
Sulphate

The aesthetic objective for sulphate in drinking water is ≤ 500 mg/L, based on taste considerations. Because of the possibility of adverse physiological effects at higher concentrations, it is also recommended that health authorities be notified of sources of drinking water that contain sulphate concentrations in excess of 500 mg/L.

General

Sulphur is a non-metallic element; its common valences are -2 , -1 , 0 , $+4$ and $+6$. The three most important sources of sulphur for commercial use are elemental sulphur, hydrogen sulphide (H_2S , found in natural gas and crude oil) and metal sulphides such as iron pyrites. Hexavalent sulphur combines with oxygen to form the divalent sulphate ion (SO_4^{2-}). Sulphates occur naturally in numerous minerals, including barite (BaSO_4), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).⁽¹⁾ The reversible interconversion of sulphate and sulphide in the natural environment is known as the "sulphur cycle."^(2,3)

Sulphur, principally in the form of sulphuric acid, is one of the most widely used chemicals in industrialized society. Most sulphur is converted into sulphuric acid, close to 60% of which is used for the production of phosphate and ammonium sulphate fertilizers. World production of sodium sulphate in 1988 was estimated to be approximately 4 million tonnes; 342 076 t were produced in Canada in 1987, whereas the United States and Europe produced 985 000 t and 1.8 million tonnes, respectively.⁽⁴⁾

Sulphates or sulphuric acid products are also used in the manufacture of numerous chemicals, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents and emetics. They are also used in the mining, pulping, metal and plating industries, in sewage treatment and in leather processing.⁽¹⁾ Aluminum sulphate (alum) is used as a sedimentation agent in the treatment of drinking water, and copper sulphate has been used for the control of blue-green algae in both raw water and public water supplies in the United States.^(5,6)

Salt cake (sodium sulphate) is often produced in regions where natural brine deposits occur. Salt cake consumption has declined in recent years owing to the introduction of new methods in the chemical pulping of

wood (the major use for this mineral), which require less salt cake. In 1975, 256 385 t were consumed in Canada, compared with 188 626 t in 1984. The use of salt cake as a diluent in detergents has been estimated to account for 10% of total consumption.⁽⁴⁾

Occurrence

Sodium, potassium and magnesium sulphates are all soluble in water, whereas calcium and barium sulphates and the heavy metal sulphates are not. Dissolved sulphate may be reduced to sulphide, volatilized to the air as hydrogen sulphide, precipitated as an insoluble salt or incorporated in living organisms.⁽⁷⁾

Sulphates are discharged into the aquatic environment in wastes from industries that use sulphates and sulphuric acid, such as mining and smelting operations, kraft pulp and paper mills, textile mills and tanneries.^(7,8) Atmospheric sulphur dioxide (SO_2), formed by the combustion of fossil fuels and by the metallurgical roasting process, may also contribute to the sulphate content of surface waters. It has frequently been observed that the levels of sulphate in surface water correlate with the levels of sulphur dioxide in emissions from anthropogenic sources. In the Sudbury region in Ontario, for example, it was found that water quality changes such as an increase in pH and a decrease in sulphate, nickel and copper levels coincided with a reduction in sulphur dioxide emissions from the Sudbury metal smelters.⁽⁹⁾

Sulphur trioxide (SO_3), produced by the photolytic or catalytic oxidation of sulphur dioxide, combines with water vapour to form dilute sulphuric acid, which falls as "acid" rain or snow.⁽⁷⁾ Sulphate concentrations in rain in Canada ranged between 1.0 and 3.8 mg/L in 1980,⁽¹⁰⁾ whereas concentrations ranging from 3 to 7 mg/L had previously been measured in Toronto.⁽¹¹⁾ Measurements of snowpack (March) and rainfall (between March and April) sulphate deposition in the Algoma region of Ontario indicate levels of 7.81 and 11.01 meq/m², respectively.⁽¹²⁾

Sulphate levels in Canadian lakes typically range from 3 to 30 mg/L.⁽¹³⁾ Recent data from Ontario show similar levels in small lakes (12.7 ± 11.3 mg/L); sulphate concentrations were 7.6 mg/L in Lake Superior at Thunder Bay and 19 mg/L in Lake Huron at

Goderich.⁽¹⁴⁾ In a survey of river waters in western Canada, concentrations of sulphate ranged from 1 to 3040 mg/L; most concentrations were below 580 mg/L.⁽¹⁵⁾

Data compiled by three Canadian provinces (Nova Scotia, Saskatchewan and Alberta) indicate that, in the years 1976 to 1977, sulphate concentrations in municipal water supplies ranged from less than 10 mg/L to 1795 mg/L.⁽¹⁶⁻¹⁸⁾ Levels in central Canada were particularly high; approximately 13% of the 428 sampling locations in Saskatchewan and Alberta had sulphate concentrations in excess of 500 mg/L. In Saskatchewan, between 1970 and 1989, median levels of 368 mg/L and 97 mg/L were determined for treated drinking water from groundwater and surface water supplies, respectively, with a range of 3 to 2170 mg/L.⁽¹⁹⁾ The mean sulphate level in municipal drinking water supplies in 78 locations in Nova Scotia during 1987 to 1988 was 14.2 mg/L (range 2.0 to 110.0 mg/L).⁽²⁰⁾ In a 1989 municipal water supply survey in Nova Scotia, mean sulphate concentrations were 12.1 mg/L (N=102) in treated supplies and 15.0 mg/L (N=87) in raw supplies; a maximum of 79.0 mg/L was recorded.⁽²¹⁾ Monitoring of 17 municipal water supplies in Ontario during 1985 and 1986 found the mean sulphate concentration in the untreated water to be 12.5 mg/L, increasing to 22.5 mg/L after treatment; a maximum concentration of 83.6 mg/L was recorded in the distribution system of one water treatment plant where the sulphate concentration prior to treatment had been only 1.9 mg/L.⁽¹⁴⁾

Seawater contains about 2700 mg sulphate per litre,⁽²²⁾ and it has been estimated that 1.7 million tonnes of sulphate are added annually to the Canadian atmosphere from sea spray.⁽¹³⁾ Canadian anthropogenic sources such as base metal smelting, sour gas processing and fuel combustion contribute an estimated 3.0 million tonnes of sulphate to the atmosphere, and transboundary flow from 20 major northern U.S. locations contributes another 3.4 million tonnes.⁽¹³⁾

The level of sulphate in air has been monitored in a number of Canadian locations. A temporal study undertaken in Edmonton from 1978 to 1979 showed that the mean concentration in air was $2.1 \pm 1.1 \mu\text{g}/\text{m}^3$ (N=15, range 0.3 to $4.1 \mu\text{g}/\text{m}^3$), with the lowest mean values being recorded in November ($1.7 \mu\text{g}/\text{m}^3$) and the highest in July/August ($2.7 \mu\text{g}/\text{m}^3$).⁽¹⁰⁾ During the winter of 1983 to 1984, a sulphate concentration of $0.72 \mu\text{g}/\text{m}^3$ was measured in Portage la Prairie, Manitoba, and a concentration of $2.75 \mu\text{g}/\text{m}^3$ was measured in Tillsonburg, Ontario.⁽²³⁾ The mean sulphate concentration in air recorded in 52 stations in Ontario during 1985 was $7.0 \pm 1.7 \mu\text{g}/\text{m}^3$, with a range of 3.0 to $12.6 \mu\text{g}/\text{m}^3$.⁽²⁴⁾ In a recent survey of sulphate concentrations from 31 mostly urban sites across Canada between 1984 and 1993, mean concentrations

(N=8123) ranged from $1.6 \mu\text{g}/\text{m}^3$ (Edmonton) to $6.3 \mu\text{g}/\text{m}^3$ (Windsor); a maximum of $41.5 \mu\text{g}/\text{m}^3$ was also recorded in Windsor.⁽²⁵⁾ The data also indicate that average ambient sulphate concentrations in eastern Canada are nearly twice as high as those in western Canada. In a nationwide (U.S.) survey of 23 664 ambient air samples from 405 sites over the period 1976 to 1981, sulphate concentrations ranged between 0.5 and $228.4 \mu\text{g}/\text{m}^3$, with the mean values in each city ranging from 0.82 to $31.49 \mu\text{g}/\text{m}^3$.⁽²⁶⁾

No data on the sulphate content of foodstuffs were identified; however, both sulphites and sulphates are used as firming agents and preservatives in the food industry.^(27,28) A portion of the sulphide present in foods may also be oxidized to sulphate in the gastrointestinal tract.⁽²⁹⁾

Canadian Exposure

Data concerning the daily dietary intake of sulphates by Canadians were not found. Tabulations of possible dietary intakes of a variety of sulphate compounds used as additives in U.S. foods are available. Estimates from these data, based on food consumption values and reported usage of sulphates as additives, indicate that these substances contribute an average of 453 mg to the daily sulphate intake of Americans.^(30,31) The average daily intake of sulphur in food by adults is estimated to be 930 mg, based on dietary surveys and data on food composition, and 1100 mg, based on the assumption that the sulphur content of foods is derived from protein and is proportionately related to the nitrogen content.⁽³²⁾

If one assumes a daily drinking water consumption of 1.5 L and a sulphate concentration in drinking water of 22.5 mg/L (the mean concentration in treated drinking water from the Ontario survey),⁽¹⁴⁾ the daily intake of sulphate from this source would be less than 35 mg. However, in areas with much higher sulphate levels in drinking water, such as Saskatchewan,⁽¹⁹⁾ daily intake from this source could be over 3000 mg.

If one assumes sulphate concentrations in air of $0.006 \text{ mg}/\text{m}^3$ for eastern Canada and $0.002 \text{ mg}/\text{m}^3$ for western Canada,⁽²⁵⁾ and if daily respiratory volume is 20 m^3 of air, then daily exposure of an adult to sulphate via the inhalation route would be 0.1 mg in eastern Canada and 0.04 mg in western Canada.

Average daily intake of sulphate from drinking water, air and food is therefore approximately 500 mg, with food being the major source. However, in areas where drinking water supplies contain high levels of sulphate, such as Saskatchewan, drinking water may constitute the principal source of intake.

Analytical Methods and Treatment Technology

Sulphate in aqueous solutions may be determined by ion chromatography using a conductivity detector; the detection limit for this method is about 0.05 mg/L.⁽³³⁾

Because sulphate is highly soluble and relatively stable in water, it cannot be effectively removed using conventional water treatment processes. However, the addition of sulphate-containing chemicals to the water during the water treatment process can be reduced or eliminated.⁽³⁴⁾ In general, only demineralization techniques are effective for sulphate removal.⁽³⁵⁾

Health Considerations

Essentiality

No symptoms of sulphate deficiency have been reported in humans. No optimum dietary intake for inorganic sulphate has been suggested, mainly because the cysteine and methionine contained in dietary proteins may be oxidized to provide sulphate.

Absorption, Distribution and Excretion

In a study on seven human volunteers, it was found that about 30% or more of an orally administered dose of 13.9 g of radioactively labelled magnesium sulphate heptahydrate was recovered in the urine within 24 hours.⁽³⁶⁾ In a similar study in which five healthy men ingested 18.1 g of sodium sulphate decahydrate, 43.5% of the dose was recovered in the urine within 24 hours.⁽³⁷⁾ Approximately 73% of the dietary dose of calcium or magnesium sulphate salts administered to adult male Wistar rats was absorbed.⁽³⁸⁾ However, the amount ingested, the nature of the accompanying anion and the presence of certain dietary components influence the amount of sulphate absorbed.⁽³⁸⁾ Low doses are generally absorbed well; at higher doses (such as would be used to induce catharsis), however, the absorptive capacity is probably exceeded, so that much of the dose is excreted in the faeces.

The serum concentration of sulphate in humans ranges between 1.4 and 4.8 mg/100 mL, with a mean of about 3.1 mg/100 mL. Sulphate is present in all body tissues but is found in the highest concentration in the connective tissues, where it is present as chondroitin sulphates,^(39,40) and in the metabolically active areas of bone and teeth formation. It has been suggested that sulphated protein polysaccharides may be involved in the regulation of bone development.⁽⁴¹⁾

Excess sulphate in the blood is rapidly eliminated by urinary excretion,^(42,43) although some may be excreted in the bile^(44,45) and pancreatic fluid⁽⁴⁴⁾; as well, some reabsorption may occur in the renal proximal tubule,⁽⁴⁶⁾ especially if the quantities of sulphate ingested are sufficiently large to saturate tubular

reabsorption.⁽⁴⁷⁾ About 800 mg of elemental sulphur are eliminated daily through the urine of humans, compared with 140 mg in the faeces.⁽³²⁾ Some 85% of urinary sulphur is present as inorganic sulphates and a further 10% as organic sulphates, whereas the remainder is excreted as conjugated alkyl sulphates.⁽⁴⁸⁾ In humans, sulphate excretion is usually 0.20 to 0.25 mmol/kg bw per day,⁽⁴⁹⁾ although children have a substantially higher excretion rate on a body weight basis.

Toxic Effects

Sulphate is one of the least toxic anions. The lethal dose for humans as potassium or zinc sulphate is 45 g. The reported minimum lethal dose of magnesium sulphate in mammals is 200 mg/kg.⁽⁵⁰⁾

Sulphate doses of 1000 to 2000 mg (14 to 29 mg/kg bw) have a cathartic effect on humans, resulting in purgation of the alimentary canal.⁽⁸⁾ Water containing magnesium sulphate at a concentration of 1000 mg/L acts as a purgative in normal humans, but concentrations below this are apparently physiologically harmless to the general population.^(8,50) It is reported that humans can adapt to higher concentrations with time.⁽⁵¹⁾ Dehydration has also been reported as a common side effect following the ingestion of large amounts of magnesium or sodium sulphate.⁽⁵²⁾

In short-term (28-day) studies, weanling pigs drinking water containing sulphates at 3000 mg/L experienced no adverse effects other than diarrhoea.⁽⁵³⁾ Cattle can tolerate concentrations of sodium sulphate in their drinking water up to 2610 ppm (corresponding to 527 mg/kg bw per day) for periods up to 90 days with no signs of toxicity except for changes in methaemoglobin and sulphaemoglobin levels.⁽⁵⁴⁾ However, 69 of 200 yearling calves, 22 of which subsequently died, developed polioencephalomalacia following ingestion of a protein supplement containing 1.5% organic sulphate and drinking water containing 1814 ppm sulphate.⁽⁵⁵⁾

Other Considerations

The taste threshold concentrations for the most prevalent sulphate salts are 250 to 500 mg/L (median 350 mg/L) for sodium sulphate, 250 to 900 mg/L (median 525 mg/L) for calcium sulphate and 400 to 600 mg/L (median 525 mg/L) for magnesium sulphate.⁽³⁵⁾ Concentrations of sulphate salts at which 50% of panel members considered the water to have an "offensive taste" were approximately 1000 and 850 mg/L for calcium and magnesium sulphate, respectively.⁽⁵⁶⁾

Sulphates can interfere with disinfection efficiency by scavenging residual chlorine in the distribution system.⁽⁵⁷⁾ The presence of sulphate salts in drinking water could increase corrosion of mild steel in the delivery system.⁽⁵⁸⁾ Sulphate-reducing bacteria may be involved in the tuberculation of metal pipes. The

hydrogen sulphide produced by these bacteria may lower the aesthetic quality of the water by imparting an unpleasant taste and odour and may increase corrosion in both metal and concrete pipes.^(59,60)

Rationale

1. The major physiological effects resulting from the ingestion of large quantities of sulphate are catharsis and gastrointestinal irritation. Water containing magnesium sulphate at levels above 1000 mg/L acts as a purgative in adults. Lower concentrations may affect bottle-fed infants and adults who have just been introduced to the water.

2. The presence of sulphate in drinking water can also result in a noticeable taste. Taste threshold concentrations for various sulphate salts appear to be at or above 500 mg/L for the general population, although sensitive individuals may find the taste objectionable at lower sulphate concentrations.

3. The aesthetic objective for sulphate is therefore ≤ 500 mg/L. Because of the possibility of adverse physiological effects at higher concentrations, it is also recommended that health authorities be notified of sources of drinking water that contain sulphate concentrations in excess of 500 mg/L.

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