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Cyanotoxins in groundwater; occurrence, potential sources, health impacts and knowledge gap for public health

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ABSTRACT

Groundwater is a significant source of water across the world and constitutes about 30% of the earth's freshwater. This water source is likely to be contaminated by cyanobacteria that produce secondary metabolites called cyanotoxins. Studies on contamination of groundwater by cyanobacteria have been sketchy with limited information. There is a need for better evidence regarding groundwater contamination by cyanobacteria as their presence in surface water bodies could cause contamination of groundwater via infiltration and percolation during rainfall events or during groundwater-surface water interaction, bank infiltration or water quality exchange. Therefore, this review is aimed at exploring the occurrences and potential sources of cyanotoxins in groundwater. This was achieved by summarising the existing data on the occurrence of cyanobacteria in groundwater and their potential sources across the world. Groundwater cyanobacteria contamination can possibly pose threat to water quality because many of the cyanotoxins produced by cyanobacteria pose a severe threat to human health, animals and the environment. Concentrations of microcystins (MCs) in groundwater have been recorded in China (Chaohu), Saudi Arabia, and China (Huai River Basin), with concentrations of 1.446 µg/L, 1.8 µg/L and 1.07 µg/L, respectively. In humans, exposure to these evanotoxins can cause symptoms such as vomiting, diarrhea, and skin irritation, to mention a few. This work highlights the importance of providing information or knowledge regarding public health implications of exposure to groundwater contaminated with cyanotoxins and the need to undertake risk management actions through national and international regulation. This review also points out current knowledge gaps, which could lead to future research.

1. Introduction

Cyanobacteria and their toxins are an increasing global public health menace (Otten and Paerl 2015; Rastogi et al., 2015). Population growth results to both physical and economic water scarcity (Kumar 2013; Mancosu et al., 2015; Mulwa et al., 2021), with an open water crisis in many under-developed and developing countries. Problems of water quality are both natural and anthropogenic in nature, with an increase in emerging contaminants (Khatri and Tyagi 2015; Lamastra et al., 2016; Luczaj 2016). Challenges in both quantity and quality of groundwater create problems that the world is currently facing (Luczaj 2016). Cyanotoxin contamination in natural waters may cause serious health implications to humans and the environment (Drobac et al., 2013; Zastepa et al., 2014). Groundwater plays a crucial role in providing water to humans for drinking, agriculture, and industrial purposes (Cosgrove and Loucks 2015; Dhawan 2017).

Cyanobacteria are dominating in freshwater bodies resulting in the proliferation of toxic cyanobacterial harmful algal blooms (cyanoHABs) (Gumbo et al., 2014). In most areas of the world, water is abstracted directly from underground through a borehole to a standing tap, where it is collected by water users and used for different activities without prior treatment (Drangert and Cronin 2004; Dittmann and Wiegand 2006; Mohamed and Shehri, 2009). The use of groundwater containing cyanotoxins causes detrimental health impacts to humans and animals

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since water containing cyanotoxins can present health risks if untreated. According to Alsalah et al. (2015), contamination of groundwater occurs when surface water containing cyanotoxins infiltrates the ground through pore spaces and recharges groundwater. This phenomenon normally happens in surface water bodies that are situated next to agricultural cultivations where nutrients are washed to a certain water body (Silva et al., 2019).

There is increasing concern attracted by groundwater contamination in areas with speedy industrial and agricultural development. Wu et al. (2014a, 2014b) have reported that numerous contaminants originate from human activities (landfill leachate, wastewater, petroleum pharmaceuticals, products, and pesticides) and they sink into the groundwater from the surface. Chemicals found in groundwater turn out to be more steady and hard to degrade than the ones on the surface, and this is because of low redox conditions and lack of photodegradation (Fayemiwo et al., 2017). Harmful compounds such as pharmaceuticals and pesticides have been found at high concentrations in groundwater (Lin et al., 2015). Yang et al. (2016) also reported that groundwater found close to lakes with a high mass of cyanobacteria blooms is likely to be contaminated by cyanotoxins when an interaction between groundwater and surface water occurs. Nevertheless, there is limited evidence on the concentration and distribution of cyanotoxin in groundwater closer to lakes containing cyanobacteria blooms.

This paper aims to present a review of previous work done on the occurrence of cyanotoxins in groundwater. This review also highlights sources of cyanotoxins in groundwater and contamination of groundwater by cyanotoxins and implications for human health. Furthermore, this paper explores the existing knowledge and highlights the knowledge gaps which could give birth to new research.

2. Groundwater as a vital water resource

Groundwater is a significant source of water all over the world. Of all the earth's freshwater groundwater constitutes 30% and is about 25 times more plentiful than the surface water (lakes and streams) combined (Ponce 2006). Groundwater is accessible for use in many regions around the world. It is the only reliable water source for different water uses in many areas, particularly in semi-arid and arid zones (Hosseinifard and Aminiyan 2015). It is a major freshwater resource because half of the population in the world relies on groundwater for drinking purposes (FAO 2016a, 2016b). However, groundwater is threatened by many natural and anthropogenic activities in most countries. Contamination of groundwater is normally derived from agricultural industries, disposal of solid waste on the environment, and chemical spills and leaks from chemical production/processing industries (Bouchet et al., 2019). Groundwater is commonly used across the world because of its availability, low cost for abstraction from underground, and perceived high quality for drinking, recreational, and other industrial use (Bhattacharjee et al., 2019).

Many indigenous communities, some mining operations, and remote pastoral properties depend only on groundwater for their water supply (One water 2012). Households in rural areas, farmers, and supplies of public water depend highly on groundwater (Kovacs and West 2016). There are also commercial businesses and industries that depend on groundwater for their processes and operations. Most rural communities rely on raw water from sources such as streams, rivers, lakes, and ponds for various purposes. However, people in communities that do not have sufficient surface water depend on groundwater for survival.

Groundwater remains significant as it supplies springs, and a large amount of water in our ponds, marshland, swamps, streams, rivers, and bays. Many ecosystems rely on groundwater to survive (Klausmeyer et al., 2018). It can also provide base flows to rivers and creeks on which ecosystems depend (Eamus et al., 2016). As a major earth's natural resource, groundwater is very valuable and ecologically important. Many biologists and ecologists have overlooked the vitality of groundwater to the ecosystem (Simlandy 2015; Hunt et al., 2016). It does not support only the earth's life forms but also assists in human civilization's growth.

3. Characterization of cyanotoxins in groundwater

The growth of cyanobacteria is becoming a serious issue worldwide since these species produce toxins that have been reported to be poisonous to humans and animals (Otten and Paerl 2015). There are approximately 40 of the 150 known cyanobacteria genera that are capable of producing toxins and these 40 genera include 2000 species (Caetano 2015). Numerous secondary metabolites such as hepatotoxins, dermatotoxins, and neurotoxins are produced by certain cyanobacteria species (Kultschar and Llewellyn 2018). These metabolites or cyanotoxins could pose adverse health for animals and human (Drobac et al., 2013; Cheung et al., 2013).

3.1. Hepatotoxins

Group of similar structure of small molecular weight cyclic heptaand penta-peptides, which causes acute hepatotoxicosis in human and animals is referred to as MCs and NODs (Carmichael and Boyer 2016: Essays UK 2018). Cyclic heptapeptides are composed of five common amino acids plus a pair of L-amino acids and they occur differently among the ninety variants (Carmichael et al., 2013). Hepatotoxin MCs (named after the cyanobacterium Microcystis aeruginosa) shown in (Fig. 1) is the most frequently reported cyanobacterial toxin (Dittmann et al., 2013; Nybom 2013). MCs share a common structure of cyclo-(-D-Ala¹-X²-D-MeAsp³-Z⁴-Adda⁵-D-Glu⁶-Mdha⁷) in which X and Z are variable L-amino acids, D-MeAsp is D-erythro-\beta-methylaspartic acid, and Mdha is N-methyldehydroalanine (Chorus and Welker 2021). MCs are the most common hepatotoxins that occur in natural water. MCs are chemically diverse family of peptides, with more than 250 different structural variants that have been reported to date (Chorus and Welker 2021); in addition to that, Bouaicha et al. (2019) reported 279 structurally different variants of MCs and they are named after Microcystis aeruginosa which is known to produce them (Dittmann et al., 2013; Percival and Williams 2014; Mohamed 2016; Manach et al., 2018). Nevertheless, other genera of freshwater cyanobacteria, such as Nostoc, Planktothrix, and Phormidium (Table 1) are also known to produce these toxins (Yang et al., 2016). NODs (named after the cyanobacterium Nodularia spumigena) are produced by Nodularia spumigena and are structurally related to MCs in that they regularly possess the structure cyclo -(D-MeAsp¹-L-Arg²-Adda³-D-Glu⁴-Mdhb⁵), in which Mdhb is 2-(methylamino)-2-dehydrobutyric acid. Another alkaloid cyanotoxin that has various modes of action including hepatotoxicity and cytotoxicity is cylindrospermopsin. According to Martínez-Ruiz et al. (2020), this cyanotoxin has a cyclic guanidine moiety bound to a hydroxymethyluracil group. Different cyanobacteria species (Table 1) produce cylindrospermopsin, which is most likely to cause liver failure leading to death (Lee et al., 2017).

3.2. Neurotoxins

The alkaloid neurotoxin anatoxin-a is an effective post-synaptic depolarizing neuromuscular blocking agent (McLaughlin 2013; Hameed 2013). Fig. 1 shows neurotoxin anatoxin-a, which is isolated from strains of *Dolichospermum (Anabaena) flosaquae* and *Kamptonema (Oscillatoria) formosum* and has been normally concerned with mammal and bird poisoning (Jaja-Chimedza 2014). Saxitoxins are a group of carbamate alkaloid toxins and they consist of two guanidinium moieties and a tetrahydropurine group (Duran-Riveroll and Cembella 2017). They are classified into nonsulfated, singly sulfated (gonyautoxins-GTX), doubly sulfated (C-toxins), and decarbamylated analogs (Dittmann et al., 2013). They are isolated from strains *Kamptonema (Oscillatoria) formosum, Phormidium,* and *Chroococcus* sp. A non-proteinogenic amino acid called b-methylamino-L-alanine (BMAA)



Fig. 1. Distinctive chemical structures of cyanotoxin families (Dittmann et al., 2013).

Table 1

Main toxins from cyanobacteria, including genera of main producers.

Classes	Cyanotoxins	Genera of main producers	Chemical classification
Hepatotoxins	NODs	Nodularia spumigena	Cyclic Pentapeptides
	MCs	Phormidium,	Cyclic
		Pseudanabaena,	Heptapeptides
		Microcystis, Nostoc,	
		Kamptonema	
		(Oscillatoria)	
		formosum, Planktothrix	
	Cylindrospermopsin	Aphanizomenon,	Guanidine
		Cylindrospermopsis,	Alkaloids
		Umezakia	
Neurotoxins	Anatoxin-a	Dolichospermum	Alkaloids
		(Anabaena) flosaquae,	
		Aphanizomenon,	
		Kamptonema	
		(Oscillatoria)	
		formosum, Planktothrix	
	Saxitoxins	Dolichospermum	Carbamate
		(Anabaena) flosaquae,	alkaloids
		Aphanizomenon,	
		Cylindrospermopsis,	
D		Lyngbya	
Dermatotoxins	Lyngbyatoxin-a	Lyngbya, Kamptonema	Alkyl phenols
		(Oscillatoria) formosum	
	Apiysiatoxins	Lyngbya, Schizothrix,	Aikyi phenols
		Kamptonema	
		(Oscillatoria) formosum	

(Fig. 1) is a cyanotoxin in high connection with high cases of neurodegenerative diseases such as dementia and amyotrophic lateral sclerosis (Takser et al., 2016). The BMAA, isolated from *Chroococcus*, *Merismopedia*, *Mycrocystis*, and *Nostoc* Sp. has been postulated to be a cause of neurodegenerative diseases that affect large numbers of people (Nunes-Costa et al., 2020).

3.3. Dermatotoxins

Lyngbyatoxins (Fig. 1) are found in coastal and estuarine waters in subtropical and tropical climates and are produced by *Lyngbya majuscula*

(Tamele et al., 2019). The *Lyngbya majuscule* also produce cyanotoxin Aplysiatoxin (Fig. 1), which is phenolic bislactones and similar to lyngbyatoxins, they are considered the main cause of severe contact dermatitis. These toxins have high inflammatory potential; therefore, they are capable of promoting the development of tumours (Sanseverino et al., 2017).

NODs, saxitoxin, cylindrospermopsin, and MCs are a few of the cyanotoxins of which there are almost hundred different variants (Qi et al., 2015; Miller and Russel 2017) and are shown in Table 1. The most studied cyanotoxins in groundwater are MCs (produced by *Anabaena*, *Planktothrix*, *Nostoc*, *Anabaenopsis*) (Mohamed and Shehri, 2009; Chatziefthimiou et al., 2016; Yang et al., 2016). Shown in Table 2, is evidence of cyanotoxins existence in groundwater. Limited studies on the investigation of cyanotoxins occurrence in groundwater have been conducted in a few countries across the world. Concentrations of MCs in groundwater have been recorded in China (Chaohu), Saudi Arabia, and China (Huai River Basin), with concentrations of 1.07 μ g/L, 1.8 μ g/L, and 0.446 μ g/L, respectively.

4. Sources and occurrence of cyanotoxins in groundwater

Cyanotoxins have been widely documented in surface water such as rivers, lakes, and dam reservoirs but their presence in groundwater presents a data gap that needs further research. Yang et al. (2016) reported in their study on the presence of MCs in groundwater collected close to a eutrophic lake in China (Fig. 2). The presence of MCs was linked to the possible interaction between the surface water (contaminated with cyanobacteria) and groundwater. Their study also showed a decrease in groundwater contamination levels away from the eutrophic sites. Previous studies have reported the presence of cyanobacteria in

Table 2
MCs concentrations found in groundwater from different regions.

Cyanotoxins	Level	Region	References
MCs MCs MCs MCs	0.446 μg/L 1.8 μg/L 1.07 μg/L 0.84 μg/L	China (Huai) Saudi Arabia China (Chaohu) Upper Egypt (Nile) China (Lake Taibu)	Tian et al. (2013) Mohamed and Shehri (2009) Yang et al. (2016) Mohamed et al. (2022) Xa et al. (2021)



Fig. 2. Temporal trends of MCs levels in the groundwater of Lake Chaohu, southeastern China (Yang et al., 2016).

soils and earth crusts in semi-arid regions such as Qatar and Saudi Arabia (Chatziefthimiou et al., 2016; Bouaicha and Corbel 2016). Previous studies suggest that MCs originate from infiltration of nearby surface water bodies into the groundwater (Zheng et al., 2018; Abesh 2019; Abesh et al., 2022), which then indicates that MCs can occur in many groundwater systems. However, these studies only focused on the presence of MCs in groundwater and not other cyanotoxins. There is lack of information on the occurrence of other cyanotoxins such as anatoxins and cylindrospermopsins in groundwater.

Apart from surface and groundwater interactions, groundwater contamination by cyanotoxins has been linked to cyanobacteriacontaminated soil. MCs are known to adsorb onto soils and other biological crusts (Mohamed and Al Shehri, 2009; Bouaïcha and Corbel, 2016). Although their adsorption is low, there could be high bioavailability for soil plants and a higher possibility of infiltration into groundwater during irrigation and precipitation events. The study of Eynard et al. (2000) showed that soil was not efficient in trapping toxins and failed to act as a filter media for groundwater protection. Chen et al. (2006) reported the ease of migration of MCs into groundwater from the soil after rain events. Low degradation of MCs in soil has been reported (Corbel et al., 2014). MCs are believed to be persistent in groundwater when found. Wu et al. (2014a, 2014b) indicated that low redox conditions and lack of photodegradation in groundwater make chemicals such as MCs more stable and harder to be degraded.

Contamination of groundwater with cyanotoxins is believed to occur from infiltration near rivers, lakes, and ponds which are eutrophic, and precipitation in agricultural used farmlands (Gerba and Goyal, 1981; Dodds 2002). The presence of cyanobacteria in groundwater becomes a potential risk to public health as in most communities groundwater is consumed without any form of treatment (Dittmann and Wiegand 2006; Mohamed and Shehri, 2009). Mohamed and Al Shehri (2009) determined cyanobacteria (Table 3) and MCs (Fig. 3) in groundwater samples from Saudi Arabia. The most dominant species determined was

Table 3

Density and frequency of cyanobacteria species in groundwater n = 10, in Abha city, Saudi Arabia.

Species	Density (cells L^{-1})			Frequency (%)
	Minimum	Maximum	Mean	
Chrococcus minor Gleocapsa spp. Oscillatoria limnetica Spirulina spp.	$\begin{array}{c} 4.5\times 10^5 \\ 0.23\times 10^5 \\ 68.1\times 10^5 \\ 0.07\times 10^5 \end{array}$	$\begin{array}{c} 7.8\times 10^5 \\ 1.9\times 10^5 \\ 92.3\times 10^5 \\ 0.18\times 10^5 \end{array}$	$\begin{array}{c} 6.33 \times 10^5 \\ 1.12 \times 10^5 \\ 86.4 \times 10^5 \\ 0.13 \times 10^5 \end{array}$	60 70 60 40



Fig. 3. Concentration of MCs in groundwater samples from Saudi Arabia (Mohamed and Shehri, 2009).

Oscillatoria limnetica producing up to 0.3 µg/L of MCs. Higher levels (0.3-1.8 µg/L) exceeding the World Health Organization (WHO) recommended guideline of 1 μ g/L for MCs were determined in some of the groundwater samples (Mohamed and Shehri, 2009). In a study conducted in Niger Delta by Odokuma and Isirima (2007), cyanobacterial species (Cylindrospermopsis sp. and Anabaena sp.) and cyanotoxins (cylindrospemopsin, microcystin, and anatoxin-a) they produce were found in groundwater from Abonnema. Findings from a study done by Tian et al. (2013) suggested that MCs contamination in groundwater originated from nearby rivers, causing potential health risks to people who drink groundwater directly. In their study, they reported MCs concentrations ranging from 0.060 to 0.446 µg/L in groundwater samples collected from Huai River Basin in China. Another study by Mohamed et al. (2022) reported MCs concentrations ranging from 0.1 to 0.84 µg/L in summer and 0–0.06 µg/L in winter. They further highlighted that their study provided evidence for the risk of cyanotoxins in groundwater close to cyanobacteria-contaminated surface water since surface water and groundwater systems are connected and interrelated in most landscapes according to Liu et al. (2016). Although the MCs levels recorded from these studies were mostly below the lifelong guideline value for drinking water, and well below the short term limit (WHO 2020c), their presence in groundwater may contribute to rendering this drinking water source unfit for domestic consumption as their presence may represent a high risk to human health.

5. Transport and fate of cyanotoxins in groundwater

Once toxic cyanobacteria come in contact with soil, cyanotoxins can be released and infiltrate from the soil surface to deeper layers and potentially contaminate groundwater. The previous study has suggested that the soil adsorption of cyanotoxins is generally low, which can potentially result in their higher bioavailability for groundwater contamination due to infiltration into the soil (Bouaicha and Corbel, 2016). This is mostly the case during surface-water and groundwater interaction. Neurotoxins cyanotoxins β-N-methylamino-L-alanine (BMAA) and its isomers N-(2-aminoethyl) glycine (AEG), and 2,4-diaminobutyric acid (DAB) were detected in soil profile samples decreasing with depth in the soil horizon (Chatziefthimiou et al., 2016). It was reported that bioaccumulation potentially exists if they are leached into the groundwater (Richer et al., 2015). Miller et al. (2005) conducted batch studies in 12 texturally diverse soils were conducted to examine the soil properties influencing the adsorption of the cyanobacterial hepatotoxins, MCs, and nodularin (NODs). In their study, they observed a significant positive correlation between hepatotoxin sorption and clay and silt contents of the soils. They further highlighted the need for a detailed understanding of factors that influence the fate and transport of contaminants to enable the assessment of the efficiency of bank filtration

as a removal strategy for cyanobacterial toxins. Miller et al. (2005) reported contents of clay, sand, and silt as factors that were significantly correlated with toxin sorption, with clay being the factor recognized for its ability to enhance adsorption of organic compounds and also adsorptive of the large hepatotoxins. In addition, they further indicated that sand has a smaller surface area than clay soils and therefore, fewer adsorption sites. Organic carbon contents of the soils have also been identified as the most important factor governing the adsorption of organic compounds. Soils with high clay and organic carbon contents have high adsorption coefficients of MCs (Machado et al., 2017). Similar findings were obtained by Miller and Fallowfield (2001), who reported that the soils with the highest organic carbon content and the highest clay content were the most effective at removing cyanobacterial toxins (NOD and MCs) in batch experiments. However, Klitzke et al. (2011) reported that, although clay and organic carbon content proved to be the most important parameters in anatoxin-a sorption to sediments, some portion of anatoxin-a is still retained by sandy porous media, which can therefore percolate during rainy events.

Previous studies suggest that MCs released from cyanoHABs in surface water could contaminate aquifers and their groundwater through surface-water and groundwater interaction (Mohamed and Shehri, 2009; Tian et al., 2013; Yang et al., 2016). Surface water cyanoHABs can negatively impact the aquifers underneath them by contaminating their groundwater with cyanotoxins transported by advection and mechanical dispersion processes. Cyanotoxin can migrate towards the aquifer along the hydraulic gradient due to pumping-induced reverse groundwater flow during or post cyanoHABs events. The transport of cyanotoxins from surface to groundwater can be facilitated by hydrogeological conditions or settings. A study has been conducted to quantitatively understand how surface-water and groundwater interaction would trigger and control the transport of MCs. The possibility that soils and groundwater adjacent to lakes, reservoirs, and other surface water bodies may be contaminated by cyanotoxins has been proven (Mohamed and Shehri, 2009; Tian et al., 2013; Yang et al., 2016). A typical hydrogeological setting or soil type can be critical for controlling the transport kinetics of cyanobacteria and cyanotoxins in the environment. Knowledge of transport parameters of cyanobacteria and cyanotoxins is essential for reliable predictions of their fate and transport in the porous medium.

The occurrence of cyanotoxins in the soils is dependent on the degradation efficiency (e.g., hydrolysis, photolysis, or microbial degradation), with microbial degradation being the major dissipation process for cvanotoxins in soil ecosystems (Machado et al., 2017). Cylindrospermopsin biodegradation has been reported in some natural waters. A study by Martínez-Ruiz et al. (2020) investigated cylindrospermopsin removal by manganese-oxidizing bacteria (Pseudomonas sp., Comamonadaceae bacterium, and Ideonella sp.) isolated from natural and technical systems. In their study, they observed cylindrospermopsin removal rates between 0.38 and 37.01 µg/L per day. Mohamed and Alamri (2012) reported that Bacillus strain, which also degrades MCs was able to degrade cylindrospermopsin; whereas, Dziga et al. (2016) reported cylindrospermopsin degradation by Aeromonas sp. Biodegradation of this toxin was found to be stronger at temperatures between 20 °C and 35 °C and at pH between 7 and 8. Moreover, biodegradation of anatoxin by bacteria under natural conditions has been previously reported. Isolated Pseudomonas sp., which also degrades cylindrospermopsin was reported to also degrade anatoxin. Organisms in sediments were able to reduce anatoxin concentrations by 25-48% in 22 days, according to Rapala et al. (1994). Cyanotoxins (MCs and cylindrospermopsins) have been reported to show high persistence in many water bodies due to their chemical stability and slow degradation (Wormer et al., 2008). Wu et al. (2014a, 2014b) reported that the lack of low redox conditions and photodegradation in the groundwater make chemicals such as MCs more stable and harder to be degraded. MCs are susceptible to breakdown by a number of aquatic bacteria that are found in sewage effluent, lake water, lake sediment, and river water worldwide

(Chorus and Welker 2021). Sphingomonas spp., Sphingopyxis spp, Pseudomonas aeruginosa, and Paucibacter toxinivorans are the documented microcystin-degrading bacteria and they perform aerobic degradation of MCs (Chorus and Welker 2021). According to Machado et al. (2017), other soil bacteria, such as *Brevibacterium* sp. *Arthrobacter* sp., and *Rhodococcus* sp. are able to break down MCs, with *Sphingomonas* sp. possessing a gene cluster that is involved in MCs degradation. Corbel et al. (2014a,b) reported that a large amount of MCs remained in the soil after it underwent weak microbial mineralization under aerobic conditions when it was introduced to silty sand soil. Therefore, the remaining portion can persist and become available in the soil and percolate during rain events.

6. Factors influencing the occurrence of cyanotoxins in groundwater

Positive correlation between temperature and MCs concentrations have been reported (Table 4). In contrast to this, Yang et al. (2016) reported that there is no significant correlation between environmental factors (e.g. temperature) and the occurrence of cyanotoxins in groundwater. Table 4 shows a strong correlation between the NO₃-N and MCs in groundwater, which implies that high concentrations of NO₃-N influenced toxin production in groundwater. Correlation analysis from Yang et al. (2016) shows that the MCs concentrations in the groundwater were positively correlated with the Total Dissolved Phosphorus in the nearby Chaohu lake water. The study also observed no correlation between the MCs concentrations and other environmental groundwater factors, such as pH, DO, depth, and temperature concentrations. They further reported that MCs in groundwater were not from endogenous production but from external inputs. These results confirm that MCs in groundwater likely originate from penetration by nearby lake water.

Studies have shown that soil type and soil clay content affect the adsorption capacity of MCs that could then percolate into the groundwater (Holst et al., 2003; Chen et al., 2006). Eynard et al. (2000) reported in their study that the soil was not efficient enough to protect groundwater contamination by MCs during the blooming period. Bank filtration is an effective method for the removal of cyanobacterial cells and their associated toxins (Rose et al., 2018). Groundwater from regions with surficial geology that is not appropriate for bank filtration is likely to be contaminated with cyanotoxins as these regions fail to control a variety of contaminants through natural physical, chemical, and biological processes that occur during ground passing (Pazouki et al., 2016). Previous studies such as Romero et al. (2014) have focused on the physicochemical parameters involved in filtration, including sorption for the effectiveness of bank filtration for the removal of cyanobacteria. Harvey et al. (2015) focused on the importance of colmation (another physicochemical parameter involved in bank filtration) layer in the removal of cells. The colmated layers are channel sediments that are characterized by reduced porosity and hydraulic conductivity as well as by consolidated textures (Brunke, 1999). In a study conducted by Pazouki et al. (2016), it was demonstrated that cyanobacteria can be found in water filtered through bank filtration, as these cyanobacterial cells are capable of penetrating the bank filter (Rose et al., 2018),

Table 4

The correlation coefficients between environmental factors and the concentrations of MCs in groundwater around the world (Yang et al., 2016).

	Temperature	pН	DO	NO ₃ –N	PO ₄ –P	MYC-con
Temperature	1.00					
pH	-0.23	1.00				
DO	-0.68	-0.06	1.00			
NO ₃ –N	0.13**	-0.15	0.06	1.00		
PO ₄ –P	0.69*	-0.06	-0.60	0.56*	1.00	
MCs-conc	0.43**	-0.04	-0.37	0.37**	0.66*	1.00

*p < 0.05; **p < 0.01.

especially species with tiny cell size (${<}10~\mu\text{m}$) such as Microcystis cells (Pazouki et al., 2016).

Groundwater contamination may occur through percolation and leaching of cyanotoxins through different soil media (Reddy et al., 2009). The degree of leaching and percolation depends on several factors including the soil type (Abd-Elaty et al., 2020). This is more likely in areas where groundwater is relatively shallow, and aquifers are sandy (Ye et al., 2021). The permeability is the soil property that provides an indication for soil stability, leakage, and settlement (El Shinawi 2017). The void ratio, grain size, and shape are some of the factors affecting soil permeability. Moreover, soil with high permeability can facilitate the vertical transport of cyanotoxins to groundwater, leading to groundwater contamination by these toxins. For example, shallow groundwater found in areas covered by silty clay may be highly vulnerable to cyanotoxins contamination as this type of soil may not offer complete protection to the shallow aquifers (Abd-Elaty et al., 2020). To verify if cyanobacteria can travel from eutrophic lakes into the groundwater quartz column penetration tests were carried out by previous researchers such as Schinner et al. (2010) and Ye et al. (2021). Schinner et al. (2010) found that Mircocystis aeruginosa and Anabaena flos-aquare were able to infiltrate through a column packed with quartz particles with an average diameter of 763 μ m. On the other hand, Ye et al. (2021) found that five cyanobacterial genera (Microcystis, Synechococcus, Nostoc, Phormidium, and Cylindrospermopsis) were able to penetrate the column packed with quartz particles ranging from 100 to 200 µm. These observations show that cyanobacteria can infiltrate into the groundwater from nearby eutrophic lakes or rivers, considering the pore size of the surficial geology, the size and shape of the cyanobacteria as the main parameters influencing the infiltration process.

7. Health impacts of cyanotoxins in groundwater

Few studies have been done on the impacts of cyanotoxins in groundwater (Mohamed and Shehri, 2009; Yang et al., 2016). Many different types of cyanotoxins (e.g. NODs, saxitoxins, cylindrospermopsins, anatoxin-a, aplysiatoxin, lyngbyatoxins, and MCs) exist, which are detrimental to public health (Table 5). WHO reported that in most settings, the most likely source of these toxins is drinking-water, inhalation of steam and aerosolized droplets of contaminated water when bathing, and consumption of food crops irrigated with water contaminated with cyanotoxins (Svircev et al., 2017; McLellana and Manderville, 2017). There are provisional guideline values for each of these toxins by WHO. The provisional guideline values for cylindrospermopsins are 0.7 µg/L, 3 µg/L, and 6 µg/L for lifetime drinking water, short-term drinking water, and recreational exposure, respectively (WHO 2020b). For anatoxin-a, recommended values are 30 µg/L and 60 µg/L for acute or short-term via drinking water and recreational exposure, respectively (WHO 2020a). The

Table 5

Types of cyanotoxins and their short- and long-term health effects (Lee et al., 2017).

cyanotoxin	Short-term health effects	Long-term health effects
MCs	1; 3; 4	2; 3
NODs	1; 3; 4	2; 3
Saxitoxin	5	8
Anatoxins	5	6
Cylindrospermopsin	1; 5	3; 7
Aplysiatoxin and	4	2
lyngbyatoxins		

Key to risks observed: 1 = Liver inflammation and hemorrhage, pneumonia; 2 = Tumor promoter; 3 = Liver failure leading to death; 4 = Gastrointestinal pain and dermatitis; <math>5 = Tingling, burning, numbness, drowsiness, incoherent speech, and respiratory paralysis leading to death; 6 = Cardiac arrhythmia leading to death; 7 = Malaise, anorexia; 8 = Unknown.

provisional guideline values for MCs are 1 µg/L for lifetime drinking water, 12 µg/L for short term drinking-water, and 24 µg/L for recreational water (WHO 2020c). The saxitoxins guideline values are $3 \mu g/L$ and 30 µg/L for drinking water and recreational, respectively (WHO 2020d). These toxins are detrimental to both human health and animals (Drobac et al., 2013; Hilborn and Beasley 2015), and different human organ systems like the nervous system, kidneys, liver, and skin among others are targeted by different toxins (Svircev et al., 2017; Miller and Russel, 2017). As for MCs poisoning, acute effects include intrahepatic hemorrhage as the cytoskeleton within liver cells breaks down, allowing blood to flow between the cells. Chronic effects of MCs include a reduced efficacy of proliferation control mechanisms within tumor cells (WHO 2020c). Normally, reported health problems are likely related to continuous exposure to low concentrations of microcystin (Drobac et al., 2013), with the liver and kidneys being the most targeted human organs (McLellana and Manderville, 2017). For cylindrospermopsin, the poisoning targets a range of organs (liver, kidneys, and testes), as well as perturbations of protein and cholesterol metabolism (WHO 2020b). Subchronic studies indicate that the liver and kidneys are major target organs for cylindrospermopsin-induced toxicity as well as structural changes in erythrocytes and a hemorrhage/coagulinopathy syndrome have also been observed. In general, human exposure to these cvanotoxins may cause symptoms such as diarrhea, skin irritation, vomiting, headache, fever, respiratory and muscular paralyses, nausea, numbness of lips and mouth, skin rash, incoordination, dizziness, and in rare cases it may lead to death (McLellana and Manderville, 2017).

Bioaccumulation of cyanotoxins (e.g. MCs) occurs in numerous food crops irrigated with water contaminated with cyanobacteria (Bittencourt-Oliveira et al., 2016). Variables are available that are used to determine to what concentration cyanotoxins bioaccumulate, such as the plant stage when exposed to cyanotoxins (e.g., germination, growing, fruiting adult plant), the composition of soil bacteria, the concentration of cyanotoxin in the water, amount of water used for irrigation, length of exposure via irrigation (Miller and Russel, 2017). In addition, MCs have caused animal and human deaths (Drobac et al., 2013). Moreover, irrigating crops with MCs contaminated water can also prevent germination and plant growth (Purkayastha et al., 2010). When edible plants are exposed to MCs, it becomes an important issue for human health, because these toxins are accumulated in plant tissues and then form part of the food chain (Mohamed and Shehri 2009).

8. Knowledge gaps on cyanotoxins in groundwater

Cyanotoxins occurrence is profound in water bodies (surface water) across the world, hence, there is a need for better evidence regarding groundwater contamination by cyanotoxins as the surface water bodies could possibly contaminate groundwater via infiltration and percolation during rainfall events or during groundwater-surface water interaction or bank infiltration or water quality exchange. Studies on cyanotoxins contamination of groundwater have been seldomly conducted. Consequently, there is very limited information on the occurrences of cyanotoxins in groundwater. Therefore, this study is very significant as it will provide information or knowledge regarding factors influencing their formation, possible sources, characterization, and possible health implications of exposure to contaminated groundwater with cyanotoxins. The cyclic structure of some MCs makes them extremely stable and resistant to chemical hydrolysis or oxidation under near-neutral pH conditions. Therefore, further experimental studies on cyanotoxins in groundwater to ascertain the possible sources, occurrences, and their health impacts on humans and animals should be conducted.

9. Conclusion and recommendations

Cyanobacteria release cyanotoxins that can contaminate groundwater, and this could be possible if infiltration occurs near surface water bodies, with rainfall infiltration migrating cyanotoxins from these water

bodies to groundwater. There is less adsorption of cyanotoxins (such as MCs) by soils, resulting in their increased bioavailability for plants and also leading to groundwater being contaminated as a result of water infiltrating the soil. This review has shown that using cyanotoxins contaminated groundwater for domestic or agricultural uses could be another route of human exposure to cyanotoxins. This work highlights the importance of providing information or knowledge regarding public health implications of exposure to groundwater contaminated with cyanotoxins as well as the need to undertake risk management actions through national and international regulation. The literature focuses more on contamination of soil and largely neglects to also focus on the fate of cyanotoxins in such soils. Few studies on groundwater contamination by cyanotoxins are available; therefore, there is a need for more extensive research with more focus on cyanotoxins contamination of groundwater. Groundwater exposure to cyanotoxins can cause severe economic damage. Chances of human intoxication and food being contaminated by cyanotoxins contaminated groundwater became a matter demanding public health, at that point, there is a need for government officers to monitor this exposure pathway.

Authorship contributions

Please indicate the specific contributions made by each author (list the authors' initials followed by their surnames, e.g., Y.L. Cheung). The name of each author must appear at least once in each of the three categories below.

Category 1

Conception and design of study: Mutoti M. I; acquisition of data: Mutoti M. I; analysis and/or interpretation of data: Mutoti M.I.

Category 2

Drafting the manuscript: **Mutoti M. I**; revising the manuscript critically for important intellectual content: **Mutoti M.I**.

Category 3

Approval of the version of the manuscript to be published (the names of all authors must be listed): **Mutoti M.I**.

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Ethical Statement

Hereby, I Mulalo I. Mutoti consciously assure that for the manuscript "Cyanotoxins in Groundwater; Occurrence, Potential Sources, Health Impacts and Knowledge Gap for Public Health" the following is fulfilled.

- 1) This material is the authors' own original work, which has not been previously published elsewhere.
- 2) The paper is not currently being considered for publication elsewhere.
- 3) The paper reflects the authors' own research and analysis in a truthful and complete manner.
- 4) The paper properly credits the meaningful contributions of coauthors and co-researchers.
- 5) The results are appropriately placed in the context of prior and existing research.
- 6) All sources used are properly disclosed (correct citation). Literally copying of text must be indicated as such by using quotation marks and giving proper reference.

 All authors have been personally and actively involved in substantial work leading to the paper, and will take public responsibility for its content.

I agree with the above statements and declare that this submission follows the policies of Solid State Ionics as outlined in the Guide for Authors and in the Ethical Statement.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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