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The impact of inorganic chemicals on water quality and health

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Summary. - Inorganic substances constitute by far the greatest proportion of chemical contaminants in drinking water. They are present in greatest quantity as a consequence of natural processes but several important contaminants are present as a result of man's activities. Some of the most important even come from the plumbing material through which water is passed. Inorganic contaminants are the most important determinands of acceptability to the consumer, affecting taste, colour and scale deposition on pipes and fittings. They are also demonstrably the most important for health, having both beneficial and adverse effects which have been shown in human populations. This is a brief review of some of the most important inorganic consituents of drinking water covering major elements such as hardness and nitrate and more minor constituents in terms of quantity, such as arsenic, selenium and lead.

Key words: inorganic chemicals, drinking water quality, risk assessment, hardness, nitrate, arsenic, selenium, lead.

Riassunto *(L'impatto dei composti inorganici sulla qualità dell'acqua e sulla salute).* - Le sostanze inorganiche rappresentano di gran lunga i principali contaminanti chimici delle acque potabili. La loro presenza nelle acque potabili è conseguenza di processi naturali ma molti importanti contaminanti sono presenti a causa di attività antropiche. Alcuni dei più importanti contaminanti provengono anche dai materiali utilizzati per il trasporto delle acque. I contaminanti inorganici rappresentano la più importante causa determinante l'accettabilità dell'acqua per i consumatori, influenzandone il sapore, il colore e la deposizione di incrostazioni nelle tubazioni e sulle guarnizioni. E' anche possibile dimostrare che essi sono i contaminanti più importanti ai fini della salute poiché, come è stato mostrato im popolazioni umane, possono causare effetti benefici e avversi. Questo lavoro è una breve rassegna di alcuni dei più importanti costituenti inorganici dell'acqua potabile e include, nel senso della quantità, alcuni elementi maggiori, quali durezza e nitrati, e alcuni minori, quali arsenico, selenio e piombo.

Parole chiave: sostanze inorganiche, qualità dell'acqua potabile, valutazione del rischio, durezza, nitrati, arsenico, selenio, piombo.

Introduction

Inorganic chemicals are usually present in natural waters at much higher concentrations than their organic counterparts. Many of these chemicals are naturally occurring and should be considered as an integral part of those particular waters e.g. calcium carbonate and bicarbonate in hard waters, rather than as "contaminants".

It is of course these major inorganic contaminants which make the differences in taste of various waters. The very highly mineralised waters have been prized for their supposed health giving properties over the years and "taking the waters" was a recognised medical and social activity in spa towns all over Europe. The taste of these waters is often very strong and would be unacceptable in normal drinking water. However there are many inorganic components usually present in much smaller concentrations, which could be considered as "contaminants" and which are of greater interest in terms of their effect on water quality and health than the major components.

Sometimes the most startling differences in the inorganic content of drinking water arise as a consequence of the differences between groundwater and surface water. Such differences are usually a reflection of the solution of minerals as water percolates through the ground. However some are due to relatively low groundwater flows compared to surface water, and the subsequent build-up of pollutants such as nitrate.

An assessment of the potential health effects of inorganic contaminants in drinking water is greatly complicated by the limited database on the toxicity of these chemicals by the oral route and the fact that many of these elements are essential for human nutrition.

The number of inorganic chemicals of importance for water is large and it is not possible to cover them in depth here. Therefore only a few of particular significance or interest are considered and the important features of each are summarised. Where possible reference has been made to reviews of the data in order to lead the reader to more detailed evaluations.

Major elements

These are the components of drinking water usually present in the highest concentrations, and which have a major impact on taste and aesthetic quality e.g. the ability of a water to deposit scale.

Hardness

Hardness is not related to a specific constituent but is caused by a variety of polyvalent metallic ions, predominantly calcium and magnesium, although some other cations such as barium, iron, manganese and strontium may make a minor contribution. Water hardness is traditionally the measure of reactivity with soap, with hard water requiring large amounts to form a lather. This was of some economic importance, particularly to the wool industry in the 18th and 19th centuries in the degreasing of fleeces.

The most common measure of hardness is milligrams of calcium carbonate equivalent per litre. In general hardness in drinking water ranges from about 10 to 500 mg calcium carbonate/litre with less than 60 mg/l being considered soft water. Although hardness is caused by cations it may also be considered in terms of temporary (bicarbonate) and permanent (non-carbonate) hardness. The former is removed by boiling and the latter consisting primarily of sulphates is not. Hardness occurs in water principally because of slightly acid water seeping through sedimentary rocks and dissolving polyvalent metallic ions. The two most common such rocks are limestone and chalk. Concentrations of up to about 100 mg calcium/litre are fairly common while sources containing over 200 mg calcium/litre are rare. Magnesium is commonly found at concentrations up to about 10 mg/l but occasionally concentrations of 100 mg magnesium/l can be encountered.

Both calcium and magnesium are essential elements and virtually all foods contain both. Typical diets provide about 1000 mg calcium/day and 200-400 mg magnesium/day. The typical contribution of water to daily intake of these elements is between 5 and 20% and it is possible that in some instances water could be an important source of calcium and magnesium in those who are receiving a marginally deficient diet. Evidence that consumption of hard water causes adverse health effects is not convincing, although there have been suggestions that very high calcium intakes can exacerbate kidney stones. In view of the relatively minor contribution that water makes to calcium and magnesium nutrition and the physiological control of calcium and magnesium absorption, this seems unlikely under normal circumstances.

There are a number of studies which show an inverse relationship between water hardness and cardio-vascular disease [1-9]. However, some studies have reported no such relationship [10, 11]. In addition a reduction in cardiovascular events has been observed following changes in the source of drinking water resulting in changes in hardness [9]. The evidence certainly does seem to support a small statistically significant relationship but the mechanism for such a relationship remains to be determined. At present the data are inadequate to prove that the relationship between lower cardio-vascular disease rates and consumption of hard water is causal.

Sodium

Sodium salts are usually highly soluble in water and can leach from strata bearing such salts. However the highest levels of sodium in water are usually associated with saline intrusion at the coast or from underground salt deposits. Sewage effluents and salt used for de-icing roads can make a significant contribution. A number of water treatment chemicals also contain sodium and domestic water softeners can substantially increase sodium levels in water. Most water supplies contain less than 20 mg sodium/litre but levels can exceed 400 mg/l in exceptional circumstances. Drinking water sodium normally makes only a very minor contribution to total sodium intake.

Sodium is of extremely low toxicity but evidence from animal studies does indicate that high levels of salt in the diet may result in hypertension [12-14].

There is considerable controversy as to whether the findings in laboratory rats can be extrapolated to humans and the data do not support the view that high sodium intake is likely to contribute substantially to the development of hypertension in human populations. There have been studies which suggest that increased drinking water sodium may lead to increases in blood pressure in children [15, 16] however other studies have failed to confirm this [17, 18]. In addition the very minor contribution of sodium in drinking water to total sodium intake would not seem to be sufficient to have any biological impact considering the very high bioavailability of sodium in food.

Two groups for which excessively high sodium intakes, including intake from drinking water, could be of concern are infants and those with chronic congestive heart failure. The immature infant kidney is less efficient at excreting sodium and infants with fluid loss, usually through diarrhoea, may develop elevated plasma sodium levels (hypernatraemia) which can result in permanent neurological damage. In such cases infant formula made up with tap water with elevated sodium levels may exacerbate this problem. Exacerbation of congestive heart failure, which is aggravated by excessive salt intake, has also been reported as a consequence of high sodium levels in drinking water [12].

The major effect of high sodium levels in drinking water for most individuals is an adverse effect on taste. The taste threshold in water depends on both the associated anion and the temperature. The taste thresholds for sodium chloride, nitrate and sulphate at room temperature are 150 mg/l, 190 mg/l and 420 mg/l respectively [19].

Sulphate

Sulphates are usually soluble in water and levels in public water supplies range from about 3 mg/l to over 2000 mg/l in Saskatchewan [19] although concentrations in Europe rarely exceed 200 mg/l. Sulphur dioxide emissions to air, discharges from a variety of industries such as mining and smelting, kraft pulp and paper mills and water treatment chemicals, particularly aluminium sulphate, all contribute to sulphate concentrations in drinking water, augmenting naturally occurring sulphate.

Although there are only limited data on sulphate in food this appears to be the major source of exposure when drinking water sulphate concentrations are below 100 mg/l. The average daily intake of sulphates in food in the USA is estimated to be about 450 mg [20], including sulphates used as food additives.

Sulphates appear to be well absorbed at low doses but less well at high doses [21] and sulphate is one of the least toxic anions. However high doses of sulphate, particularly magnesium sulphate, cause catharsis or purging of the bowels, and magnesium sulphate or epsom salts has been used as a purgative. These effects are not uncommon in individuals drinking water with sulphate concentrations in excess of 700 mg/l although they will adapt in time to even higher concentrations [22]. Some sensitive individuals may even suffer mild catharsis at concentrations as low as 400 mg/l [19]. The taste thresholds of sulphates are 200-500 mg/l for sodium, 250-900 mg/l for calcium and 400-600 mg/l for magnesium [22].

Chloride

Chlorides are highly soluble and are leached from rocks and soil, eventually reaching the sea. Sodium, potassium, calcium and magnesium chloride are widely used in industry in the production of industrial chemicals and fertilisers and in snow and ice control. Industrial and sewage discharges, run off from de-icing operations and saline intrusion all contribute to chloride levels in surface and ground water [23]. Chloride levels in unpolluted waters can be below 10 mg/l but concentrations in drinking water are often higher than this. In the UK, chloride concentrations in a number of rivers ranged between 11 and 42 mg/l [24] while in the USA, aquifers prone to seawater intrusion have reached 460 mg/l [25].

Chloride in drinking water normally contributes less than 2% to the average dietary intake of about 6 g/day [19]. Chloride is an essential element and the chloride ion does not appear to have an adverse effect on health itself. The toxicity of chlorides depends on the associated cation.

The primary problem with chloride in drinking water, apart from a contribution to the corrosivity of the water, is its effect on taste. The taste threshold of the chloride anion is dependent on the associated cations and the taste thresholds for sodium, calcium and potassium chloride are 210, 222 and 310 mg/l, respectively [19].

Nitrate

The major source of nitrates in drinking water is from agricultural activity, particularly the breakdown of plant material in the soil when there is no plant growth to take up the released nitrate. Excess fertiliser and wastes containing organic nitrogen first decompose to ammonia and then undergo oxidation to nitrate. Concentrations of nitrate in surface water are usually less than about 18 mg/l but may be higher where there is agricultural run off or contamination with animal waste or sewage effluent. In groundwater, natural levels of nitrate do not normally exceed 10 mg/l [26] however in aquifers in regions of significant agricultural activity, concentrations of nitrate may reach several hundred milligrams [27].

As a consequence of changes in land use and more intensive agriculture, concentrations in affected groundwater have been steadily rising over the past 20 years [28]. There is often a long delay in nitrates reaching groundwater which can mean that even when surface inputs stop the levels in groundwater will continue to rise for some time after. In some cases this can be for 10 years or more.

For most individuals, vegetables are the main source of nitrates although meats, particularly cured meats, may contain significant levels. Vegetable and fruits usually contain between 200 and 2500 mg/kg nitrate with vegetables such as betroot, lettuce and spinach being particularly high in nitrate [29]. The intake of nitrate from the diet varies between about 40 to 130 mg/day [27] so water with nitrate levels at or above the most common drinking water standard of 50 mg nitrate/l can make a significant contribution to nitrate intake.

The impact of nitrate on health primarily relates to bottle-fed infants and is caused by the reduction of nitrate to nitrite in the body and the subsequent oxidation of haemoglobin to methaemoglobin. This leads to a reduction in oxygen transport which manifests itself as blue-baby syndrome or methaemoglobinaemia when the proportion of methaemoglobin reaches 10%, compared to normal levels of <1 to 3%. The problem seems to be confined to infants since older children appear to be much more resistant to the formation of methaemoglobin [30].

Bottle-fed infants under 3 months of age are particularly vulnerable to methaemoglobin formation for four reasons:

1) a high intake of water in relation to body weight;

2) a high stomach pH allowing growth of bacteria which convert nitrate to nitrite;

3) foetal haemoglobin which is present in the first few months of life is more readily oxidised to methaemoglobin;

4) deficiency of the enzymes which convert methaemoglobin back to haemoglobin [19].

Most cases of methaemoglobinaemia occur at nitrate concentrations in excess of 100 mg/l but a tiny proportion of cases do occur at concentrations between 50 and 100 mg/l. Most instances of infantile methaemoglobinaemia are associated with the use of microbiologically contaminated well water, and the presence of concomitant gastro-intestinal infections is strongly implicated in the formation of clinical blue-baby syndrome [19, 27, 31].

These findings are the basis of the commonly adopted drinking water standards of 50 mg/l which would appear to give a reasonable margin of safety if the microbiological quality of the supply is maintained.

There have been suggestions that nitrate when reduced to nitrite can react with nitrosatable compounds, such as certain amines, in the human gastro-intestinal tract to form N-nitroso compounds many of which are carcinogenic in laboratory animals. There have been a number of epidemiological studies which have been assessed by WHO [27] who found no convincing evidence for an association between gastric cancer and drinking water nitrate concentrations up to 45 mg/l. The evidence for an association with higher levels was difficult to assess because the data are inadequate. Further studies have been carried out since the WHO review [31] and the association of gastric cancer and drinking water nitrate remains unproven. It must be considered that, at present, the weight of evidence is heavily against there being such an association.

Other effects which have been suggested to be associated with nitrate in drinking water are congenital malformation, cardiovascular effects and effects on the thyroid (goitre). However the observations were either not confirmed in subsequent studies, as with the data on congenital malformations and goitre or the data are inconsistent [27, 31].

Other inorganic contaminants

There are many inorganic contaminants found in water which are usually present at lower concentrations than the major components. Some of these are of major interest either because of demonstrated health effects or suggestions of possible associations with health effects.

Aluminium

Aluminium occurs naturally in surface and groundwaters but it is increased in acid conditions, and acid precipitation facilitates leaching from soils to water. In surface waters aluminium appears to be associated with particulate and colloidal matter and with high molecular weight organic complexes [32]. It is also widely used in the form of aluminium sulphate as a coagulant in water treatment. This can lead to residual aluminium in supply and, particularly in older treatment works or those not operating under optimal conditions, these residuals can reach several hundred micrograms per litre. Aluminium in treated water appears to be present as low molecular weight hydroxides [32]. When residuals exceed about 100 μg/l, deposition of floc in distribution can occur and this can lead to dirty water problems for consumers, particularly if iron is present.

In the 1970's a condition was identified in dialysis patients which was characterised by insidious onset of altered behaviour, dementia, speech disturbance, muscular twitching and convulsions and was termed dialysis dementia. Patients were shown to have substantially elevated serum aluminium levels and high concentrations in many tissues including brain. A correlation between aluminium in water used to prepare dialysate fluid was established and controlling this and other sources of aluminium, including phosphate binders, resulted in control of the condition [33].

The first symptoms of Alzheimer's disease, a progressive form of senile dementia, are memory lapses, disorientation and confusion which mark the start of progressive mental deterioration. The identification of aluminium associated with the two characteristic lesions in the brain led to the hypothesis that aluminium may play a key role in the aetiology of the disease, particularly since aluminium appeared to be causal in dialysis dementia. Three ecological epidemiological studies showed some association between aluminium in drinking water and the incidence of Alzheimer's disease. However care must always be taken in interpreting the results of such studies and these associations do not prove causality. In addition the biological plausibility of a simple causal role for aluminium in drinking water, a relatively minor source of aluminium exposure, would need to be demonstrated. There are many hypotheses for the aetiology of Alzheimer's disease and there is evidence for a genetic component. It is of course still possible that aluminium will be shown to play a role in Alzheimer's disease but, at present, this still remains unproven.

Arsenic

Arsenic is usually only present in waters at concentrations of 1-2 μg/l but in waters associated with arsenic containing rocks, such as in some parts of Taiwan or Chile, then concentrations of milligrams per litre have been observed [34, 35]. The speciation of arsenic in drinking water is not well characterised, but it is apparently present in the inorganic form. This is in contrast to food in which about 75% is present as organic arsenic [36]. The mean intake of arsenic from food ranges from about 16 to 130 µg for adults but only about 1 to 16 µg for children. However intakes may be higher in areas with arsenic rich soils [36, 37].

Soluble inorganic and organic arsenicals are readily absorbed from the gastrointestinal tract and excretion is primarily in urine [19]. There is evidence for arsenic being an essential element [36] and this is still under investigation. However arsenic in drinking water is clearly associated with cardio-vascular and skin pathology and with skin cancer and there is strong evidence of causality. Arsenic is one of the few compounds classified by IARC in group 1, known to be carcinogenic to humans [38]. There are data relating to effects in human populations as a consequence of exposure to arsenic from drinking water from Taiwan, Chile, Mexico, the United States and Canada [39]. Dermal lesions are the most common symptoms observed in chronically exposed populations, followed by peripheral vascular lesions.

The most extensive data relate to small communities in Taiwan in which there was a dose related increase in skin cancer, dermal lesions and peripheral vascular disease in groups consuming well water containing from 0.3 mg/l, to in excess of 0.6 mg/l [40]. The data are however complicated by the presence of other compounds and there appears to be little information on exposure to arsenic from food. This makes quantitative extrapolation difficult. These findings were confirmed by a study in a Mexican population exposed to about 0.1 mg/l compared to a similar population exposed to between 0.005 and 0.007 mg/l [41].

There is still considerable controversy relating to the quantitative relationship between arsenic in drinking water and skin cancer. Borzsonyi *et al.* [42] have not found an increase in arsenic related disease, observed in other studies, in populations in Hungary exposed to significantly elevated concentrations of arsenic in drinking water. Further studies will be required before the true position with regard to the risks from arsenic contamination of drinking water can be established.

Barium

Barium is found in both igneous and sedimentary rocks and can be leached by water of low pH, as the nitrate or one of the halides. These natural sources are the prime reason for the presence of barium in drinking water and barium can be found at concentrations ranging from a few micrograms to several milligrams per litre [43]. Levels of barium in food are low and the total intake of barium at low water concentrations is about 1 mg/day. At higher concentrations, water is clearly the major source of barium in all except occupationally exposed individuals.

Barium is primarily of interest because it has been shown to cause significant and persistent increases in mean systolic blood pressure in a study in rats, with a no observed adverse effect level of 0.51 mg/kg body weight/day and a lowest observed adverse effect level of 5.1 mg/kg body weight/day [44].

Studies in exposed human populations indicate that there is no correlation between barium intake and changes in cardiovascular disease. Some studies have shown a negative association [45, 46]. However a study of Illinois communities showed significantly higher death rates for all cardiovascular disease and heart disease, when the data were adjusted for age and sex, in those with concentrations of barium from 2-10 mg/l compared to those with <0.2 mg/l [47] although there were some confounding factors such as use of domestic water softeners for which it was not possible to control. In a subsequent study in Illinois which included measurements of blood pressure, these data were not confirmed and there appeared to be no adverse effects measurable in a population drinking water with barium concentrations in excess of 7 mg/l [48]. No changes were observed, other than an increase in total serum calcium in a small number of healthy volunteers given barium in drinking water for 8 weeks but the number of subjects was small and the period of exposure short [49].

The significance, if any, of barium in drinking water remains to be determined. At present the human data indicate that man is not more sensitive than the rat and that barium in drinking water is probably of little concern except perhaps at extreme concentrations.

Boron

Boron is found in sea and estuarine water at concentrations of between about 3 to 5 mg/l and in fresh and drinking waters it can be found at concentrations varying from a few micrograms to 18 mg/l [23, 50]. The median concentration measured in US drinking waters was 0.12 mg/l [51].

Boron chemistry in water is poorly characterised but it would appear that boron is probably normally present in the form of undissociated boric acid [51]. The total intake of boron from the diet is estimated to be between 1 and 5 mg/day. Boron as boric acid is rapidly absorbed from the gastrointestinal tract in humans [51].

Boron appears to be of low toxicity but the main adverse effect in laboratory animals associated with high doses, in excess of about 9 mg/kg body weight per day, appears to be testicular atrophy [52-54]. The significance for humans is not clear at present since no epidemiological studies of human populations exposed to the higher levels of boron found in drinking water appear to be available.

However total human exposure is more than an order of magnitude below the lowest no observed adverse effect levels in animals even as a worst case, and more that two orders of magnitude in most cases. It would therefore appear that boron in drinking water at the reported typical concentrations is of little concern.

Chromium

Chromium from natural sources is only found in drinking waters at low concentrations of up to 2 or 3 µg/l. Chromium occurs as Cr (VI) and Cr (III) with the former being the more soluble form. The major source of chromium in most surface water and some shallow groundwaters is human industrial activity and concentrations in excess of 50 µg/l have occasionally been reported [19, 55, 56]. Food is normally the major source of chromium in the diet, but drinking water can make a significant contribution in some circumstances. The total intake of chromium from food and water is estimated to be between 52 and 943 µg/day [56].

Absorption of chromium is dependent on the speciation, with chromium (VI), due largely to its greater solubility, being more readily absorbed than chromium (III). In human studies absorption from the gastrointestinal tract has been shown to be up to about 10% [56, 57]. In the body, Cr (VI) is readily transported though the cell membrane where it is rapidly reduced to Cr (III), the form which binds to macromolecules. Cr (III) does not penetrate the cell membrane.

Chromium is an essential element in human nutrition and is necessary for glucose metabolism in particular. The daily requirement for adults is estimated to be from 0.5 to 2 µg of absorbed chromium (III).

Chromium (VI) has been shown to be carcinogenic to humans by inhalation in occupationally exposed populations. IARC classify Cr (VI) in group 1 but Cr (III) is considered to be not classifiable as to carcinogenicity to humans. The difference probably reflects the differing ability of the different forms of chromium to penetrate cell membranes. There is also evidence that Cr (VI) is genotoxic *in vitro*, and *in vivo* in occupationally exposed human groups [58, 59].

In laboratory animals, Cr (VI) has been studied for carcinogenicity by the oral route [60, 61] but the data are inadequate for proper evaluation.

The dogma relating to chromium in drinking water has been that chromium is not carcinogenic by the oral route.

Although there is evidence to support the view that it is not likely to be very potent, it has not been demonstrated satisfactorily that high concentrations are not carcinogenic. However chromium is an essential element and at present it would appear that although the basis of the drinking water value of 50 µg/l commonly used as a standard [19] is not very clear, this concentration is unlikely to have any adverse impact on human health.

Fluoride

Fluoride commonly occurs in the form of minerals such as fluorspar, cryolite and fluorapatite. Aluminium, calcium and magnesium fluorides are of low solubility in water but sodium fluoride is highly soluble. Many waters contain low levels of fluoride, less than 1 mg/l, but in supplies associated with fluoride rich minerals, particularly from underground sources, concentrations may exceed this and may even reach 10 mg/l [19, 62]. However fluorides are added to drinking water in many parts of the world in order to prevent dental caries and in these circumstances drinking water concentrations are usually adjusted to somewhere between 0.6 and 1.5 mg/l.

Most foodstuffs contain traces of fluoride and some plants, such as the tea plant, accumulate high concentrations while fluoride is added to dental preparation such as toothpaste. In some parts of the world, particularly China, there is a high fluoride level in coal and inhalation can be a major source of exposure.

Fluorine, as fluoride, is an essential element which is involved in mineralisation of teeth and bones. There is a significant body of data which indicates that fluoride concentrations in drinking water between 0.6 and 1.0 mg/l, depending on consumption, has a beneficial effect in reducing dental caries [19]. Above a concentration of between 1.5 and 2.0 mg/l in a temperate climate there is sometimes an objectionable increase in mottling of tooth enamel which appears to be primarily of cosmetic significance [19, 62, 63]. However the exact concentration at which such effects occur is clearly dependent on the quantity of drinking water consumed and exposure from other sources. This will also apply to changes in bone discussed below, but water usually becomes the single most important source at concentrations in excess of about 5 mg/l.

Increasing bone density is observed at concentrations in excess of 3-6 mg/l and crippling skeletal fluorosis with significant deformation of the skeleton occurs with long term exposure to concentrations in excess of about 10 mg/l [19, 62, 64]. The USEPA have considered fluoride from the point of view of skeletal fluorosis and consider a standard of 4 mg/l to be sufficiently protective [63].

Concern over fluoridation and cancer has been expressed, often in association with the activities of anti-fluoridation pressure groups. IARC have evaluated the several epidemiological studies of fluoride in drinking water and cancer and have concluded that they do not provide adequate evidence of carcinogenicity in humans [65]. More recently, studies in laboratory animals given very high doses of fluoride do not provide any significant evidence for the carcinogenicity of fluoride [66, 67].

The controversy over the artificial fluoridation of drinking water will doubtless continue. That fluoride can cause adverse effects is beyond dispute and concentrations in drinking water can make a major contribution to fluoride exposure. There is however a gradual spectrum of change with increasing concentration which takes fluoride through the range of benefits into the range in which serious adverse effects can occur, although this latter circumstance is very unusual.

Iron

Iron is one of the most abundant elements in the earth's crust and is found as a range of salts and minerals, e.g. oxides, hydroxides, carbonates and sulphides both as Fe (II) and Fe (III).

In anaerobic groundwaters, where iron is present as ferrous ion (Fe II), concentrations can be up to 10 mg/l but less than 3 mg/l is more typical. Iron salts are used as coagulants in drinking water and cast iron pipes may increase the concentrations of iron in drinking water.

However, except in some anaerobic groundwaters, the concentration of iron in drinking water is usually less than 0.3 mg/l [19]. Above about 0.1 mg/l deposition of iron in pipes may occur and if aluminium is also present this can lead to dirty water problems. At concentrations above 0.3 mg/l staining of laundry and plumbing fittings such as basins can occur and such water may impart an unpleasant taste to beverages. Ferrous salts are unstable under normal drinking water conditions and will precipitate as rust coloured ferric salts such as ferric hydroxide.

Iron is an essential element and the daily requirement is approximately 1.0 mg for males and 1.5 mg for females but iron is poorly absorbed and the adequate intake is about 10 mg and 18 mg, respectively, for adults [68].

The Joint FAO/WHO Expert Committee on Food Additives [69] established a provisional maximum tolerable daily intake of 0.8 mg/kg body weight for iron from all sources except iron oxides used for colouring agents and iron supplements taken during pregnancy or for specific clinical requirements. This figure was proposed as a precaution against excessive iron storage in the body.

Under these circumstances it is difficult to identify a realistic situation in which iron in drinking water would have an adverse effect on health, particularly since the aesthetic condition of the water would be very unpleasant.

Manganese

Manganese is an extremely abundant element, occurring mainly with iron, and concentrations in lakes and rivers range from 1 to about 600 µg/l [70, 71]. Like iron, higher concentrations can occur under reducing conditions found in some deep lakes and groundwaters. Levels in drinking water are usually less than about 30 µg/l but higher concentrations are encountered. Concentrations from about 20 µg/l can lead to precipitation in distribution systems as manganous compounds which tend to be oxidised to manganese oxides which in turn, can give rise to dirty water problems [19].

Manganese is an essential element but no manganese deficiency has been identified in humans. WHO [72] indicated that the usual daily manganese intake of 2 to 3 mg appeared to be adequate and NRC [68] estimated an intake of 2.5 to 5.0 mg as safe and adequate for adults, with corresponding lower levels for children.

In general, manganese has been considered to be of low toxicity but it is a well established neurotoxin at high doses by the inhalation route. Manganese is observed in individuals occupationally exposed to elevated concentrations of 0.1 to 1.0 mg/m^3 [73]. However manganese appears to be poorly absorbed from the gastrointestinal tract although it is possible that soluble manganese in drinking water is more bio-available than manganese from food. There is little evidence to support the contention that manganese is a significant environmental toxin by the oral route. In Japan, symptoms of neurotoxicity were reported in a number of individuals, particularly among the elderly, in a population exposed to contaminated well water containing manganese at a concentration which was probably close to 30 mg/l [74].

However there were also high concentrations of other metals present so the conclusions are not clear cut.

More recently, an epidemiological study in elderly people in Greece concluded that progressive increases in manganese levels in drinking water were associated with higher prevalences of the signs of neurological deterioration in elderly people. The authors concluded that this was consistent with chronic manganese poisoning.

The concentrations of manganese in the control region was 3.6-14.6 µg/l and in the test regions 81-282 µg/l and 1800-2300 µg/l, but no data were given on exposure from other sources [75]. By contrast a population in Japan, drinking water containing 0.75 mg/l, showed no apparent adverse effects [76] nor were adverse effects noted in an early study of patients given 9 mg manganese per day for an extended period [77].

The questions over the health impact of high levels of manganese in drinking water still remain to be resolved.

However it is highly probable that aesthetic degradation of waters will occur at concentrations well below those which could be suspected of causing even minor neurological changes.

Selenium

Selenium concentrations in drinking water are usually less than 10 µg/l but in areas with seleniferous rocks, concentrations can reach several hundred micrograms/litre [78]. For example concentrations of 50 to 160 µg/l have been determined in such an area in China. Exposure from food is usually from meat and sea-food, although selenium can be significantly elevated in crops grown in high selenium soils. The intake from food is estimated to be about 60 µg/day and even in areas with high selenium in drinking water, selenium intakes from this source may still be much smaller than from local food grown on selenium rich soils. There appears to be evidence that selenium is well absorbed from both food and drinking water [79].

Selenium is an essential element although there are few reports of selenium deficiency in humans. The recommended daily intakes for adults and infants are 0.9 µg/kg and 1.7 µg/kg, respectively [68].

There are many instances of adverse effects in human populations exposed to high levels of selenium in food.

These are primarily manifested as brittle hair and nails, skin lesions, mottled teeth and, in some cases, changes in peripheral nerves [78]. The levels of exposure resulting in clinically detectable adverse effects appear to be in excess of about 0.6 mg/day, but other factors relating to nutritional status may also be important. Recent studies by Yang *et al.* [80, 81] seem to indicate that a no adverse effect level in humans is about 4 µg/kg body weight/day which is not greatly in excess of the recommended daily intakes. Further research is required on the toxicity of selenium, its essentiality and the contribution from drinking water to total intake.

Metals primarily associated with plumbing materials

There are several metals which are primarily found in drinking water as a consequence of their use in domestic plumbing for service connections or in distribution systems. The most notable of these is lead which has been used in water supply since Roman times. Concentrations of lead are likely to be high following overnight or longer periods of stagnation in lead pipes, particularly in areas with soft acidic waters.

In the past 10 years there has been increasing evidence that children in particular can suffer neurological changes at concentrations lower than previously anticipated. This has in turn led to action in many countries to reduce exposure from food by banning lead solders, from dust by the removal of lead from paint and from air and dust by the removal of lead anti-knock agents from petrol. In addition efforts have been made to reduce the plumbosolvency of, and therefore lead levels in, drinking water in vulnerable areas. It is against this background, coupled with improved methods of analysis, that blood lead levels in the general population appear to be falling.

The Joint WHO/FAO Expert Committee on Food Additives and Contaminants [82] has established a provisional tolerable weekly intake (PTWI) of 25 µg lead/kg body weight on the basis that lead is a cumulative toxin and there should be no accumulation of body burden. This figure was derived from metabolic studies in infants which showed that 3-4 µg/kg body weight was not associated with an increase in blood lead levels or lead retention [82-84]. The PTWI would be exceeded by a 5 kg bottle fed infant receiving 0.75 l water per day at the current drinking water standard in Europe of 50 µg/l. Under these circumstances treating water to reduce plumbosolvency can only achieve limited success and a programme of replacing lead plumbing and service connections and some kinds of fittings, in conjunction with a ban on lead solder for other types of metal plumbing will be required to significantly reduce lead in drinking water.

Other metals associated with plumbing are copper from copper piping, zinc from galvanised pipe and brass fittings, cadmium from galvanised pipe and nickel from nickel plated fittings. Copper and zinc both give rise to aesthetic problems as a consequence of high levels due to corrosion or from long retention times in service pipes or the distribution system. Copper gives rise to taste problems at concentrations above about 5 mg/l and will stain fittings at concentrations in excess of 1 mg/l. It is rarely present in drinking water at concentrations sufficient to cause adverse health effects but it is a gastric irritant and may cause gastric disturbances, such as vomiting, in susceptible individuals at concentrations above about 3 mg/l. Recently a number of cases of infantile cirrhosis have been associated with elevated waterborne copper in Germany. However this appears to be due to a defect in biliary copper excretion.

Zinc gives rise to an astringent taste and opalescence at concentrations of about 5 mg/l. There have been suggestions that high zinc intakes may cause a reduction in serum high-density lipoprotein [85] but this remains to be confirmed. However zinc levels in water seem unlikely to be significant with regard to human health.

Nickel concentrations of several hundred micrograms may be found in water as a consequence of leaching from nickel-chromium plated fittings [86]. Nickel is a common skin allergen and, at this concentration, it is probable that at least some sensitised individuals would react to a challenge of nickel in water used for washing or drinking.

Discussion

Inorganic substances occur in drinking water as a consequence of dissolution from natural sources and, in some cases, as a consequence of man's activities. This includes pollution of raw water sources but it also includes the use of inorganic substances in water treatment, distribution and plumbing systems. There is insufficient scope here to discuss all of the different inorganics found in drinking water. However this note is an attempt to present some of the most significant and some of the more controversial.

The aesthetic characteristics of drinking water are largely determined by both the quantitative and qualitative nature of the inorganic substances present.

These substances play a major role in the operation of drinking water supplies, influencing corrosion and scale deposition. In addition they may have a significant impact on public health, both positively and negatively.

The inorganics have been less well studied than might be expected and questions relating even to hardness remain to be resolved. The difficulties which are encountered are the need, in many cases, to study human populations with all the attendant problems of confounding variables such as the measurement of effects and exposure, since often there are no good animal models of the relevant disease process. Knowledge of the speciation in drinking water is frequently limited and speciation may be complex.

Often it is not known whether bioavailability is different from food and water and the daily requirements for essential elements may be poorly understood.

The bioavailability question is of particular importance since this can have a substantial impact on how the levels of a particular element in food and water are viewed. It will be a major factor in determining how much of an acceptable daily intake should be allocated to either food or water. Speciation can also be important in this context since variations in the availability of different chemical species will be a major determining factor in quantitative risk assessment from epidemiological studies.

Inorganic substances will continue to be of major importance as an integral part of, or as contaminants in, drinking water. There is a continuing need for research on these substances, many of which have been clearly demonstrated to have both beneficial and adverse effects on human populations as a consequence of exposure through drinking water.

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