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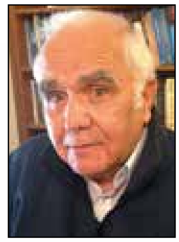
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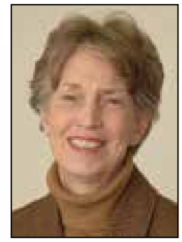
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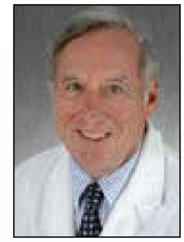
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Magnesium, Hard Water, and Health

The risk relationship between hard water and reduced cardiovascular disease is well known, but it's the magnesium portion of the hardness that accounts for most of the beneficial effect. Magnesium is important in hundreds of biochemical processes, and adult daily requirements are approximately 300–350 mg/day. Most Americans consume less than the optimal daily amount of magnesium recommended for good health. Although diet is the major source of magnesium, drinking water can be an important contributor, and the uptake of magnesium from drinking water is more efficient than from most dietary components except milk/dairy. Dairy intake tends to decline with age, so even a small (~10 mg/L) consistent lifetime contribution from water can be an important supplement as we age. Bottled waters and naturally soft and softened waters tend to have little or no magnesium.

WATER AND MAGNESIUM CONSUMPTION

Approximately half of the US population has been shown to consume less than the daily requirement of magnesium from foods (USDA & HHS 2015). The 2015 Dietary Guidelines Advisory Committee considered magnesium to be a shortfall nutrient that was under-consumed relative to the estimated average requirement (EAR) for many Americans. Magnesium deficiency and hypomagnesemia manifest in numerous disorders and diseases. Although diet is the primary source of intake, drinking water can be a lifetime contributor of supplemental magnesium to one's total daily intake depending on the source water composition and the treatment it has received.

Natural water can contain high or low concentrations of dissolved salts. Rain water has minimal salts content, but most surface waters and groundwaters accumulate salts by extraction from the geology they contact. Conventional water treatment should not significantly affect many salts and magnesium and calcium content; however, softening and ion exchange technologies can remove multivalent cations such as magnesium and calcium, while desalination technology can treat water to remove virtually all salts.

Hard water. The term "hard water" refers to water that has high mineral content—mainly calcium and magnesium—but in some cases barium, copper, lead, zinc, cadmium, iron, and radium can also be contributors to total hardness. Hard water is probably the most common and noticeable water quality problem in the United States, where perhaps 80–85% of the United States has hard water, as defined in Table 1 (McGowan & Harrison 2000).

Hardness at elevated levels is not known to cause any adverse human health concerns, except perhaps eczema resulting from incomplete rinsing, but it can have aesthetic and economic consequences. Hard water forms precipitates of insoluble metal carbonates when heated, and these scale deposits can clog pipes and reduce the heat transfer capability in cooling systems. When combined with soap, lathering and rinsing become difficult, commonly resulting in a "bathtub ring" where deposits accumulate. Detergents for clothes washing, dishwashing, and shampoos are formulated for specific purposes and are much less affected by hard water.

Quality of water in domestic wells. Table 2 summarizes pertinent data from the US Geological Survey's National Water-Quality Assessment Program 1991–2004 study of water from domestic wells (De Simone 2009). The raw water in domestic wells is not necessarily the same as in nearby municipal wells. The data illustrate the prevalence of hard water, alkalinity, magnesium, and calcium, and demonstrate the greater amounts of calcium compared with magnesium in typical groundwater.

Calcium and magnesium are commonly present in water as soluble bicarbonates in equilibrium with carbonate, carbon dioxide, and water. Bicarbonates predominate in the pH range of about 6 to 10. Higher pH or heat cause loss of carbon dioxide and conversion of the bicarbonate to carbonate. Calcium bicarbonate is soluble at 165 g/L at 25°C (77°F), but calcium carbonate solubility is only 0.013 g/L; at this temperature, magnesium bicarbonate solubility is 0.77 g/L, and magnesium carbonate solubility is 0.139 g/L. Carbonates will precipitate when conditions favor their presence, and magnesium will be present in significantly lower levels than calcium in hard water.

TABLE 1 Water hardness measured as calcium hardness of $CaCO_3$ equivalent

Water Hardness	Calcium Hardness *mg/L* $CaCO_3$
Soft	<17
Slightly hard	17–60
Moderately hard	60–120
Hard	120–180
Very hard	>180

$CaCO_3$—calcium carbonate

The term "grains/gallon" is commonly used in the water softening industry; 17.1 mg/L as calcium carbonate is equivalent to 1 grain/gallon (McGowan & Harrison 2000).

WATER SOFTENING

Water hardness can be overcome by softening, a common practice in homes, drinking water treatment plants, and industrial facilities. Precipitative softening at municipal water plants is commonly achieved using calcium hydroxide and lime–soda ash, and clarification following softening can also remove contaminants such as radium and *Cryptosporidium* oocysts.

Possibly 10 to 15 million home water softeners are in current use, and about one million are installed annually (Regunathan 2017, Wilker 2017). The two most common home water-softening techniques are cation exchange for point of entry and low-pressure reverse osmosis for point of use. Point-of-entry home water softening uses a cation exchange resin that is neutralized with sodium ions. As hard water passes through the resin, calcium and magnesium displace sodium ions from the resin into the water, and the resin retains the calcium and magnesium and other "hard" ions. The resin is periodically regenerated by treating with a concentrated sodium chloride brine solution that goes down the drain. Some communities restrict ion-exchange softeners because of the effect of brine discharge on groundwater.

DIETARY MAGNESIUM, EARs, AND FOOD VERSUS WATER SOURCES

EARs are defined as the average level of daily intake estimated to meet 50% of the requirements of healthy individuals. For magnesium, US levels are 330–350 mg/day for

TABLE 2 Summary statistics for water samples collected from domestic wells 1991–2004

Property/Ion *mg/L*	Samples	Detections	Concentration Percentile				
			10th	25th	Median	75th	90th
Alkalinity/$CaCO_3$	2,033	2,030	32	78	156	241	325
Calcium	2,160	2,160	7.2	20.6	43.0	70.0	95.3
Magnesium	2,160	2,159	1.7	4.4	11.0	23	36
Hardness as $CaCO_3$	2,160	2,160	30.3	76.2	162	267	370

Source: De Simone 2009

$CaCO_3$—calcium carbonate

adult males, 255–265 mg/day for adult females, and 290–335 mg/day during pregnancy (IOM 2014). The efficiency of the uptake of magnesium after ingestion is affected by the chemical form of magnesium in the food, and the presence of other natural chemicals that modulate the uptake of metal ions.

Magnesium is present in fruits, vegetables, whole grains, legumes, nuts, milk, meat, and fish, as well as in some fortified foods such as breakfast cereals (NIH 2016). Dairy foods are a key source of magnesium, contributing 17% of the magnesium in the diet for individuals aged two years and older (USDA & HHS 2015), and dairy and water are among the most efficient uptake sources. Magnesium is chelated as the central atom in chlorophyll, so it is present in all green plants (Rosanoff 2013). Some 75% of leaf magnesium is involved in protein synthesis, and 15–20% of total magnesium is associated with chlorophyll pigments, acting mainly as a co-factor of a series of enzymes involved in photosynthetic carbon fixation and metabolism (Guo et al. 2016).

Magnesium absorption is dose dependent, and following ingestion its levels are curvilinear, reflecting the active saturable process and passive diffusion of magnesium within the small intestine. Net magnesium absorption increases with increasing magnesium intake; however, fractional magnesium absorption falls (Rude 2012). Magnesium absorption varies on the basis of the composition of the diet, which may contain enhancers (lactose, fructose, and glucose) or inhibitors (fiber, free fatty acids, oxalate, phytate, and high levels of zinc) of absorption. Under normal intake, perhaps 30 to 40% of dietary magnesium is absorbed; however, data on absorption fractions from well-controlled balance studies in humans using differing diets have been quite variable, ranging from 35 to 70% (Sabatier et al. 2002).

Magnesium is also present in tap, mineral, and bottled waters at varying concentrations (Quattrini et al. 2016); however, most deionized bottled waters sold in the United States contain little or no magnesium (NIH 2016), and a few have some magnesium and other salts added back for taste.

In a group of 10 healthy women, magnesium from magnesium-rich mineral water, as measured by a stable magnesium isotope study, was found to be highly bioavailable ($52.3 \pm 3.9\%$) when consumed with a light meal compared with $45.7 \pm 4.6\%$ without a meal, a relative difference of 11.0%. These authors concluded that magnesium-rich mineral water could make a valuable contribution to meeting an individual's magnesium requirement (Sabatier et al. 2002).

Dietary supplements. Multiple salts of magnesium are available as dietary supplements including oxide, hydroxide, citrate, chloride, gluconate, lactate, and aspartate. The fractional absorption of a salt depends on its solubility in intestinal fluids as well as transport mechanisms and inhibitors. Small studies have found that magnesium in the aspartate, citrate, lactate, and chloride forms is absorbed more completely and is somewhat more bioavailable than magnesium oxide and magnesium hydroxide.

The diarrhea and laxative effects of magnesium salts are due to the osmotic activity of the unabsorbed salts in the intestine and colon and the stimulation of gastric motility. Magnesium carbonate, chloride, gluconate, and oxide are the forms most reported to cause gastrointestinal effects (NIH 2016). In a study using data from the National Health and Nutrition Examination Survey 2003–2006 (NHANES IV) to assess mineral intakes among adults, average intakes of magnesium from food alone were found to be higher among users of dietary supplements than nonusers. When supplements were included in the average total intakes, men consumed 449 mg/d and women consumed 387 mg/d, placing them in a more favorable intake level above the EAR (NIH 2016). The Institute of Medicine (IOM) upper level of 350 mg for magnesium intake only applies to supplemental use of magnesium for healthy individuals (IOM 1997).

Water consumption and magnesium intake. Good hydration is essential to maintain the body's water equilibrium. Although needs may vary among people because of age, physical activity, personal circumstances, and weather conditions, a minimum daily intake of 1.5 to 2 L of water is advised. Adequate intakes (AIs) for water are defined on the basis of three factors: observed water intakes in population groups, desirable water volumes per energy intake, and desirable osmolality values in urine or plasma (EFSA 2010, Manz et al. 2002, Armstrong et al. 1994). The AI values for water from beverages and foods according to the IOM are 2,700 mL/day for adult women and 3,700 mL/d for adult men. These values were based on median intake estimates among younger adults from NHANES III (CDC 2013).

Data from a national survey showed that water and other beverages contributed 75–84% of dietary water, with 17–25% provided by water in foods, depending on the age group. Plain water, from tap or bottled sources, contributed 30–37% of total dietary water. Overall, 56% of drinking water volume was from tap water, while bottled water provided 44% (Drewnowski et al. 2013).

The composition of tap water can contribute to dietary intake of minerals to some degree. The Nutrient Data Laboratory of the US Department of Agriculture conducted a study of the mineral content of residential tap water. Sodium, potassium, calcium, magnesium, iron, copper, manganese, phosphorus, and zinc content of drinking water were determined in a nationally representative sampling; 144 locations for water collection in winter and spring from home taps were sampled.

Assuming a daily consumption of 1 L of tap water, only four minerals (copper, calcium, magnesium, and sodium) provided more than 1% on average of the US dietary reference intake, showing a mean calcium intake of 3% (range <1–10%) and mean magnesium intake of 2.4% (range <1–14%). There were no significant differences in overall mineral content between municipal and well water. This nationally representative data set of mineral values for drinking water available from home taps provides valuable additional information for assessment of dietary mineral intake (Patterson et al. 2013). These authors concluded that the average content of US drinking water magnesium meets the 10 mg/L magnesium benchmark as suggested by epidemiological research for health benefits (Calderon & Hunter 2009).

HUMAN HEALTH ASPECTS OF MAGNESIUM DEFICIENCY

Magnesium is the fourth most abundant mineral in the body after calcium, potassium, and sodium. Magnesium is essential for numerous biochemical functions, but it is present at much lower levels than calcium, in the diet and in the body. A person typically carries about 1,200 g of calcium with about 99% in teeth and bone as a durable phosphate compound called hydroxyapatite (Rosanoff et al. 2015). On the other hand, magnesium burden is only about 25 g primarily in bone and soft tissues, and the bone magnesium is not readily accessible (Joy et al. 2013, IOM 2004).

Numerous diseases and disorders have been related to inadequate magnesium levels from clinical and epidemiological studies. Magnesium deficiency can cause or exacerbate numerous diseases, including cardiovascular disease, hypertension, and diabetes (Costello et al. 2016).

The kidney manages the urinary reabsorption and excretion of magnesium and maintains systemic levels; at typical daily intake levels, virtually all of the urinary magnesium is reabsorbed (Romani 2013). Alcohol will increase the renal loss of magnesium, and alcoholics can exhibit many of the manifestations of magnesium deficiency. Normal serum levels of magnesium in humans are approximately 1.82–2.33 mg/DL (CDC 2013). Magnesium deficiency and hypomagnesemia are caused by inadequate intake or impaired intestinal absorption of magnesium. Hypomagnesemia can be defined as a magnesium concentration <1.6 meq/L (<1.9 mg/dL)

(Epilepsy Foundation 2017, Agus 1999). It can also be associated with alcoholism, chronic diarrhea, or acid-reducing proton pump inhibitors and use of diuretics (Romani 2013).

Magnesium also functions in interactions involving calcium, sodium, and potassium with an essential role in electrolytic homeostasis. It is necessary for DNA synthesis; maintaining bone mineral density; and protein, carbohydrate, and fat metabolism (Romani 2013). Hundreds of magnesium-dependent enzymes are involved in phosphorylation kinases that transfer a phosphate group to the recipient small organic molecule. Kinases regulate cell-cycle growth and apoptosis (programmed cell death), in which the kinases switch on inactive molecules to functional ones.

WATER EPIDEMIOLOGY STUDIES

A large number of studies have investigated the potential health effects of hardness in drinking water. Most of these have been ecologic studies, which can only provide inferences that may warrant more detailed research. Many found an inverse relationship between water hardness and cardiovascular mortality (higher hardness is associated with lower mortality). Many studies have suggested a benefit of reduced cardiovascular mortality from consumption of hard water; however, it has now been concluded that if there is a benefit, it is associated specifically with the magnesium content rather than hardness per se.

In more detailed analyses, Catling et al. (2005) identified six case-control studies, five of which involved magnesium, and concluded that although not all of them had statistically significant outcomes, all five showed the same inverse trend of lower risk of cardiovascular mortality and magnesium in drinking water, especially at levels greater than 5 mg/L. Calcium in drinking water did not show an association with mortality from cardiovascular disease.

In a recent meta-analysis, the authors reviewed abstracts and titles from 632 published articles; 72 were reviewed in full and 63 were subsequently excluded (Jiang et al. 2016). Nine articles with 10 studies that were mostly European were quantitatively examined. They included seven case-control studies and three cohort studies of acceptable quality investigating calcium or magnesium and cardiovascular disease or mortality with a total of 77,821 cases. These case-control and cohort studies were much more rigorous than ecologic studies. Of the case-control studies, one addressed the association between calcium and acute myocardial infarction, and three evaluated the association with death from cardiovascular disease. One study from Taiwan indicated beneficial effects from calcium in water (Yang et al. 2006).

On the basis of the case-control and cohort studies that were analyzed, the meta-analysis concluded that the drinking water level of magnesium was significantly and inversely associated with coronary heart disease mortality, particularly in the European populations that were studied (Jiang et al. 2016). Although this association does not necessarily demonstrate causality, it is consistent with the well-known effects of magnesium on cardiovascular function. There are mixed results regarding an association between drinking water magnesium and calcium and acute myocardial infarction.

WORLD HEALTH ORGANIZATION (WHO) REVIEW

In November 2003, the WHO held a workshop in Rome, Italy, in which 21 international experts reviewed the "nutrient minerals in drinking water and the potential health consequences of long-term consumption of demineralised and remineralised and altered mineral content drinking waters" (WHO 2005). They dealt with more than 80 reports on the subject and developed a consensus document that was published on the WHO's website for public comment, along with 14 support papers that were presented at the workshop. The consensus document made these conclusions, among others:

- On balance, the hypothesis that consumption of hard water is associated with a somewhat lowered risk of cardiovascular disease was probably valid, and magnesium was the more likely contributor of those benefits.
- Demineralized and corrosive drinking water should be stabilized where possible with additives that will increase or reestablish calcium and magnesium levels. Water bottlers could consider providing some waters with mineral compositions that are beneficial for some population segments.
- Water utilities are encouraged to periodically analyze their waters for calcium, magnesium, and trace elements to help assess trends and conduct future epidemiologic studies.
- Studies should evaluate a number of potentially relevant health outcomes (e.g., renal stone formation, cardiovascular disease, hypertension incidence, osteoporosis, stroke, mineral balance, mineral nutritional deficiencies). Studies should include analyses for calcium, magnesium, and trace elements.
- Information should be provided on methods of application of home water-softening devices so that consumers will also have access to mineralized water for drinking and cooking.
- In the revisions of the *Guidelines for Drinking-Water Quality,* the WHO should consider the beneficial roles of nutrient minerals including water hardness characteristics (WHO 2017).

CONCLUSION

Most people in the United States are consuming less than the estimated requirement of magnesium to support good health. Drinking water can provide a baseline lifetime contribution to dietary magnesium intake. The removal of essential minerals like calcium and magnesium from water by softening can result in lower lifetime intakes of those essential elements without their replacement from the diet or supplementation. Magnesium from plant-derived food is less efficiently absorbed than from dairy and water. Dietary consumption of magnesium (and calcium) tends to decline beyond childhood, and the body's stores of magnesium may ultimately become depleted, and intake may not supply sufficient replacement. Numerous adverse health effects have associations with inadequate magnesium levels. There are several case-control and cohort epidemiological studies that indicate beneficial effects of reduced cardiovascular mortality associated levels of magnesium in drinking water.

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