The Science of the Total Environment, 54 (1986) 207—216
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHEMICAL QUALITIES OF WATER THAT CONTRIBUTE TO HUMAN HEALTH IN A POSITIVE WAY

HOWARD C. HOPPS

Medical College of Ohio, Department of Pathology, Toledo, OH 43699 (U.S.A.)

GERALD L. FEDER

U.S. Geological Survey, Lakewood, CO 80225 (U.S.A.)

ABSTRACT

The emphasis on harmful substances that may occur in potable waters has almost obscured the fact that important beneficial constituents are commonly present.

The chemical substances in water that make positive contributions to human health act mainly in two ways: (i) nutritionally, by supplying essential macro and micro elements that the diet (excluding water) may not provide in adequate amounts (for example, Mg, I and Zn); and (ii) by providing macro and micro elements that inhibit the absorbtion and/or effects of toxic elements such as Hg, Pb and Cd. Specific examples of these beneficial effects will be given, also examples of harmful effects on health that may result from excessive intake of these ordinarily beneficial elements.

Because concentrations of the essential macro and micro elements that occur in natural, potable waters vary greatly, depending upon their source, geographic considerations are very important in any studies attempting to relate water quality to health. In this context, the inverse relationship between hard water and cardiovascular disease will be discussed. Specific data relating hardness and Mg and Ca content of potable waters to specific geographic regions of the U.S.A. will be presented. These data show a strong positive correlation between low Mg content and decreased longevity, and between high Ca and Mg content and increased longevity. In the regions considered, increased longevity correlates strongly with decreased cardiovascular mortality, and the decreased longevity with increased cardiovascular mortality.

INTRODUCTION

Some toxic substances in water are *not* health threatening, at least not to human beings. They may be toxic only to certain species other than *H. sapiens* or, more important to our considerations, toxic to *H. sapiens*, but ordinarily found at concentrations insufficient to threaten human health. This consideration influenced the title of our paper, with its emphasis on contribution to health in a *positive* way, implying that we shall not focus on the healthful aspects of certain waters merely because they do not contain toxic substances in health-threatening concentrations.

0048-9697/86/$03.50

TABLE 1
ESSENTIAL[a] MICRO AND MACRO ELEMENTS THAT MAY BE SUPPLIED IN NUTRITIONALLY SIGNIFICANT AMOUNTS BY POTABLE WATERS (arranged in order of atomic number)

Fluorine
Sodium
Magnesium
Calcium
Chromium
Zinc
Selenium
Iodine

[a] This list does not include those trace elements proved essential for various experimental animals, but for which deficiency disorders in humans are rare or unknown, e.g. Si, V, Mn, Ni, As, Mo and Sn.

The importance of many natural, potable waters in human nutrition has been largely ignored in the concern for health-threatening, toxic substances that some waters contain. In the context of positive contributions to human health, the *beneficial* qualities of drinking water should also be emphasized.

There are two major categories of these positive contributions to health (aside from the obvious fact that water (H_2O) is essential to life and comprises about 60% of the total body mass of the average normal adult human) — nutritional and antitoxic.

Nutritional, through contributions of macro and micro elements essential for health

These elements (Table 1), mainly ingested in the form of inorganic ions, have many biological functions. For example, they contribute to the formation of vitally important metalloenzymes, carriers (e.g., hemoglobin), and selective membrane permeability; and to the physical integrity of structures such as bone, cartilage, and various fibrous materials (e.g., collagen and elastica).

The practical significance of the first category depends upon (a) the amount of the element in question that is often or occasionally found in potable water, which varies greatly with the geographic region; (b) whether or not the element, as it occurs in potable water, is in a biologically active form (for example, cobalt, as such, is not biologically active in terms of human nutrition; to be nutritionally effective it must be ingested and absorbed as a preformed complex, cobalamin); (c) the extent to which the (regional) diet often or occasionally fails to meet the individual's needs (this consideration must take into account common physiologic and pathologic events that may require amounts of the element that will exceed the recommended dietary allowance (RDA) (NAS, 1980) for average humans).

Antitoxic contributions of certain macro and micro elements that inhibit the adsorption and/or effects of toxic elements such as mercury, lead and cadmium

These protective effects are, of course, limited, but may be quite significant. Levander (1977) has reviewed much of the evidence in support of this category. Stated very briefly, protective action against toxicity from *mercury* is provided by selenium; a high zinc intake appears to offer some protection against the toxic effects of *lead*, whereas a deficiency of *calcium* (also iron and copper to a lesser extent) increases susceptibility to lead; selenium (also zinc and iron to a lesser extent) decreases the toxicity of cadmium, whereas a deficiency of calcium (also iron and copper to a lesser extent) aggravates toxicity.

With respect to the nutritional qualities of potable waters, we are mainly concerned with those macro and micro elements that can be contributed in significant amounts by natural potable waters, particularly if food alone (excluding water) may be inadequate to provide the recommended daily allowances (RDA). The elements that fall into this category are shown in Table 1.

Based upon an average consumption of 2 l of water per day for adults (including the water content of coffee, tea, milk, fruit juice, soft drinks, beer, soup, etc.) some natural potable waters can supply all of the RDA for magnesium, fluorine, sodium, iodine, and selenium, and more than one-third of the RDA of calcium (Feder and Hopps, 1981). As much as 15% of the RDA of zinc can also be supplied; this amount, although a relatively small percentage of the RDA, can be quite significant because of the widespread deficiency of zinc in the United States. The nutritional significance of chromium in drinking water has not been demonstrated, but the predominant valance state of chromium in natural potable waters (Cr^{3+}) is the biologically active state and, since the minimal requirement for absorbed chromium is approximately 1 μg per day (NAS, 1980), it is reasonable to assume that some waters can provide nutritionally significant amounts of this essential element. Chromium deficiency is relatively common in the United States, and several investigators have shown that it results in demonstrable states of diabetes-like altered carbohydrate metabolism (Mertz, 1969; Jeejeebhoy et al., 1977; Freund et al., 1979). Iron represents a special case in that natural, nontoxic waters may supply more than the RDA; however, waters containing concentrations of iron in solution $> 1\ \mathrm{mg\ l^{-1}}$ are distasteful and are rejected for aesthetic reasons.

Important consequences from deficiency of these elements may become apparent only after many years and then, perhaps, only when triggered by *a pathologic event* (for example, deficiency of magnesium, when complicated by acute myocardial ischemia, contributes to a lethal arrythymia), or a *physiological stress* (for example, deficiency of calcium, in association with the post menopausal state and its associated endocrine disturbances, contributes to osteoporosis). In experimental animals, it is clear the deficiency of certain essential micro elements early in life, or even during the fetal period, can lead to a disease or disorder that manifests itself only many years later — and perhaps this manifestation may be as subtle as a relatively slight decrease in life span. Such delay is most likely to occur when the deficiency is slight or moderate. These observations imply that an adequate, balanced intake of essential macro and microelements (coupled with otherwise good nutrition) may increase life span compared with the average (Mertz, 1981). A National Academy of Science sponsored study, Aging and the Geochemical Environment (NAS, 1981), supports this view.

Although we are focussing upon ill effects that result from deficiency of essential elements, it is important to point out that too much of even an essential element can cause ill effects. As in the case of deficiency, sometimes slight excesses may require many years to manifest themselves in forms such as increased risk of cancer, acceleration or exaggeration of atherosclerosis, increased susceptibility to other "degenerative diseases", and so on. The admonition of Paracelsus (1493—1541) is very pertinent in this context: "All substances are poison; there is none which is not a poison. The right dose differentiates a poison and a remedy". Of the elements listed in Table 1, fluorine and selenium deserve comment in this connection.

The effects of too much fluorine derived from natural drinking waters are well known, ranging from slight cosmetic effects (mottled tooth enamel) to incapacitating skeletal abnormalities. Overt toxic effects from too much selenium also occur (rarely) from ingestion of natural waters that contain high levels of selenium, but, as with fluorine, occurrence is limited to small geographic regions. Although selenium poisoning, i.e. selenosis of livestock, has been recognized for many years (Underwood, 1977), human disease from naturally-occurring selenium poisoning has been shown only recently; the occasional, poorly-documented reports of past decades were not scientifically acceptable. Yang et al., (1983) have reported selenium intoxication in the Hubei Province of China involving several hundred individuals, apparently the result of consuming vegetables with high concentrations of Se in association with a low-protein diet. Selenium intoxication in human beings from drinking water rich in selenium has been reported in southwestern Colorado. On a Ute reservation, some wells that provide drinking water for humans contain very high concentrations of selenium — as high as $13000\,\mu g\,l^{-1}$ (Brogden et al., 1979). It is from the consumption of very high selenium content waters that overt manifestations of toxicity have been observed (Beath, 1962). It may be that the toxicity of selenium to human beings has been exaggerated because, in some areas of southwestern Colorado, waters with 400—$500\,\mu g\,l^{-1}$ of selenium have been consumed by humans over many years without apparent harmful effects (E.C. Hutchinson, U.S. Geological Survey, personal communication, 1982). Data pertaining to selenium content of drinking waters illustrate well the tremendous variation in concentrations of trace elements in natural waters even within relatively small geographic regions. In one 3-square mile area, the Oxford Tract, selenium values in ground water ranged from <10 to $13000\,\mu g\,l^{-1}$ (Brogden et al., 1979). Vertical changes in Se concentrations are also important. In one well that taps water at several depths on the Oxford Tract installed by the U.S. Geological Survey, water samples collected had selenium concentrations that ranged from 90 to 540 $\mu g\,l^{-1}$ (Brogden et al., 1979).

The most important benefit to human health associated with the macro and micro elements contained in drinking water is probably that related to *cardiovascular mortality* (CVM). Many epidemiologic studies have shown an *inverse* relationship between hard water and CVM, but the precise characteristics of the "hard-water factor" remain elusive. Some (NAS, 1979) have considered that substances contained in hard water may not be directly responsible for *decreased* CVM; rather, soft water may cause *increased* CVM because many soft waters are corrosive and dissolve cadmium and/or lead from pipes that distribute the water. In "Geochemistry of Water in Relation to Cardiovascular Disease" (NAS, 1979), Comstock states". . . there can be little doubt that the negative associations of water hardness with cardiovascular mortality are not spurious", and he evaluates several reports on the level of increased risk of cardiovascular deaths in soft versus hard water areas in the United States, Canada, and England and Wales. The data are not entirely compatible because the grouping according to precise cause of death varies, but the risk factor in the United States appears to be about 1.15. This seems a weak association, but when one considers that nearly 1 million persons in the U.S.A. die each year from cardiovascular disease, approximately 2.5 times as many as from cancer, an increased risk of death of 15% becomes very significant indeed.

Many diseases contribute to deaths from cardiovascular disease (CVM). Examples include certain developmental defects of the heart, brain, or kidney; rheumatic fever; various other infectious diseases; diabetes mellitus; hypertension; and, most important of all, atherosclerosis. The decreased CVM associated with water hardness appears to be most strongly related to *ischemic heart disease* (NAS, 1981), the category which is responsible for slightly more than half of all cardiovascular deaths occurring in the United States. A weaker relationship probably exists for stroke.

Virtually all diseases are multicausal, and ischemic heart disease is no exception. Atherosclerosis of the coronary arteries, which in itself has many causes, is the major contributor to fatal ischemic heart disease. A thrombus imposed upon an atherosclerotic plaque within a coronary artery, totally blocking the flow of blood, is often the event that precipitates sudden death; thus, blood-coagulation factors also play a role. Furthermore, because the ultimate terminal event that causes cessation of circulation is usually a cardiac arrythymia (including asystole), reactivity of the myocardium to electrical stimuli is also an important factor. The predominant current view is that hard water probably does not significantly affect the degree or extent of atherosclerosis, but may influence coagulative mechanisms and, more likely, may increase the possibility that acute ischemic injury will result in fatal cardiac arrythmia (Aikawa, 1981).

The study we are reporting here is not primarily concerned with the

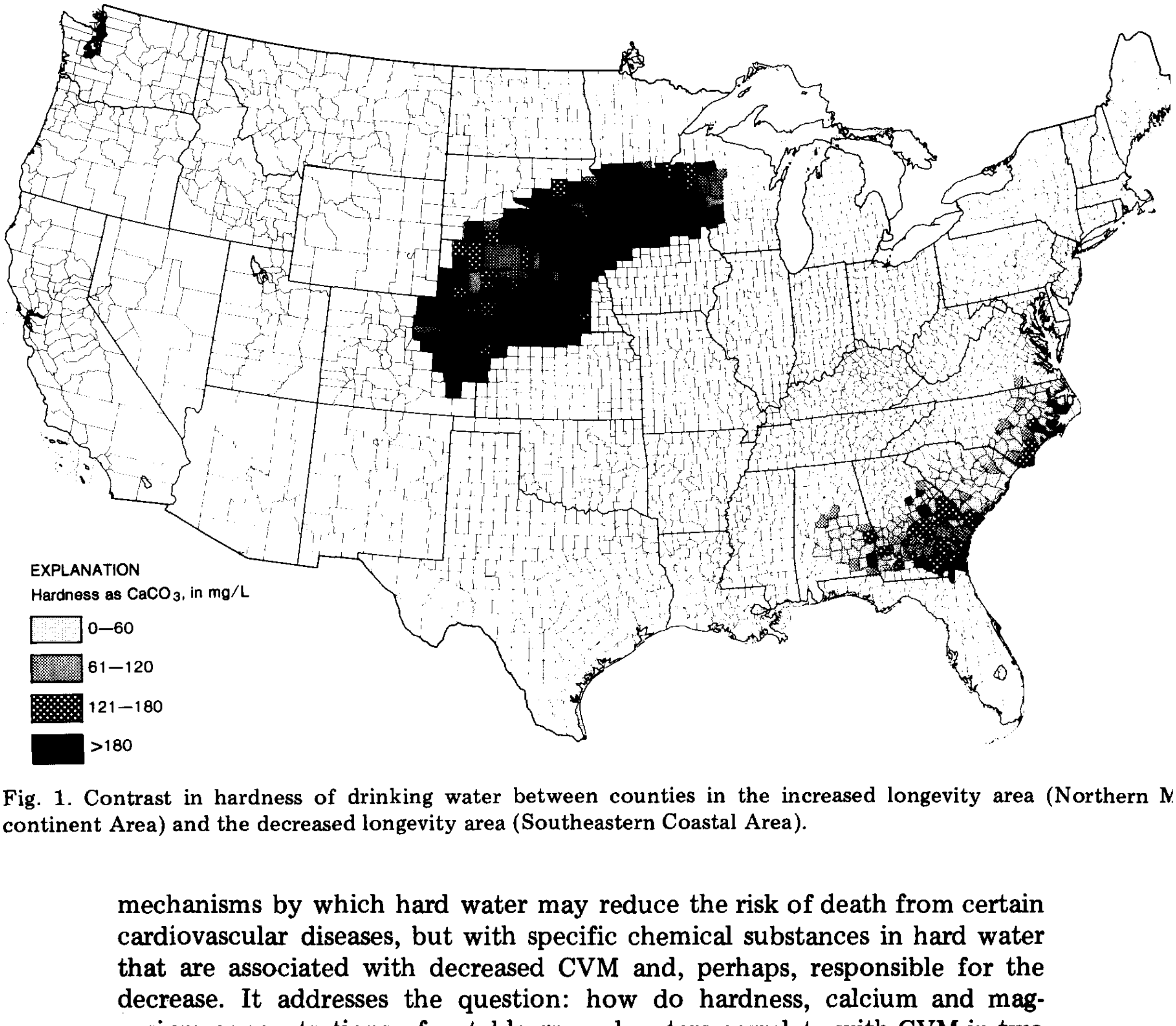

Fig. 1. Contrast in hardness of drinking water between counties in the increased longevity area (Northern M continent Area) and the decreased longevity area (Southeastern Coastal Area).

mechanisms by which hard water may reduce the risk of death from certain cardiovascular diseases, but with specific chemical substances in hard water that are associated with decreased CVM and, perhaps, responsible for the decrease. It addresses the question: how do hardness, calcium and magnesium concentrations of potable ground waters correlate with CVM in two large regions of the United States. The two contiguous regions selected, each comprising more than 100 000 square miles, had been identified and characterized in a previous National Academy of Science sponsored study described in the monograph, "Aging and the Geochemical Environment" (NAS, 1981). Longevity was determined indirectly by measuring death rates (for natural causes) of white males aged 35—74, *age adjusted*. The difference in mortality of the two geographic regions was striking. The decreased longevity region had a death rate nearly twice as large as the region of increased longevity. The reader is referred to the original source (NAS, 1981) for a detailed description of the epidemiologic data (by H.I. Sauer), also the reasons for the indirect method assessing longevity.

The two large areas identified in each of the maps shown as Figs 1—3 represent the regions of increased longevity (Northern Midcontinent Area)

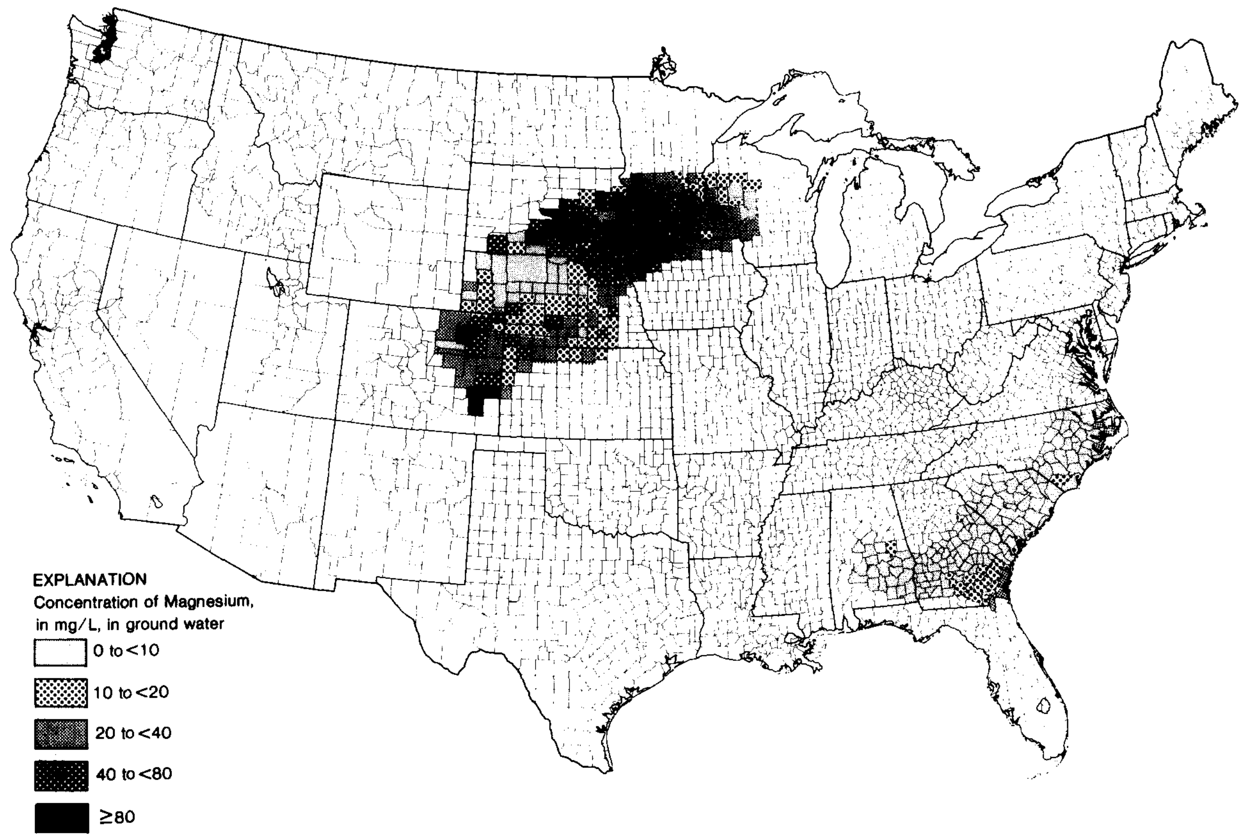

Fig. 2. Contrast in Magnesium content of drinking water between counties in the increased longevity area (Northern Midcontinent Area) and the decreased longevity area (South-eastern Coastal Area).

and decreased longevity (Southeastern Coastal Area). The previous studies, referred to above, showed clearly that the area of increased longevity was characterized by markedly *decreased* CVM and, conversely, the decreased longevity area by markedly *increased* CVM. In fact, CVM was the major factor responsible for the increased and decreased (compared with the average) longevity in the two regions. The average water compositions for each county are shown for hardness (Fig. 1) and for concentrations of magnesium (Fig. 2) and calcium (Fig. 3). Magnesium and calcium were chosen for study, not only because they are the most consistent, major cations present in hard water, but also because one or the other or both are generally regarded as the most probable cause of the hard water effect on CVM (Marier et al., 1979). Hard water usually contains considerable calcium, and may also contain considerable magnesium. Limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are both major sources of calcium in water. Of the two, only dolomite contributes magnesium, however. Therefore, some natural hard waters have a high Ca:Mg ratio, others a low Ca:Mg ratio, and many fall in an intermediate range.

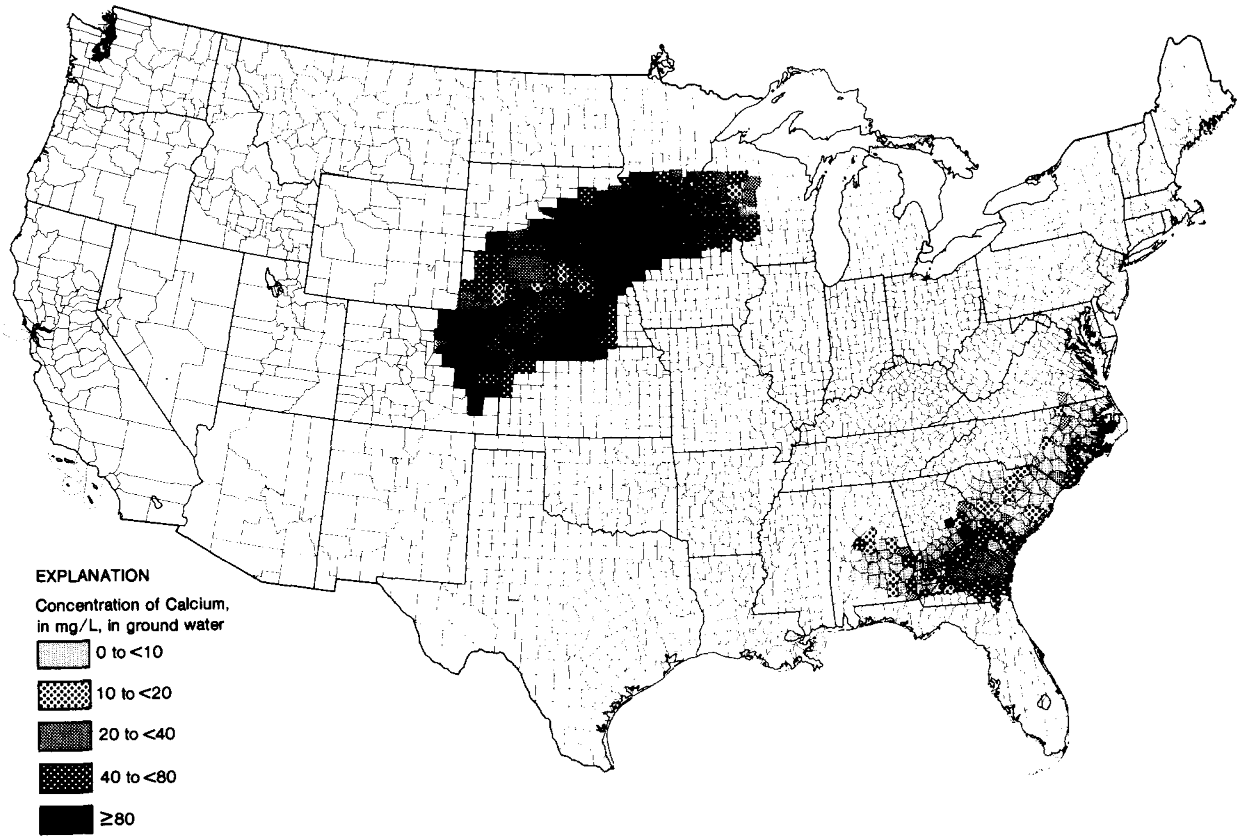

Fig. 3. Contrast in calcium content of drinking water between counties in the increased longevity area (Northern Midcontinent Area) and the decreased longevity area (South-eastern Coastal Area).

Figure 1 shows a striking, positive relationship between *water hardness* and the region of increased longevity (*decreased* CVM), and the converse relationship is also quite good — that is, a negative relationship with the region of decreased longevity (*increased* CVM). In Fig. 2 the relationship between low concentrations of *magnesium* and decreased longevity (increased CVM) is very good, but the converse is not as obvious. In Fig. 3 the high concentrations of calcium correlate well with increased longevity (decreased CVM), but the converse is questionable.

The decreased longevity (high CVM) region that we have studied contains highly leached rocks and soil; this feature profoundly influences the geochemical environment. The great majority of potable waters there have very low total dissolved solids; *all* cations and anions are in low concentrations. This characteristic of many soft waters, coupled with the great variations of calcium and magnesium concentrations (as well as other elements) among hard waters makes it difficult to establish a correlation between the concentration of a particular element and mortality from cardiovascular disease, if indeed a prime component exists. At any rate, it is unlikely that *the* hard-water factor will be identified until more studies that relate cardiovascular mortality to hardness of drinking water characterize chemically the hard water and examine relationships between CVM and *specific* chemical components of the hard water.

Given these caveats, our findings are compatible with the hypothesis that magnesium at moderate concentrations provides a modest degree of protection from CVM; thus, most hard waters will satisfy this requirement, although other characteristics of the water may overshadow magnesium, the prime component (?). Calcium appears to provide *additional* protection from CVM. Thus, geographic regions with very low CVM (compared with average CVM) may best correlate with high-calcium content hard water, whereas regions with very high CVM (compared with average rates) will best correlate with very low Mg concentrations (e.g., very soft waters).

SUMMARY

Many natural, potable waters contribute significant amounts of macro and micro nutrients that are essential for human health. Ordinarily, hard waters have greater nutritional benefits than soft waters, but geographic variations are large, depending on the geochemical environment. A major health benefit from drinking hard water is a decreased risk of dying from cardiovascular disease.

Two large contiguous geographic regions of the United States — one characterized by higher than average cardiovascular mortality (CVM), the other by lower than average CVM — are compared in terms of the concentrations of hardness, and magnesium and calcium in their natural, potable, ground waters. Striking positive relationships exist between elevated hardness and concentrations of calcium in water and *decreased* CVM. In addition, the data show very good relationships between softness and low concentrations of magnesium in water with *increased* CVM. These findings are compatible with the hypothesis that magnesium, in concentrations $>20\ \mathrm{mg\,l^{-1}}$, is the major factor in hard water responsible for decreased risk of CVM. The data also suggest that calcium in concentrations >40–$80\ \mathrm{mg\,l^{-1}}$ provide additional protection.

ACKNOWLEDGEMENT

This paper is an extension of material presented at the "Medical Geology Conference on Health Threatening Toxins in Water", 3 May 1984, directed by Dr E. Lynn Savage, Brooklyn College, City University of New York.

REFERENCES

Aikawa, J.K., 1981. Magnesium: Its Biologic Significance. CRC Press, Boca Raton, Florida.

Beath, O.A., 1962. Selenium poisons Indians. Sci. News Lett. 81: 254.

Brogden, R.E., E.C. Hutchinson and D.E. Hillier, 1979. Availability and quality of ground water, Southern Ute Reservation, Southwestern Colorado. U.S. Geological Survey Water-Supply Paper 1576-J.

Feder, G.L. and H.C. Hopps, 1981. Variations in drinking water quality and the possible effects on human health. In: D.D. Hemphill (Ed.), Trace Substances in Environmental Health — XV. University of Missouri, Columbia, Missouri, pp. 96—103.

Freund, H., S. Atamian and J.E. Fischer, 1979. Chromium deficiency during total parenteral nutrition. J. Am. Med. Assoc., 241: 496—498.

Jeejeebhoy, K.N., R.C. Chu, E.B. Marliss, G.R. Greenberg and A. Bruce-Robertson, 1977. Chromium deficiency, glucose intolerance, and neuropathy reversed by chromium supplementation, in a patient receiving long-term total parenteral nutrition. Am. J. Clin. Nutr., 30: 531—538.

Levander, O.A., 1977. Nutritional factors in relation to heavy metal toxicants. Fed. Proc., Fed. Am. Soc. Exp. Biol., 36: 1683—1687.

Marier, J.R., L.C. Neri and T.W. Anderson, 1979. Water Hardness Human Health, and the Importance of Magnesium. NRCC Publication No. 7581, Ottawa, Ontario.

Mertz, W., 1969. Chromium occurrence and function in biological systems. Physiol Rev., 49: 163—239.

Mertz, W., 1981. The essential trace elements. Science, 213: 1332—1338.

National Academy of Sciences (NAS), 1979. Geochemistry of Water in Relation to Cardiovascular Disease. National Academy Press, Washington, DC.

NAS, 1980. Recommended Dietary Allowances, 9th edn. National Academy of Sciences, Washington, D.C.

NAS, 1981. Panel on Aging and the Geochemical Environment of the U.S. National Committee for Geochemistry, The National Research Council, Aging and the Geochemical Environment. National Academy Press, Washington, D.C.

Underwood, E.J., 1977. Trace Elements in Human and Animal Nutrition, 4th edn. Academic Press, New York.

Yang, G., S. Wang, R. Zhow and S. Sun, 1983. Intoxication of humans in China. Am. J. Clin. Nutr., 37: 872—881.