

HEALTH AND REGULATORY ASPECTS OF CALCIUM AND MAGNESIUM IN DRINKING WATER

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Calcium and magnesium as major representatives of natural water constituents have been extensively studied for years, but surprisingly, the extensive data available and the knowledge acquired has had a low effect on the regulatory field. This situation cannot be considered as satisfactory from public health point of view.

If we want to work on calcium and magnesium in drinking water, a third parameter is to be taken into account: water hardness, even if this term is incorrect and obsolete from a strictly chemical point of view. That is to say that both of these elements largely have not been analysed individually in drinking water in the past, but just non-specifically in summary as hardness. This approach was applied in many studies focused on health effects of this "water factor". Initially, water hardness was understood to be a measure of the capacity of water to precipitate soap, which is in practice the sum of concentrations of all polyvalent cations present in water (Ca, Mg, Sr, Ba, Fe, Al, Mn, etc.); nevertheless, since the other ions (apart from Ca and Mg) play a minor role in this regard, later it has been generally accepted that hardness is defined as the sum of the Ca and Mg concentrations, determined by the EDTA titrimetric method, and expressed in mmol/L (ISO 1984) or as CaCO₃ equivalent in mg/L (*Standard Methods* 1998), less frequently as the CaO equivalent.

Although it is generally acknowledged that research boom on health effects of water hardness over the last 50 years was started with the paper of the Japanese chemist Kobayashi published in 1957 (who showed, based on epidemiological analysis, higher mortality rates from stroke in the areas of Japanese rivers with more acid water compared to those with more alkaline, i.e. harder water used for drinking purposes), it is possible to document that such interest is in fact much older and may be traced back before the World War 1 (*The Lancet*, 1913) and even in the 1870s when Dr. Letheby studied relationships between total mortality and water hardness in 19 cities in England and Scotland (*Journal für Gasbeleuchtung und Wasserversorgung*, 1871).

Results of number of epidemiologic studies done in the 1960s - 1970s were summarized in compelling dictum "soft water, hard arteries", widely accepted by both water and public health experts. Although this knowledge was called later in question by some parties, extensive and systematic review done by the University of East Anglia (2005), summarizing data from several thousands of papers on water hardness and health published in English, found significant evidence of an inverse association between magnesium levels in drinking water and cardiovascular mortality. Following meta-analysis of case control and cohort studies (i.e. the most valid epidemiological studies) calculated a pooled odds ratio 0.75 (95%CI 0.68,

0.82; $p < 0.001$) which means that people consuming drinking water with magnesium 8.3-19.4 mg/L had the risk of cardiovascular mortality lower by 25 %, in comparison with people using water with Mg content of 2.5-8.2 mg/L. Protective role of water calcium towards cardiovascular disease was also confirmed by some studies, but the evidence is not so strong as for magnesium.

A number of other papers suggest also beneficial or protective effect of water calcium and magnesium on other diseases like neurological disturbances, amyotrophic lateral sclerosis, stroke, preeclampsia, osteoporosis, etc. In the late 1990's several epidemiological studies were carried out in Taiwan by one research team to focus on relationships between drinking water hardness and mortality from type of cancers showing significant geographical variation. Water hardness was found to have protective effect against cancer of oesophagus, pancreas, rectum and breast, drinking water calcium proved protective against colorectal and gastric cancers. However, further studies from other countries are needed to confirm these results.

Calcium and magnesium to a lower extent also in both drinking water and food were previously found to have a beneficial antitoxic effect since they prevent - via either a direct reaction resulting in a nonabsorbable compound or competition for binding sites - absorption or reduce harmful effects of some toxic elements such as lead, cadmium, etc.

Contrary to beneficial effects, there is no evidence about any harmful health effects if calcium is present in drinking water below 200 mg/L and magnesium below 100 mg/L. Perhaps only a high magnesium content (hundreds of mg/L) coupled with a high sulphate content (above 500 mg/L) may cause transient diarrhoea. Nevertheless, such cases are rather rare; other harmful health effects (e.g. higher incidence rates of cholelithiasis, urolithiasis, arthrosis and arthropathies) observed in some older ecological epidemiological studies due to high water hardness, i.e. more than 5 mmol/L, were observed in waters rich in total dissolved solids (above 1000 mg/L) showing mineral levels which are not typical of most drinking waters. It is not

possible to determine if these effects are caused solely by calcium and magnesium (probably not) or by other cation(s) and anion(s) present or by total dissolved solids. Hard water is also rarely reported to cause increase in the risk for atopic eczema in school children which can probably be explained by its higher drying effect on the skin (similar to that of overchlorinated water), but in this case water is used externally and is not intended for consumption.

Higher water hardness may worsen aesthetic (organoleptic) characteristics of drinking water or drinks and meals prepared with such water: formation of a layer on the surface of coffee or tea, loss of aromatic substances from meals and drinks (due to bonding to calcium carbonate), unpleasant taste of water itself for some consumers (calcium taste threshold is about 100-300 mg/L, unpleasant taste starts from 500 mg/L, but it also depends upon the presence of other ions; the magnesium content exceeding 170 mg/L together with the presence of chloride and sulphate anions are responsible for the bitter taste of water). On the other side, very soft water, such as distilled and rain water as two extreme examples, is of unacceptable taste for most people who usually report it to be of unpleasant to soapy taste. It means that a certain minimum content of minerals, the most crucial of which are calcium and magnesium salts, is essential for the pleasant and refreshing taste of drinking water.

Based on the available data, the desirable minimum of magnesium and calcium can be estimated to be >10 mg/L (for Mg) and >20-30 mg/L (for Ca), respectively. Nevertheless, this does not mean that if low levels of these elements were increased to remain below the minimum mentioned above (e.g. if the magnesium level were increased from 2 to 5 mg/L), it would be of no importance. It seems that any increase of Ca or Mg in water, even by several mg/L, could have a beneficial or protective health effect (not speaking about technical effect - reduction of aggressivity of water). Although a certain minimum quantity of these elements is desirable, it definitely does not mean the more the better. What can be called the optimum levels in

drinking water (from health point of view) ranges from 20 to 30 mg/L for magnesium and from 40 to 80 mg/L for calcium, respectively, and for water hardness as Ca+Mg from about 2 to 4 mmol/L.

Introduction of regulatory measures concerning the minimum levels of calcium and magnesium in drinking water seems to be justified and highly desirable. They should be based on the fact that it is much simpler and much more effective to keep the existing Ca and Mg drinking water levels than to add these minerals to water artificially. Practically, this means restricting the use of technologies leading to removal of Ca and Mg from water only to the cases where the Mg and Ca levels are too high (i.e. of hundreds of mg/L or more) provided that the required minimum of Ca+Mg is kept in the water after treatment.

Considering high number of epidemiological studies confirming beneficial effects of certain amount of Ca and Mg in drinking water and multitude supporting evidence from experimental and clinical studies, as well as zero health risk relating to usual levels found in drinking water (dozens of mg/L), it is surprising to see the restrained attitude of the World Health Organization over the last 20 years to recommend any guideline value. After all, a deficiency of Ca and Mg poses at least comparable health risk as exceeding the limit for some toxic substances does (which are regulated even the evidence of their toxicity is much less convincing than evidence of beneficial effect of Ca or Mg). One can just try to guess the true motives behind such position.

Nevertheless, apart from this WHO approach and the fact that hardness (Ca or Mg) is not regulated by current EU Drinking Water Directive (98/93/EC), about 10 European countries have established some form of minimum requirements on hardness level after softening or generally optimum range. Some countries have this requirements legally based, while others issued just recommendation in form of technical standard or guidelines. Other countries try to educate the consumers through information leaflets or websites how to use any softening device in respect to keep calcium and magnesium in water for drinking and cooking purposes.