



REVIEW ON CHEMICAL AND BIOLOGICAL ASPECTS OF HARDNESS IN WATER

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ABSTRACT

Water is one of the most essential natural resource for existence of life on this planet. With increasing human population and rapid development, the global water consumption demand have been increased many folds and physico-chemical and microbiological parameters of large proportion of the water sources have been altered due to anthropogenic activities. Physico-chemical parameters are influenced by both geogenic and anthropogenic agents. Hardness of water is one of them. Hardness is an essential parameter for drinking water from both aesthetic and quality aspects. A common source of natural pollutants in groundwater is the dissolution of minerals in some aquifers under certain physical conditions. Water having very high amount of minerals is reported to be detrimental to human health. Several epidemiological investigations have demonstrated the relation between hardness of drinking water and risk for cardiovascular disease, cancer, growth retardation, reproductive failure, and other health problems. It is therefore requisite to assess drinking water quality parameters at regular interval for preventing diseases and improving quality of life. This review is an attempt to explore the causes and effects of its constituents (calcium and magnesium) on humans and animals.

Key words: Hardness, calcium, magnesium, cardiovascular, drinking water, health

INTRODUCTION

Water quality assessment is of vital concern as it is directly linked to human welfare and the definition of water quality depends on the desired use of water (Kirda 1997, Jain et al. 2009). Consumption of deteriorating water quality affects livelihoods at risk (Leelavathi et al. 2016). Groundwater quality is affected by both geogenic and anthropogenic agents (Sheikhy et al. 2014). About 70% of Earth's surface is covered by water of which 97.5% is salty and 2.5% is freshwater. Less than 1% of this 2.5% amount of freshwater is accessible (Mishra and Dubey 2015). Groundwater accounts for about 98% of global freshwater on the Earth (Kibona et al. 2009, Cassardo and Jones 2011, Lui et al. 2011) which is used by approximately 2.5 billion people worldwide for their daily needs (Margat 2008, Margat and van der Gun 2013). Total global population is reported to be 7.6 billion, out of which 1.1 billion people in the world, or 15 % of the global population lack access to safe drinking water (Sobsey 2006). Chemical characteristics of the groundwater are influenced by rock-water interactions and several anthropogenic factors (Alfy et al. 2017). A common source of natural pollutants in groundwater is the dissolution of minerals in some aquifers under certain pH and redox conditions (Rasool et al. 2015, Singh and Mukherjee 2015). The dominant factors in controlling the groundwater hydro geochemistry are chiefly evaporation

and weathering (Ghalib 2017). Furthermore, increased use of chemical fertilizers to improve agricultural yields enhanced groundwater pollution (Bouzourra et al. 2015, Milhome et al. 2015, El Alfy and Faraj 2016).

One of the major causes of health issues in the developing countries is largely due to lack of safe drinking water (Cairncross and Valdmani 2006). Due to expansion in human population, intensive industrialization, excessive use of fertilizers in the agriculture and other human activity water is highly polluted with harmful contaminants (Patil et al. 2012, Nag and Lahiri 2012). The groundwater is reported to be comparatively clean and free from pollutants than surface water but prolonged discharge of industrial effluents such as glass and porcelain industries, enamel industries, steel industries, domestic sewage and solid waste dump caused groundwater pollution and raised human health issues (Raja et al. 2002). Those water sources that do not conform the national standard result in human health problem in long time exposure (Alemu et al. 2015). It is necessary that the quality of drinking water should be checked at regular time interval because due to use of contaminated drinking water, human population suffers from varied water borne diseases (cholera, typhoid, diarrhea etc.).

Water is essential for life. But water having very high degrees of hardness is reported to be harmful to human health (Ramya

et al. 2015). Hardness is the property of water which prevents lather formation with soap and increases the boiling point of water (Khan and Khan 1985). Total hardness is one of the most important properties of drinking water. It is a measure of the quantity of divalent ions (salts with two positive charges) such as calcium (Ca), magnesium (Mg) and/or iron (Fe) in water. These ions enter in water supply by leaching and dissolution of minerals from rocks and soil. Calcium contributes to the hardness of water within the bicarbonate (HCO_3^-) forming temporal carbonate hardness while sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-) forming permanent or non-carbonate hardness (Twort and Dickson 1994). Water with higher hardness is considered to be unsuitable for domestic and industrial purposes (Sarath et al. 2012, Gopinath et al. 2015).

as compared to surface water makes it a preferred choice for many purposes (Rajanka et al. 2009). Chemical composition of water depends to a great extent on the chemical composition of geological substrata. The principal processes that influence the quality of water in an aquifer are physical, geochemical, hydrogeochemical and biochemical. The quality of groundwater depends on the source, the degree to which it has been evaporated, the composition of recharge water, the interaction between the water and the soil, the soil-gas, the rock with which it comes into contact in the unsaturated zone, and the residence time and reactions that take place within the aquifer (Caj and Postma 2005). It has been reported that chemical characteristics of the groundwater are majorly influenced by rock-water interactions (dissolution/precipitation, ion exchange processes, oxidation, and reduction) and

Table 1. Carbonated and non-carbonated hardness

Compounds responsible for carbonated hardness	References
Calcium carbonate (CaCO_3)	Amor et al. 2004, Ahnet al. 2018
Magnesium carbonate (MgCO_3)	Sengupta 2013, Ahnet al. 2018
Calcium hydroxide [$\text{Ca}(\text{OH})_2$]	Kabayet al. 2002, Gunten 2003
Magnesium hydroxide [$\text{Mg}(\text{OH})_2$]	Entezari&Tahmasbi 2009, Sengupta 2013
Calcium bicarbonate [$\text{Ca}(\text{HCO}_3)_2$]	Kabayet al. 2002, Amor et al. 2004
Magnesium bicarbonate [$\text{Mg}(\text{HCO}_3)_2$]	Entezari&Tahmasbi 2009, Gumashtaet al. 2012
Compounds responsible for non-carbonated hardness	References
Calcium chloride (CaCl_2)	Kabayet al. 2002, Sengupta 2013
Magnesium chloride (MgCl_2)	Sengupta 2013, Ahnet al. 2018
Calcium sulfate (CaSO_4)	Gumashtaet al. 2012, Ahnet al. 2018
Magnesium sulfate (MgSO_4)	Kabayet al. 2002, Sengupta 2013

Table 2. Classification of water hardness (WHO 1996, APHA 2012)

Hardness	CaCO_3 (mg/L)
Soft	0-75
Medium hard	75-150
Hard	150-300
Very hard	300-500
Need treatment	500 and above

Earlier researchers have reported various chemical compounds to cause carbonated hardness and non-carbonated hardness (Table 1).

Causes of hardness in water

The principal natural source of hardness in water are dissolved polyvalent metallic ions from sedimentary rocks, seepage and runoff from soils (WHO 2010). The presence of dissolved minerals coupled with special characteristics of groundwater

anthropogenic factors (Freeze and Cherry 1979, Matthes 1982, Kumar et al.2006, Liu et al. 2008, Zhu and Schwartz 2011, Rajesh et al. 2012, Alfy et al. 2017).

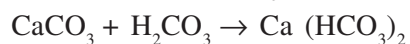
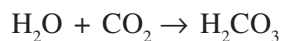
The most common source responsible for hardness in water are calcium-containing limestone (CaCO_3) and magnesium-containing dolomite ($\text{CaMg}(\text{CO}_3)_2$). Therefore, groundwater obtained from deep tube wells usually has a greater hardness than does surface water (Prepas et al. 2001, Khound et al. 2012, Ahn et al. 2018).

Elementary calcium reacts with water at room temperature, according to the following reaction mechanism:

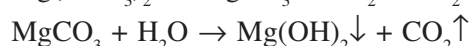


This reaction forms calcium hydroxide that dissolves in water as a soda (NaHCO_3), and hydrogen gas. Other important calcium reaction mechanisms are erosion reactions which usually occur when carbon dioxide is present. Under normal conditions calcium carbonate is water insoluble. In the

presence of carbon dioxide carbonic acid (H_2CO_3) is formed, affecting calcium compounds. The reaction mechanism for carbon weathering is



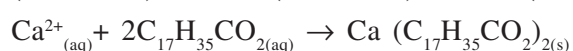
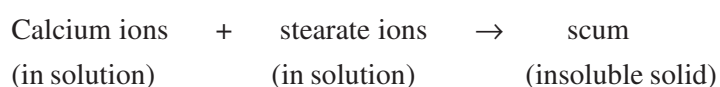
Hardness, a physico-chemical property of water, is a measure of calcium (Ca) and magnesium (Mg) ions in water. However, hardness can be caused by several other dissolved metals, those forms divalent or multivalent cations including aluminum (Al), barium (Ba), strontium (Sr), iron (Fe), zinc (Zn), and manganese (Mn). However, they are generally present in very low concentrations (Sengupta 2013). The types of anion present in these salts distinguish between two types of hardness i.e carbonate hardness and non-carbonate hardness. Carbonate hardness is known as temporary hardness because it can be removed by boiling of water to expel the CO_2 , as indicated by the following equations:



Whereas non-carbonate hardness cannot be broken down by boiling the water as it contains either calcium or magnesium sulfates ($CaSO_4$ or $MgSO_4$) as well as other salts that are not precipitated by boiling, known as permanent hardness. Permanent hard water may only be softened by the use of chemical softeners (Skipton and Dvorak 2014). Hardness is expressed in terms of equivalent quantity of $CaCO_3$. The water containing excess hardness is not desirable for domestic purpose as it forms scales on water heater and utensils when used for cooking and consume more soap during washing of clothes (Gupta et al. 2009, Ranjeeta et al. 2011). Lime scale is insoluble calcium carbonate that precipitated during thermal decomposition of calcium bicarbonate $Ca(HCO_3)_2$ as:



Hard water containing calcium (Ca) or magnesium (Mg) ions react with the sodium stearate (soap). The soluble calcium and magnesium ions combine with stearate ions in the soap to form insoluble calcium and magnesium stearates. These compounds are the insoluble scum that floats on the water, for example, with calcium ions (Brown 1997, Itsadanont et al. 2014).



Ions in water combine with soap to form insoluble precipitates, prevents lather formation during washing clothes can therefore be used to estimate the hardness of water.

Significance of calcium and magnesium in water

Water calcium and magnesium result from decomposition of calcium and magnesium aluminosilicates and, at higher concentrations, from dissolution of limestone ($CaCO_3$), magnesium limestone ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and other minerals. The acceptable limits of Ca^{2+} and Mg^{2+} in water for domestic use are 75 and 30 mg/L respectively (BIS 2012). In case of non-availability of alternate source of water, Ca^{2+} & Mg^{2+} limit can be extended upto 200 and 100 mg/L. The readily observable adverse effect of magnesium in drinking water is the laxative effect, particularly with magnesium sulphate at concentrations above 700 mg/L (Arabi et al. 2013).

The ratio of calcium and magnesium in water is also a crucial factor to cause several hard water related health problems. The reduction in Mg: Ca ratio is associated with increasing risk for mortality from ischemic heart disease (IHD) and acute myocardial infarction (AMI) (Itokawa 1991, Rubenowitz et

Table 3. Drinking water quality standards for hardness (mg/L)

Parameters	BIS (2012)		WHO (1996)
	Acceptable limit	Permissible limit in the absence of alternate source	
Total hardness	200	600	100
Calcium	75	200	75
Magnesium	30	100	50

al. 1996) while the increase in Mg : Ca ratio is associated with increasing risk for gastric cancer (Sakamoto et al. 1997). Durlach's recommended that the Mg to Ca total intake ratio should be 1 to 2 (Durlach 1989) as required for the best Mg absorption.

Human health issues of excess hardness in water

Although hard water pose serious problem in industrial settings and hardness is monitored to avoid breakdown in expensive equipment, hard water is generally said to be not harmful to health. According to World Health Organization "there does not appear to be any convincing evidence that water hardness causes adverse health effects in humans" (WHO 2003). Water hardness has no known adverse effects, however, some studies indicates its correlation with heart diseases (Schroeder 1960, Park and Park 1980). Hardness is also reported to cause Urolithiasis (urinary stone formation) (Chari and Lavanya 1994).

According to BIS acceptable limit of total hardness i.e. 200 mg/L and permissible limit in the absence of alternate source is 600 mg/L. Hardness of 150- 300 mg/L and above is reported

Table 4. Earlier studies of various human health issues associated with hardness

S.No	Study	Conclusion	Author
1	Potential health impacts of hard water	Hardness influenced cardiovascular mortality, growth retardation, reproductive failure	Sengupta 2013
2	Effect of water hardness on non-communicable diseases, including chronic kidney disease of multifactorial origin (CKDmfo/CKDuo)	Consumption of hard water associated with chronic dehydration with urinary stones	Wimalawansa 2016
3	Urolithiasis, urinary cancer, and home drinking water source in the United States territory of Guam, 2006–2010	Deep well water having high calcium carbonate may be at increased risk for urolithiasis as compared to surface water	Haddock et al. 2016
4	Hydrogeochemistry and groundwater quality of Singhari river basin, district Chatarpur (M.P)	High hardness in water may cause kidney stone and heart diseases in human	Jain 1996
5	Domestic water hardness and prevalence of atopic eczema in Castellon (Spain) school children.	correlated domestic hard water usage with increased eczema in children	Amedo-Pena 2007

Table 5. Earlier studies of animal health issues associated with hardness

S. No	Study	Conclusion	Author
1	Water quality management in aquaculture, In: Course Manual of summer school on development of sustainable aquaculture technology in fresh and saline waters, CCS Haryana Agricultural, Hisar (India)	hardness values less than 20ppm causes stress, 75-150ppm is optimum for fish culture and >300ppm is lethal to fish life as it increases pH, resulting in non-availability of nutrients.	Bhatnagar et al. 2004
2	Effect of water hardness on egg hatchability and larval viability of Angelfish (<i>Pterophyllum scalare</i> (Schultze 1823)	too soft water (10 mg/L CaCO ₃) and too hard water (300 mg/L CaCO ₃) are not suitable for <i>Pterophyllum scalare</i> incubation and larval rearing	Kasiri et al. 2011
3	Low water hardness and pH affect growth and survival of silver catfish juveniles	Juveniles kept at zero water hardness presented higher mortality at pH 7.0 and 8.0 than those submitted to other treatments	Copatti et al. 2011
4	Effects of water hardness and Cu and Zn on LC ₅₀ in <i>Gambusia holbrooki</i>	Water hardness had a much smaller effect upon the acute toxicity of Cu than that of Zn.	Pourkhabbaz et al. 2011
5	Effects of total hardness and Ca: Mg ratio of water during early stages of rare Minnows (<i>Gobio cyprisrurus</i>)	an imbalance between Ca ²⁺ and Mg ²⁺ in water is toxic to <i>Gobio cyprisrurus</i>	Luo et al. 2016

to cause kidney problems and kidney stone formation (Jain 1998). However, there is no guideline value for total hardness in drinking water from World Health Organization (WHO 2003).

Effect of hardness on cardiovascular system

Water hardness and human health issues were surfaced in the late 1950's. The relationship between water hardness and

the incidence of vascular diseases was first described by a Japanese chemist Kobayashi (Kobayashi 1957) as he concluded, based on epidemiological analysis, higher mortality rates from cerebrovascular diseases (stroke) in the areas of Japanese rivers with more acid (i.e. softer) water compared to those with more alkaline (i.e. harder) water used for drinking purposes.

Table 6. Human health aspects of calcium and magnesium

Parameter	Calcium	Reference	Magnesium	Reference
Significance	Essential for bone and teeth, reducing the risk for preterm birth and low birth weight	Yang et al. 1996, 2002	Essential for metabolism, cell permeability, bone	Ebel and Gunther 1980, Lipkin and Newmark 1985, Furihata et al. 1989, Nishikawa et al. 1992
Deficiency	Increased risks of osteoporosis, nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity	Kohri et al., 1989, 1993, Chari and Lavanya 1994, Floyd 2004	risk of motor neuron disease, hypomagnesaemia	Mildred 1989, Altura and Altura 1991, Iwami et al. 1994, Nadler and Rude 1995
Toxicity	Calcium can interact with iron, zinc, magnesium, and phosphorus within the intestine, thereby reducing the absorption, Hypercalcemia	Sengupta 2013	Hyper magnesemia, renal insufficiency associated with a significantly decreased ability to excrete magnesium, diarrhea, laxative effect	Swaminathan 1998, Chandra et al. 2013

The effect of hardness of water on human health is still controversial (Crawford and Crawford 1967, Heyden 1976, Hall and Jungner 1993). Some studies concluded that the higher the hardness of water, the lower the incidence of cardiovascular diseases (CVD) (Malpas et al. 1973, Masironi et al. 1979, Leoni et al. 1985) but many other studies do not corroborate this finding (Mackinnon and Taylor 1980, Morris et al. 2008). Schroeder (1960) demonstrated correlation between mortality from CVD in males aged 45-64 years and water hardness in 163 large cities of the USA.

Crawford et al. (1971) studied variations in mortality from CVD depending on water hardness

in 11 British cities between 1950 and 1960 and found hardness in water increased in five cities and decreased in six cities. Water hardness exhibited protective effect against CVD (Yang et al, 1996). In Asia, several studies have suggested an inverse association between water hardness or magnesium and CVD mortality. A low dietary magnesium intake was associated with a higher risk of coronary artery disease in north India (Singh et al. 1996). Inverse association between magnesium levels in drinking water with mortality due to CHD in the age group of 15-64 years in 12 South African districts has also been reported (Anne 2011). Human population studies exhibit that populations with less than 3-6ppm magnesium drinking water have very high rates of mortality from heart disease, and that rate goes down as the magnesium

concentration of their water goes up, the higher the better (Calderon et al. 2009).

Effect of hardness on the development of cancer diseases

Several epidemiological studies were carried out in the late 1990's in Taiwan to focus on relationships between drinking water hardness and mortality from various diseases showing significant geographical variation. Water hardness showed protective effect against cancer of oesophagus (Yang et al. 1999c), pancreas (Yang et al. 1999d), rectum (Yang et al. 1999e) and breast (Yang et al. 2000).

Hardness in drinking water has also been suspected to be associated with stomach cancer (Turner 1962, Malnasi et al. 1976, Zemla 1980). Animal studies indicate that salt-induced damage to the gastric mucosa might be inhibited by increased intake of calcium (Lipkin and Newmark 1985, Furihata et al. 1989, Nishikawa et al. 1992). Yang et al. (1998) studied possible association between the risk of esophageal cancer and hardness levels in drinking water from municipal supplies in Taiwan and reported 42% excess risk of mortality from esophageal cancer in relation to the use of soft water. Magnesium may protect against deaths from cancer (Durlach et al. 1986, Van Rensburg et al. 1986). However, in a more recent study, it was found that magnesium did not show any protective effect on the risk of esophageal cancer (Hashemian et al. 2015). Calcium in drinking water protects against

colorectal cancer (Yang et al. 1997) and gastric cancer (Yang et al. 1998). However, an increased risk of esophageal cancer has been attributed to diets high in calcium (Graham et al. 1990, Chen et al. 1992, Rogers et al. 1993). Magnesium is reported to have protective effect against cerebrovascular diseases (Yang 1998) and hypertension (Yang et al. 1999b).

Effect of hardness on urinary system

Urolithiasis is a process of urinary stone formation involving multiple factors, i.e. not only intake of water, liquids, but also genetic predisposition, eating habits, climatic and social conditions, gender etc. Several studies reported that higher water hardness is associated with higher risk of urolithiasis. However in contrast, more studies found softer water to be associated with higher risk for urolithiasis.

Some study reported lower Mg to Ca ratio to be associated with a higher risk for urolithiasis regardless of type and incidence of urolithiasis to correlate with the type of geological subsoil (Kohri et al. 1989) and another study found correlation between the higher Mg to Ca ratio and higher incidence of infectious phosphate urolithiasis (Kohri et al. 1993).

Effect of hardness on prevalence of dermatitis problem

Among several other environmental factors, water hardness has been suggested as a risk factor for childhood eczema (Flohrs et al. 2014). Eczema (atopic dermatitis) is a chronic inflammatory skin disease currently affecting 15–30% of children characterized by a persistent itching (Bieber 2008). Around 60% of eczema cases begin within the first year of life and 85% before 5 year of age (Bieber 2008). Exposure to hard water has been suggested as a risk factor for eczema in childhood. Earlier studies found a positive association between residential water hardness and prevalence of eczema disease among school aged children of specific aged groups (McNally et al. 1998, Miyake et al. 2004, Arnedo-Pena et al. 2007, Chaumont et al. 2012). However, a randomized control trial of installation of a water softener at home failed to show an improvement in eczema severity in children 0–16 year of age (Thomas et al. 2011). Font-Riberia et al. (2015) carried out a study on prevalence of eczema due to exposure to hard water in childhood. However, no association was detected between water hardness at home and current or ever eczema at 1 and 4 year of age. The Japanese study conducted among children aged 6–12 year aged group found a positive association among the oldest but not among the youngest children (Miyake et al. 2004).

Effect of hardness on Fisheries

Water hardness is reported to be very important for fish culture and is commonly reported as an important aspect of water quality. Calcium and magnesium are reported to be essential in the metabolic processes of fish (bone and scale

formation, blood clotting and other metabolic reactions). Fish can absorb calcium and magnesium directly from the water or from food (Wurts and Durborow 1992). Different species of fish have varied water hardness requirements. For most pond fish species, i.e. koi and goldfish, moderate to hard water is best. Water hardness affects fish health as it influences the process of osmo-regulation. Being open systems, fish is reported to be affected by the makeup of the surrounding water. As a consequence of osmosis, freshwater fish are subject to encounter a continuous influx of water, while marine fish have to live with a continuous outflow of water (Frank 2017). Hardness is reported to reduce the toxicity of various metals to fish and other aquatic life through competitive inhibition of metal binding to gill surfaces by Ca^{2+} (Hollis et al. 1997).

Because water chemistry is a major driver of aquatic invertebrate, species presence, health, and community composition, drastic changes in the ionic composition of water are of concern. New (2002) recommended an ideal total hardness range of 50 to 150 mg/L CaCO_3 to be suitable for nursery and grow-out facilities for *M. rosenbergii*, while Vasquez et al. (1989) found 20 to 200 mg/L to be optimal. Very high water hardness often results in encrustation with *Bryozoa sp.* and *Epistylis sp.* which retard growth rate. However, earlier study of Bartlett & Enkerlin (1983) postulated that high calcium levels may not be detrimental unless combined with high carbonate levels. Adhikari et al. (2007) investigated the effect of calcium hardness levels from 92 to 384 mg/L CaCO_3 for 42 days on the performance of *M. rosenbergii* juveniles (0.045 ± 0.007 g, 25 days old), found that the maximum survival rate (100%) was observed at a level of 92 mg/L CaCO_3 . The lowest survival (60%) was at the highest calcium hardness level (384 mg/L). An extreme, concomitant increase in water hardness and alkalinity resulting in CaCO_3 precipitation was >98% lethal to *D. magna*, yet also that <10% mortality occurred in the same alkalinity water if hardness was reduced (Bogart et al. 2016).

Effect of hardness on animals

The hardness of water has no effect on animal performance or water intake (Looper and Waldner 2002). Water intake of cattle and milk production were unaffected by water containing up to 290ppm of hardness (NRC 1974). There is very limited research on the impact of hardness, all of which indicate no effect on milk production, weight gain, or water consumption (Graf and Holdaway 1952, Blosser and Soni 1957, Allen et al. 1958).

Effect of hardness on poultry

The response to water hardness increase varies from species to species. Too soft water (10 mg/L CaCO_3) and too hard water (300 mg/L CaCO_3) are not suitable for *Pterophyllum*

scalare incubation and larval rearing (Kasiri et al. 2011). Calcium is necessary for the development and survival of rainbow shark minnow eggs. Calcium, although necessary, was found to have a detrimental effect at higher concentrations due to its increasing osmotic concentration of the incubation water which directly affected the swelling of the eggs, reducing larval survival (Abernathy 2004).

Irrigational effect of water hardness on plant metabolism

The use of saline irrigation water poses adverse effect on soil–water–plant relations, occasionally severely affecting normal physiological activity and productive capacity of the crops (Pascale et al. 2013, Plaut et al. 2013). Irrigation water containing a high proportion of soluble calcium may form scale inside the irrigation component (Haman 1990) and form scale like deposits on plant parts when overhead sprinkler irrigation system is used (Haman and Yeager 2000). Magnesium is an important element in the groundwater which may reduce crop yield by inducing Ca deficiency at high concentration of Mg (Ayers and Westcot 1985). If the soil water salt concentration is too high, the plant will not be able to absorb water. It will wilt and begin to die. The point at which this happens depends on the type of species; some crops are more tolerant to salts than others. Saeed et al. (2015) reported utilization of grey (soap) water is beneficial for the cultivation of medicinal plant (*Sesbania grandiflora* L.) under scarcity of freshwater irrigation. Soap water is a source of compounds like, surfactants, soaps, oils, boron and other salts (sodium) which can alter the soil and plant characters (Travis et al. 2008, Wiel-Shafran et al. 2006).

Effect of water hardness on soil microbiology

The microbial communities of the soil perform an ecological role in biogeochemical cycling of nutrients, in the volume of organic matter in the soil and in maintaining plant productivity. Thus it is important to understand the microbial response to environmental stress, such as water content of soil, high concentrations of heavy metals of salts. Stress can be detrimental for sensitive microorganisms and decrease the activity of surviving cells, due to the metabolic load imposed by the need for stress tolerance mechanisms (Schimel et al. 2007, Yuan et al. 2007, Ibekwe et al. 2010, Chowdhury 2011). The excessive amounts of salts provided by irrigation waters can have adverse effects on the chemical and physical properties of the soils and on their biological processes (Garcia & Hernandez 1996, Rietz & Haynes 2003, Tejada & Gonzalez 2005). These effects include mineralization of the carbon and nitrogen and enzymatic activity, which are crucial for the decomposition of organic matter and liberation of the nutrients necessary for sustainability of the production (Azam and Ifzal

2006, Wong et al. 2008). The agricultural practices influence the microbial population, thus altering the activity, source and persistence of the enzymes in the soil (Parham et al. 2003). Vincent (1962) studied effect of calcium and magnesium on the growth of *Rhizobium trijoli* and reported that deficiency of calcium (Ca), in the presence of sufficient magnesium (Mg), caused reduction in growth rate, the level of maximum growth and the proportion of viable cells. On the other hand, although shortage of Mg (Ca sufficient) was without effect on growth rate down to the lowest concentration at which growth occurred, maximum growth and the proportion of viable organisms were markedly decreased.

Cytotoxicity of aluminum (Al) has been earlier reported in plants (Delhaize and Ryan 1995, Horst et al. 1999, Kollmeier et al. 2000, Marienfeld et al. 2000, Teresa 2001). It is generally known that plants grown in acid soils due to Al solubility at low pH have reduced root systems and exhibit a variety of nutrient-deficiency symptoms, with a consequent decrease in yield. With respect to growth determinants (auxin, gibberelic acid and ethylene), aluminum (Al) apparently interacts directly and/or indirectly with the factors that influence organization of the cytoskeleton, such as cytosolic levels of Ca²⁺ (Jones et al. 1998), Mg²⁺ and calmodulin (Grabski et al. 1998), cell-surface electrical potential (Takabatake & Shimmen 1997), callose formation (Horst et al. 1997), and lipid composition of the plasma membrane (Zhang et al. 1997).

Hardness and metal toxicity

Heavy metals are ubiquitous pollutants and occur in water from natural sources as well. Several important factors are known to make heavy metals biologically less active and therefore less toxic. Heavy metals are more toxic in the soft water than in hard water because they are more soluble in soft water and it is known that the dissolved forms of heavy metals are the active toxic agents. Spear and Pierce (1979) discussed the lethal levels of copper for fish, as determined by several investigators, and find that Cu toxicity decreased with an increase in water hardness. Brown (1968) found a correlation between total hardness of water and 48 hr LC₅₀ of rainbow trout for nickel, lead, zinc, cadmium and copper. Hardness is also reported to lowers the toxicity of some heavy metals (Pb, Cd, Cr, Zn) (Taylor et al. 2000).

Correlation between hardness and occurrence of diseases

The correlation helps in the study of existence and magnitude of the direction of the relation between two or more variables. The role of water hardness as a risk factor for cardiovascular disease has been widely investigated and evaluated in cardiovascular disease. Nerbrand et al. (2003) reported that individuals living in soft and hard water areas showed

significant correlations between the content of calcium in water and major cardiovascular risk factors. Various researchers have reported positive correlations between water and dietary magnesium and calcium and blood pressure (Kesteloot 1985, Kesteloot and Joossens 1988). In Finland and South Africa it was reported that the incidence of death ascribed to ischaemic heart disease is inversely correlated with the concentration of magnesium in drinking water (Luoma et al. 1983, Leary et al. 1983). Landin (1989) reported that magnesium levels in the skeletal muscle were significantly higher in persons living in an area with higher water magnesium. Maheswaran et al. (1999) reported an association between magnesium and cardiovascular mortality in a study of magnesium in drinking water supplies and mortality from acute myocardial infarction in north-west England. Nerbrand et al. (2003) found negative correlations between calcium in water and s-cholesterol and s-LDL indicated that a high content of calcium could lower the levels of s-cholesterol and s-LDL but on the other hand may increase systolic blood pressure (SBP). A recent study on cancer mortality found a significant negative relationship between drinking water hardness and gastric, pancreatic, and colorectal cancer mortality (Yang et al. 1997, 1999a, b, Yang and Hung 1998).

Hard water can cause some chemicals to precipitate. Chemicals that tend to do this often have agents added to overcome this problem. Hard water can also affect the balance of the surfactant system and affect properties such as wetting, emulsification and dispersion. Chemicals with amine formulations, which include the herbicides: glyphosate, 2, 4-D amine, MCPA amine and dicamba are adversely affected by hard water. The solubility of the herbicide is reduced which leads to it being less absorbed by the weeds (McDougall 2012). Increasing carrier water hardness from 0 to 1,000 mg L⁻¹ reduced mesotrione efficacy 28, 18, and 18% (or greater) on giant ragweed, horseweed, and *Palmer amaranth*, respectively (Devkota et al. 2016).

Impact of hardness on other water quality parameters

Hardness is often confused with salinity or TDS, but the two are not necessarily related meaningfully. For example, high saline water may contain an abundance of Na salts of chloride and sulfate and yet be quite soft if relatively low concentrations of Mg and Ca are present. Hardness is a chemical parameter of water that represents the total concentration of calcium and magnesium ions. Calcium typically represents 2/3 of total hardness, Mg typically about 1/3. It is commonly confused with alkalinity. The confusion relates to the term used to report both measures, mg/L CaCO₃. If limestone is primary source of both hardness and alkalinity, the concentrations will be similar if not identical. However, where sodium bicarbonate (NaHCO₃) is responsible for high alkalinity it is possible to

have low hardness and low calcium. The carbonate fraction of hardness (expressed as CaCO₃ equivalents) is chemically equivalent to the bicarbonates of alkalinity present in water (Burton and Pitt 2002) in areas where the water interacts with limestone (Timmons et al. 2002). Any hardness greater than alkalinity represents non-carbonate hardness. Hard water is naturally likely to also have a high pH because it is also high in carbonates that buffer the pH toward the alkaline side (due to carbonate hardness).

Remedial technologies

Hardness in water is an aesthetic and health concern because of the unpleasant taste. It is reported to cause scale formations in pipes and applied distribution system (BCC 2007). The most common method for hardness removal at household level in the drinking water is boiling. However, there are various methods for removal of calcium and magnesium hardness from groundwater such as reverse osmosis, ion exchange, combination of ultrasound and ion exchange and chemical treatment with lime-soda ash method.

Water softening: Water softening uses an ion exchange process. The ion exchange process is one of the most effective methods to remove hardness in the groundwater (Entezari and Tahmasbi 2009, Entezari and Tahmasbi 2011). An ion exchange water softener replaces calcium and magnesium ions with sodium or, less commonly, potassium ions. Pentawma et al. (2011) studied removal of hardness from groundwater by synthetic resin from waste polystyrene plastics. The results revealed that the hardness removal efficiency of added made resins in the system was higher than no added resin (43% vs. 12%).

Membrane separation: Because hardness ions are larger, a coarser, less expensive, membrane can be used. This membrane is known as a nanofiltration membrane. The nanofiltration can also be used for hardness removal from groundwater. It is an effective process in term of higher recovery for hardness removal (Schaep et al. 1998). Presently, nanotechnology such as zero valent iron and carbon nano tube is a new and promising technology for groundwater remediation for drinking and reuse. Nano-remediation has emerged to have the potential to clean up large contaminate site and reducing the contaminant concentration to near zero (Rajan 2011). Reverse osmosis (RO) is one of the most popular membrane processes.

Bioremediation: Algae based remediation technology can provide an excellent solution for water hardness quality problems. Many micro and macro algae are being used in various bioremediation techniques especially in polluted hard waters. Sivasubramanian et al. (2012) studied application of algal technology (Phycoremediation) to reduce total hardness

in waste waters and industrial effluents. Worku and Sahu (2014) reported that by using micro algae (*Synechocystis salina*) almost 60% Cr, 66% Fe, 70% Ni, 77% Hg, 65% Ca²⁺, 63% Mg²⁺ and 78% of total hardness was reduced in 15 days of treatment.

CONCLUSION

Hard water is unsuitable for drinking, recreation, agriculture, and industry. It diminishes the aesthetic quality of water resources. The effects of water pollution are not only devastating to people, but also affect animals, fish, and birds; also destroy aquatic life and reduce their reproductive ability. It affects the ecosystem services thereby affecting the overall set up of an ecosystem. Hard water in the municipal water supply also raises economic issues as a considerable amount of money is spent yearly to ensure that water is softened to avoid its negative impacts such as degrading soaps and precipitate deposition on faucets. Eventually, it is a hazard to human health. Higher Mg and Ca levels in water are mostly associated with higher levels of the other dissolved solids that may not be beneficial to health. Individuals living in soft and hard water areas showed significant correlations between the content of calcium in water and major cardiovascular risk factors. However, the use of softened drinking water in the households has several positive effects such as reduced consumption of energy and laundry detergents and prolonged service lives of household appliance. Hard water lowers the toxicity of heavy metals also. Heavy metals are more toxic in soft water than in hard water as dissolved forms of heavy metals are the active toxic agents. Although hardness affects taste of water, magnesium and calcium are having some protective effect on cardiovascular mortality and other diseases as reported by many researchers. When hardness of drinking water went up, the rate of death from cardiovascular disease went down. Although a certain minimum quantity of these elements is desirable, it definitely does not mean the more the better. Thus, regular monitoring of the status of water resources and development of low cost technology for rural population of India is needed. The quality of our water is directly linked to the quality of our lives. Access to safe, clean water is to access the life.

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