Sulfate in Drinking-water

Background document for development of
WHO *Guidelines for Drinking-water Quality*

Preface

One of the primary goals of WHO and its member states is that "all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water." A major WHO function to achieve such goals is the responsibility "to propose ... regulations, and to make recommendations with respect to international health matters ...."

The first WHO document dealing specifically with public drinking-water quality was published in 1958 as *International Standards for Drinking-water*. It was subsequently revised in 1963 and in 1971 under the same title. In 1984–1985, the first edition of the WHO *Guidelines for Drinking-water Quality* (GDWQ) was published in three volumes: Volume 1, Recommendations; Volume 2, Health criteria and other supporting information; and Volume 3, Surveillance and control of community supplies. Second editions of these volumes were published in 1993, 1996 and 1997, respectively. Addenda to Volumes 1 and 2 of the second edition were published in 1998, addressing selected chemicals. An addendum on microbiological aspects reviewing selected microorganisms was published in 2002.

The GDWQ are subject to a rolling revision process. Through this process, microbial, chemical and radiological aspects of drinking-water are subject to periodic review, and documentation related to aspects of protection and control of public drinking-water quality is accordingly prepared/updated.

Since the first edition of the GDWQ, WHO has published information on health criteria and other supporting information to the GDWQ, describing the approaches used in deriving guideline values and presenting critical reviews and evaluations of the effects on human health of the substances or contaminants examined in drinking-water.

For each chemical contaminant or substance considered, a lead institution prepared a health criteria document evaluating the risks for human health from exposure to the particular chemical in drinking-water. Institutions from Canada, Denmark, Finland, France, Germany, Italy, Japan, Netherlands, Norway, Poland, Sweden, United Kingdom and United States of America prepared the requested health criteria documents.

Under the responsibility of the coordinators for a group of chemicals considered in the guidelines, the draft health criteria documents were submitted to a number of scientific institutions and selected experts for peer review. Comments were taken into consideration by the coordinators and authors before the documents were submitted for final evaluation by the experts meetings. A "final task force" meeting reviewed the health risk assessments and public and peer review comments and, where appropriate, decided upon guideline values. During preparation of the third edition of the GDWQ, it was decided to include a public review via the world wide web in the process of development of the health criteria documents.

During the preparation of health criteria documents and at experts meetings, careful consideration was given to information available in previous risk assessments carried out by the International Programme on Chemical Safety, in its Environmental Health Criteria monographs and Concise International Chemical Assessment Documents, the International Agency for Research on Cancer, the joint FAO/WHO Meetings on Pesticide Residues and the joint FAO/WHO Expert Committee on Food Additives (which evaluates contaminants such as lead, cadmium, nitrate and nitrite, in addition to food additives).

Further up-to-date information on the GDWQ and the process of their development is available on the WHO internet site and in the current edition of the GDWQ.

Acknowledgements

Acronyms and abbreviations used in the text

EPA   Environmental Protection Agency (USA)

OME   Ontario Ministry of the Environment

USA   United States of America

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1. GENERAL DESCRIPTION

1.1 Identity

Sulfates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) (Greenwood & Earnshaw, 1984). These dissolved minerals contribute to the mineral content of many drinking-waters.

1.2 Organoleptic properties

Reported taste threshold concentrations in drinking-water are 250–500 mg/litre (median 350 mg/litre) for sodium sulfate, 250–1000 mg/litre (median 525 mg/litre) for calcium sulfate and 400–600 mg/litre (median 525 mg/litre) for magnesium sulfate (NAS, 1977). In a survey of 10–20 people, the median concentrations that could be detected by taste were 237, 370 and 419 mg/litre for the sodium, calcium and magnesium salts, respectively (Whipple, 1907). Concentrations of sulfates at which 50% of panel members considered the water to have an "offensive taste" were approximately 1000 and 850 mg/litre for calcium and magnesium sulfate, respectively (Zoeteman, 1980).

Addition of calcium and magnesium sulfate (but not sodium sulfate) to distilled water was found to improve the taste; an optimal taste was found at 270 and 90 mg/litre for calcium and magnesium sulfate, respectively (Zoeteman, 1980).

1.3 Major uses

Sulfates and sulfuric acid products are used in the production of fertilizers, chemicals, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents and emetics. They are also used in the mining, wood pulp, metal and plating industries, in sewage treatment and in leather processing (Greenwood & Earnshaw, 1984). Aluminium sulfate (alum) is used as a sedimentation agent in the treatment of drinking-water. Copper sulfate has been used for the control of algae in raw and public water supplies (McGuire et al., 1984).

1.4 Environmental fate

Sulfates are discharged into water from mines and smelters and from kraft pulp and paper mills, textile mills and tanneries. Sodium, potassium and magnesium sulfates are all highly soluble in water, whereas calcium and barium sulfates and many heavy metal sulfates are less soluble. Atmospheric sulfur dioxide, formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulfate content of surface waters. Sulfur trioxide, produced by the photolytic or catalytic oxidation of sulfur dioxide, combines with water vapour to form dilute sulfuric acid, which falls as "acid rain" (Delisle & Schmidt, 1977).

2. ANALYTICAL METHODS

Sulfate in aqueous solutions may be determined by a gravimetric method in which sulfate is precipitated as barium sulfate; the method is suitable for sulfate concentrations above 10 mg/litre (ISO, 1990).

3. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

3.1 Air

Levels of sulfate in air in Ontario, Canada, have been found to range from 3.0 to 12.6 $\mu g/m^3$, with a mean of 7.0 $\mu g/m^3$ (OME, 1987). In a nationwide survey in the USA, sulfate concentrations in air ranged from 0.5 to 228 $\mu g/m^3$, the means ranging from 0.8 to 31.5 $\mu g/m^3$ (US EPA, unpublished data, 1984). The average daily intake of sulfate from air based on these means and on the assumption that 20 m^3 of air are inhaled daily would be in the range 0.02–0.63 mg.

3.2 Water

Sulfate concentrations in rain in Canada ranged between 1.0 and 3.8 mg/litre in 1980 (Franklin et al., 1985). An annual mean value of about 6 mg/litre in precipitation over central Europe has been reported (WHO/UNEP, 1989). Levels of sulfate in rainwater and surface water correlate with emissions of sulfur dioxide from anthropogenic sources (Keller & Pitblade, 1986).

Seawater contains about 2700 mg of sulfate per litre (Hitchcock, 1975). According to GEMS/Water, a global network of water monitoring stations, typical sulfate levels in fresh water are in the vicinity of 20 mg/litre and range from 0 to 630 mg/litre in rivers (the highest values are found in Belgium and Mexico), from 2 to 250 mg/litre in lakes (the highest value is found in Mexico) and from 0 to 230 mg/litre in groundwater (the highest values are found in Chile and Morocco) (UNEP, 1990). Levels of sulfate in rivers in western Canada ranged from 1 to 3040 mg/litre, most concentrations being below 580 mg/litre (Environment Canada, unpublished data, 1984). Levels of sulfate in groundwater in the Netherlands were below 150 mg/litre (van Dijk-Looijaard & Fonds, 1985). In 1970, the US Public Health Service measured sulfate levels in the drinking-water sources of nine geographic areas. Sulfate was found to be present in 645 of 658 groundwater supplies and in all of the 106 surface water supplies sampled. Sulfate levels ranged from <1 to 770 mg/litre, with a median of 4.6 mg/litre. Only 3% of the water supplies sampled had sulfate levels in excess of 250 mg/litre (US EPA, 1999a).

The mean sulfate level in municipal drinking-water supplies may be increased by treatment. Thus, the mean sulfate level was 12.5 mg/litre in untreated water in municipal water supplies in Ontario, Canada, but 22.5 mg/litre in treated water (OME, unpublished data, 1987). Levels in central Canada are particularly high; in Saskatchewan, median levels of 368 and 97 mg/litre were found in treated drinking-water from groundwater and surface water supplies, respectively, with a range of 3–

2170 mg/litre (Saskatchewan Environment and Public Safety, unpublished data, 1989). In the Netherlands, the sulfate concentration of drinking-water from 65% of water treatment plants was below 25 mg/litre in 1985 (van Dijk-Looijaard & Fonds, 1985). A water quality survey carried out on British tap water supplies indicated a mean sulfate concentration of 59.5 mg/litre, with a maximum of 236 mg/litre (Powell et al., 1984).

3.3 Food

No data on the sulfate content of foodstuffs were found; however, sulfates are used as additives in the food industry (Codex Alimentarius Commission, 1992). The estimated average daily intake of sulfate in food in the USA is 453 mg, based on data on food consumption and reported usage of sulfates as additives (NAS, 1972; Informatics Inc., 1973). Sulfites and sulfides are also present in food.

3.4 Estimated total exposure and relative contribution of drinking-water

The average daily intake of sulfate from drinking-water, air and food is approximately 500 mg, food being the major source. However, in areas with drinking-water supplies containing high levels of sulfate, drinking-water may constitute the principal source of intake.

4. KINETICS AND METABOLISM IN LABORATORY ANIMALS AND HUMANS

About 30% of an oral dose of 13.9 g of magnesium sulfate heptahydrate administered in four equal hourly doses (Morris & Levy, 1983) and 43.5% of a similarly administered dose of 18.1 g of sodium sulfate decahydrate (Cocchetto & Levy, 1981) were recovered in the urine of humans within 24 h. It was estimated that approximately 73% of calcium and magnesium sulfate administered to adult male Wistar rats in the diet was absorbed (Whiting & Cole, 1986). The amount ingested, the nature of the accompanying anion and the presence of certain dietary components influence the amount of sulfate absorbed. Low doses are generally absorbed well; at high doses (such as those used to induce catharsis), the absorptive capacity is probably exceeded, so that much of the dose is excreted in the faeces.

5. EFFECTS ON LABORATORY ANIMALS AND IN VITRO TEST SYSTEMS

5.1 Short-term exposure

In short-term (28-day) studies, there were no adverse effects other than diarrhoea in weanling pigs drinking water containing 3000 mg of sulfate per litre (Paterson et al., 1979). Cattle can tolerate concentrations of sodium sulfate in their drinking-water up to 2610 mg/litre (corresponding to 527 mg/kg of body weight per day) for periods up to 90 days with no signs of toxicity except for changes in methaemoglobin and sulfhaemoglobin levels (Digesti & Weeth, 1976).

Groups of 20 male and 20 female Sprague-Dawley rats were given either tap water or bottled mineral water containing sulfate at concentrations of 9–10, 280 or 1595 mg/litre for 90 days. No gastrointestinal disturbances or other effects were noted in any group, based on the evaluation of biochemical and haematological parameters as well as a histopathological examination (Würzner, 1979).

A study was carried out in which artificially reared neonatal piglets were used as a model to evaluate the effect of inorganic sulfate on bowel function in human infants. Two experiments (an 18-day and a 16-day study) were conducted to evaluate the effects of high levels of sulfate on growth, feed intake and faecal consistency of the piglets and to determine the dose at which 50% of the pigs developed non-pathogenic diarrhoea. The study involved newborn piglets being left with the dams for a period of 48 h and then transferred to an isolated room containing an automated feeding device that dispensed liquid diet, the amount being dependent on the weight of each piglet. Initially, the piglets were fed a basal diet with no added sulfate in order to allow them to adapt to their new environment. This was done for 3–4 days, following which 40 piglets were weighed and distributed into four groups of 10, according to sex, body weight and litter origin. The groups were fed the liquid diet containing inorganic sulfate (as anhydrous sodium sulfate) at 0, 1200, 1600 or 2000 mg/litre of diet for experiment 1 over 18 days and at 0, 1800, 2000 or 2200 mg/litre of diet for experiment 2 over 16 days. The results of these studies indicated that addition of sulfate did not affect the growth of the piglets or their feed intake. At 1200 mg/litre, there was no effect on faecal consistency, but at 1800 mg/litre, the piglets displayed a persistent non-pathogenic diarrhoea. The study indicated that the level of added dietary sulfate at which 50% of the piglets developed non-pathogenic diarrhoea was between 1600 and 1800 mg/litre (Gomez et al., 1995).

6. EFFECTS ON HUMANS

Ingestion of 8 g of sodium sulfate and 7 g of magnesium sulfate caused catharsis in adult males (Cocchetto & Levy, 1981; Morris & Levy, 1983). Cathartic effects are commonly reported to be experienced by people consuming drinking-water containing sulfate in concentrations exceeding 600 mg/litre (US DHEW, 1962; Chien et al., 1968), although it is also reported that humans can adapt to higher concentrations with time (US EPA, 1985). Dehydration has also been reported as a common side-effect following the ingestion of large amounts of magnesium or sodium sulfate (Fingl, 1980).

There are subpopulations that may be more sensitive to the cathartic effects of exposure to high concentrations of sulfate. Children, transients and the elderly are such populations because of the potentially high risk of dehydration from diarrhoea that may be caused by high levels of sulfate in drinking-water (US EPA, 1999a,b).

There have been a number of studies conducted to determine the toxicity of sulfate in humans. Case reports of diarrhoea in three infants exposed to water containing sulfate at concentrations ranging from 630 to 1150 mg/litre have been presented (Chien et al.,

1968). However, the diarrhoea could not be explained as being solely due to exposure to high sulfate levels, and other factors may have played a role (e.g., consumption of infant formula with high osmolarity or the presence of microbial pathogens). These other potential causes were not addressed by the authors.

A survey in North Dakota, USA, observed a slight increase in the percentage of people who reported a laxative effect when the drinking-water contained 500–1000 mg of sulfate per litre compared with people who reported a laxative effect with water containing <500 mg of sulfate per litre (28% versus 21%). Sixty-eight per cent of people consuming water with levels of sulfate between 1000 and 1500 mg/litre reported laxative effects. Several different conclusions were drawn from this survey by different people examining the data. It was concluded that drinking-water containing ≥750 mg of sulfate per litre was associated with a self-reported laxative effect, whereas water containing <600 mg/litre was not (Esteban et al., 1997). A reanalysis of the data found that most people experienced a laxative effect when they drank water containing >1000 mg of sulfate per litre (US EPA, 1999b).

Four healthy adult subjects were provided with drinking-water containing increasing levels of sulfate (0, 400, 600, 800, 1000 or 1200 mg/litre) from sodium sulfate for six consecutive 2-day periods. In addition, in a study in which a single dose level of sulfate was used, six other volunteers received water with 0 or 1200 mg of sulfate per litre for 2 consecutive 6-day periods. In the dose range study, there was a decrease in gastrointestinal retention of food, measured by mouth to anus appearance time (using coloured markers), with increasing sulfate concentration. In the single-dose study, there was a significant increase in stool mass for the 6 days of exposure to sulfate compared with the 6 days without exposure. None of the study subjects reported diarrhoea (Heizer et al., 1997).

In a field study that was carried out to examine the risks for diarrhoea in infants exposed to tap water containing sulfate with a median concentration of 264 mg/litre and a range of up to 2787 mg/litre, compared with the risks for those not using tap water or using low-sulfate tap water, there was no significant association between sulfate ingestion and the incidence of diarrhoea for the range of concentrations studied (US EPA, 1999a).

Reviews of the literature and a study to experimentally determine a sulfate dose that would induce effects in adults concluded that it was not possible to set a health-based standard for sulfate in drinking-water and confirmed the conclusions of other workers (Backer, 2000; Backer et al., 2001).

7. CONCLUSIONS

The existing data do not identify a level of sulfate in drinking-water that is likely to cause adverse human health effects. The data from the liquid diet piglet study and from tap water studies with human volunteers indicate a laxative effect at concentrations of 1000–1200 mg/litre, but no increase in diarrhoea, dehydration or weight loss. The presence of sulfate in drinking-water can also result in a noticeable

taste; the lowest taste threshold concentration for sulfate is approximately 250 mg/litre as the sodium salt. Sulfate may also contribute to the corrosion of distribution systems.

In the light of the above considerations, no health-based guideline value for sulfate in drinking water is proposed. However, there is an increasing likelihood of complaints arising from a noticeable taste as concentrations in water increase above 500 mg/litre.

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