADMAdda5]MCYST-LR	<i>Nostoc sp.</i>	1,022
[D-Asp3,Dha7]MCYST-LR	<i>M. aeruginos</i> <i>Anabaena sp.</i>	966	[D-Asp3,ADMAdda5] MCYST-LHar	<i>Nostoc sp.</i>	1,022
[D-Asp3,Dha7]MCYSTEE(OMe)	<i>Anabaena sp.</i>	969	[D-Asp3]MCYST-RR	<i>O. agardhiis</i> , <i>Anabaena sp.s</i> , <i>M. aeruginosas</i>	1,023
MCYST-VF	<i>M. aeruginosa</i>	971			
(D-Asp3)MCYST-LR	<i>A. flos-aquae</i> , <i>M. aeruginosas</i> , <i>M. viridisb</i> , <i>O. agardhii</i>	980	[Dha7]MCYST-RR	<i>M. aeruginosas</i> , <i>Anabaena sp.s</i> , <i>O. agardhiis</i>	1,023
[Dha7]MCYST-LR	<i>M. aeruginosa</i> <i>Anabaena sp.</i> <i>O. agardhiis</i>	980	MCYST-LW	<i>M. aeruginosas</i>	1,024
			MCYST-FR	<i>Microcystis spp.</i>	1,028
			MCYST-M(O)R	<i>Microcystis spp.</i>	1,028
[DMAdda5]MCYST-LR	<i>Microcystis. spp.</i> <i>Nostoc. sp.</i>	980	[Dha7]MCYST-HphR	<i>Anabaena sp.</i>	1,028
[Dha7]MCYST-EE(OMe)	<i>Anabaena sp.</i>	983	[D-Asp3, Dha7]MCYST-HtyR	<i>Anabaena sp.</i>	1,030
[D-Asp3,Dha7] CYSTE(OMe)E(OMe)	<i>Anabaena sp.</i>	983	[Dha7]MCYST-YR	<i>M. aeruginosas</i>	+
MCYST-LF	<i>M. aeruginosa</i>	985	[D-Asp3]MCYST-YR	<i>Microcystis spp.</i>	+
MCYST-LR	<i>M. aeruginosa</i> , <i>A. flos-aquae</i> <i>M. viridiss</i>	994	MCYST-YM(O)	<i>M. aeruginosa</i>	56
			[ADMAdda5]MCYST-LHar	<i>Nostoc sp.</i>	60
			MCYST-RR	<i>M. aeruginosas</i> , <i>M. viridiss</i> , <i>Anabaena sp.</i>	600
[D-Asp3,D-Glu(OCH3)6]MCYST-LR	<i>A. flos-aquaes</i>	994	[(6Z)-Adda5]MCYST-RR	<i>M. viridisb</i>	>1,200
[(6Z)-Adda5]MCYST-LR	<i>M. viridisb</i>	994	[D-Ser1, ADMAdda5]MCYST-LR	<i>Nostoc sp.s</i>	+
[Dha7]MCYST-E(OMe)E(OMe)	<i>Anabaena sp.</i>	997	[ADMAdda5,MeSer7]MCYST-LR	<i>Nostoc sp.</i>	+
[L-Ser7]MCYST-LR	<i>Anabaena sp.</i>	998	[L-Ser7]MCYST-RR	<i>Anabaena sp.s</i> , <i>M</i> <i>aeruginosas/b</i>	+
MCYST-LY	<i>M. aeruginosas</i>	1,001			
[L-Ser7]MCYST-EE(OMe)	<i>Anabaena sp.</i>	1,001	[D-Asp3,MeSer7]MCYST-RR	<i>O. agardhiis</i>	+
[D-Asp3,Ser7]MCYSTE-(OMe)E(OMe)	<i>Anabaena sp.</i>	1,001	MCYST-YR	<i>M. aeruginosas</i> , <i>M. viridiss</i>	70
MCYST-HiIR	<i>Microcystis spp.</i>	1,008			
[D-Asp3,ADMAdda5]MCYST-LR	<i>Nostoc sp.</i>	1,008	[D-Asp3]MCYST-HtyR	<i>A. flos-aquaes</i>	160 - 300
[D-Glu(OCH3)6]MCYST-LR	<i>A. flos-aquaes</i> , <i>Microcystis sp.</i>	1,008	[Dha7]MCYST-HtyR	<i>Anabaena sp.</i>	+
[D-Asp3,Dha7]MCYST-RR	<i>O. agardhiib</i> , <i>Anabaena sp.s</i> , <i>M. aeruginosas</i>	1,009	MCYST-(H4)YR	<i>Microcystis spp.</i>	NR
			[D-Glu-OC2H3(CH3)OH6] MCYST-LR	<i>Microcystis spp.</i>	>1,000

Table 3: Continue...



Molecular Weight	Organisms	Micro-cystin
[D-Asp3,ADMAdda5,Dhb7] MCYST-RR	<i>Nostoc sp.</i>	+
MCYST-HtyR	<i>A. flos-aquae</i>	80-100
[L-Ser7]MCYST-HtyR	<i>Anabaena sp.</i>	+
MCYST-WR	<i>Microcystis spp.</i>	150-200
[DAsp3, ADMAdda5,Dhb7] MCYSTHtyR	<i>Nostoc sp.</i>	+
[L-MeLan7]MCYST-LR	<i>Microcystis spp.</i>	1,000

Aba: Aminoisobutyric acid; ADMAdda: O-Acetyl-O-demethylAdda; Dha: Dehydroalanine; Dhb: Dehydrobutyrine; DMAdda: O-DemethylAdda; E(OMe): Glutamic acid methyl ester  $\Delta$ ; (H4)Y: 1,2,3,4,-tetrahydrotyrosine; Har: Homoarginine; Hil: Homoisoleucine; Hph: Homophenylalanine; Hty: Homotyrosine; MeLan: N-Methylanthionine; M(O): Methionine-S-oxide; MeSer: N-Methylserine; (6Z)-Adda: Stereoisomer of Adda at the  $\Delta 6$  double bond

Table 4: groups of BGA as a producers of Cyanotoxins

Toxins	No. Vari- ants	Genera
<b>Hepatotoxins</b>		
Microcystins	80+	Microcystis, Anabaena, Nostoc, Anabaenopsis, Planktothrix, Oscillatoria Hapalosiphon,
Nodularins	9	Nodularia, Theonella
Cylindrospermopsin	3	Cylindrospermopsis, Anabaena, Aphanizomenon, Raphidiopsis.
<b>Neurotoxins</b>		
Anatoxin-a	5	Anabaena, Oscillatoria, Phormidium, Aphanizomenon
Anatoxin-a(s)	1	Anabaena
Saxitoxins	20	Aphanizomenon, Anabaena, Lyngbya, Cylindrospermopsis, Planktothrix
<b>Dermatoxins</b>		
Lyngbyatoxins-a	1	Lyngbya, Schizothrix, Oscillatoria
Aphlysiatoxins	2	Lyngbya, Schizothrix, Oscillatoria

#### 4.5. Lipopolysaccharides (LPS)

External compounds of the cellular membranes of blue green algae and gram negative bacteria, the single molecule consists of three main areas: the first is the inner region and consists of non-annular sugar, termed lipid A. a central area of fatty

saccharides, associated with an internal secondary unit of specialized external carbohydrate O-specific chain figure (Zaccaroni and Scaravali, 2008)

LPS of Blue green algae BGA are differ somewhat from those evaluated by bacteria, and the difference is the appearance of very small amounts from phosphate. When exposed to these Types of toxins, the infected person will suffering from allergy, itching in the skin, allergy of eyes, irritation of digestive system and severe diarrhea in advanced cases (Funari and Testai, 2008) (Figure 6).

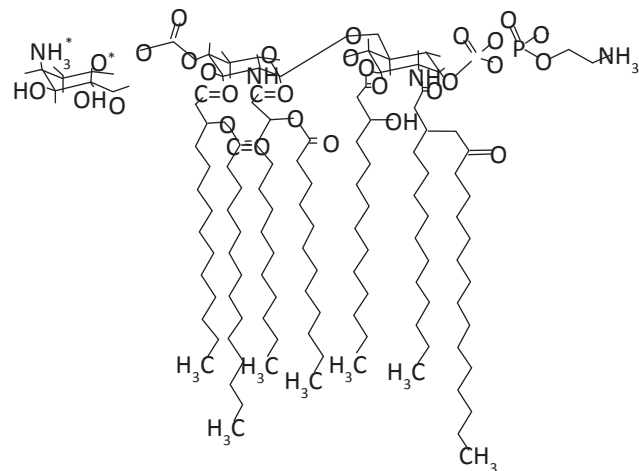


Figure 6: General structure formula of LPS endotoxins from (Funari and Testai, 2008)

#### 4.6. Biological Identification of algal toxins

The initial identification of the presence of green and blue green algae depends on the water color change to green or bluish green, accumulation of algae and floating on the water surface (Joosten and Anton, 2006), also depending on chemical analyses where blue-green algae do not need specialized chemicals such as other types of nitrogen and phosphorus as a major growth factor and depend on self-feeding via photosynthesis (Madigan et al., 2003). In addition to the above, also monitoring of dead organisms in water in the cases of eutrophication such as birds and fish, gives an evidence of the presence of Cyanotoxins (Zaccaroni and Scaravali, 2008). It is now easy to define and diagnose algae of all kinds for an acceptable classification system and for all existing algae where classification is still under constant and rapid revision and for all levels and constant updating of this information as well as genetic and structural evidence (Barasanti et al., 2008).

#### 5. Conclusion

Toxins cannot be proved from the surrounding conditions nor isolated from the toxic algae associated closely, that neglecting the study of toxic algae means, we have caused the annihilation of a complete environment that has provided food to many living organisms. It is not advisable to establish the foundations of a study

without taking into consideration the recent data of high temperature and permanent pollution as emergency data on all studies. It should be noted, as well as the results of coincidence that may change the concept of study in the field of economics and food security, also medical therapies due to relation with field of human life and economic.

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