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SUMMARY

Nitrate levels in water sources are typically 0-10 mg l^{-1} in areas where there is no intensive agriculture. The experience of the water supply industry indicates that certain agricultural activities may lead to nitrate leaching resulting in concentrations approaching 50 mg l^{-1} and in certain instances exceeding 50 mg NO_3^- l^{-1} average over a season.

Nitrogen is an essential plant nutrient, mainly absorbed in the form of nitrate or ammonium ions and is used in protein synthesis. Plant proteins are used by animals and man as a dietary source of amino acids. The nitrogen absorbed by the plants from the soil must be replaced or agricultural productivity will not be maintained in the long term ; this is done by use of animal manure or inorganic fertilizers.

There are large quantities of nitrogen in soil. A proportion of this can be mineralised to nitrate each year; a process enhanced by tillage. Nitrate leaching increases as land use progresses from forest through grassland, to arable land, and to horticulture. The main source of nitrate leaching results from release of nitrate from soil organic matter in bare land especially during the winter. The next source of nitrate leaching to water systems occurs when the use of nitrogen fertilizer or organic manure exceeds the soil and crop capacity to utilise the nitrogen. Reduction of current fertilizer nitrate application levels would not markedly reduce nitrate leaching.

Denitrification by bacterial or geochemical mechanisms is an important natural process. Other ways of reducing the nitrate content of water are improvement of agricultural practice (prevention) or removal from water supplies (cure).

Nitrate is a normal constituent of human food, vegetables being the principle source. Estimates of dietary nitrate intake show it to lie between 30-300 mg NO_3^-/day depending upon dietary habits. The nitrate intake of vegetarians is considerably higher than that of non-vegetarians. When nitrate concentrations in potable water reach 50 mg NO_3 l^{-1} the water nitrate contributes about 55% to the daily total nitrate pool. In bottle

fed infants the water used in the preparation of the feed is the main source of nitrate. Milk itself contains less than 5 mg $NO_3^- \, l^{-1}$.

Nitrate synthesis occurs in animals and man. Nitrate balance is difficult to measure in man; it has been estimated that synthesis is about 50 mg NO_3^-/day. The rate of synthesis can be increased substantially during gastrointestinal infection.

Absorbed nitrate is excreted mostly unchanged in the urine, but some is reduced by bacteria to nitrite. All the health concerns regarding nitrate relate to this potential reduction to nitrite. The extent of nitrite production under various circumstances is not known.

Nitrite is a reactive molecule and can participate in numerous reactions with food components in the gastrointestinal tract. It is also taken up in the blood where it reacts with haemoglobin to form methaemoglobin.

There is no evidence from animal experiments that nitrate or nitrite cause cancer. Nitrate is not mutagenic. Recent epidemiological research provides no evidence that nitrate induces cancer in man.

In vitro nitrosation of dietary compounds occurs in human gastric juice yielding, among other possible reaction products, N-nitrosocompounds. Many such compounds are carcinogenic to animals. Man excretes some nitrosocompounds in urine, e.g. nitrosoproline ; this excretion is increased by simultaneous ingestion of high doses of nitrate and proline. At present it is not clear whether this excretion is influenced by variations in normal dietary nitrate intake. Although N-nitrosocompounds can be detected in several body fluids evidence suggests that injestion of nitrate does not significantly increase their concentration. Increased nitrite and nitrosocompounds levels have been detected in man suffering from a deficiency in gastric acid production.

In experiments on rodents, nitrate and nitrite reduce growth, litter size and increase relative kidney weight. Nitrite increases methaemoglobin levels and brings about histopathological changes in heart, lung, liver and kidney. The highest no-effect levels are 500 mg/kgbw for nitrate and 50 mg/kgbw for nitrite.

A principle health concern is the development of methaemoglobinaemia in infants receiving high nitrate intakes.

The normal methaemoglobin level in the blood is 0.5-2%. Use of water containing 50-100 mg NO_3^- l^{-1} for infant feed preparation results in methaemoglobin levels within the normal physiological range although possibly at the high end of the normal range.

When the methaemoglobin concentration in blood exceeds 10% the skin takes on a blue tinge, a condition termed methaemoglobinaemia. Nitrate does not produce methaemoglobinaemia; it has to be reduced to nitrite to induce the condition.

Acute infantile methaemoglobinaemia can be a rare complication in gastroenteritis irrespective of nitrate intake.

Acute infantile methaemoglobinaemia resulting from bottle feeding has been associated only with the use of high nitrate well-water and was termed well-water methaemoglobinaemia. The condition is rare and has decreased in incidence in Western Europe so that in the last 20 years it has become virtually non-existent. Most cases occurred when the well-water nitrate levels exceeded 100 mg l^{-1} ; in those cases where it was associated with lower concentrations the bacteriological status of the water was poor and/or the infants were suffering from gastroenteritis.

There is no evidence that infantile methaemoglobinaemia is caused by bacteriologically sound water supplies containing nitrate concentrations up to 100 mg l^{-1}. 98% of the European population is supplied by piped mains water treated to remove bacteriological contamination. The remaining 2% is supplied with well-water of variable quality.

The recent reductions in the acceptable upper limit for nitrate in drinking water from about 100 mg l^{-1} to about 50 mg l^{-1}, and the establishment of a guide level of 25 mg l^{-1} are not justified on two grounds. Firstly the clinical data show that infant methaemoglobin levels associated with nitrate concentrations in the range 50-100 mg l^{-1} fall within the normal physiological range (0.5-2.0%). Secondly in the few cases where the use of such water causes infantile methaemoglobinaemia the condition was associated with either gastroenteritis or the use of water of poor hygienic quality, thereby casting doubts on nitrate as a causative factor in such cases.

1. INTRODUCTION

Nitrogen is an element essential for all known plant and animal life. Nitrate, generated from the soil organic matter, is naturally occurring in soil and water, and is required for primary production of biomass. Nitrate is not bound to soil and therefore moves through soil with the soil water. Plants require nitrogen for the build-up of chlorophyll, amino acids and other essential components. Yields of crops and the productivity of livestock have increased considerably in most of the world over the last 30 years. New agricultural technology, including the use of nitrogen containing fertilizers have made this progress possible. Agricultural productivity cannot be maintained without nitrogen, be it from farm yard manure, biological fixation or inorganic fertilizers.

Water not taken up by plants or lost by evaporation percolates through the soil into lower water bearing rocks, or runs to rivers. Both ground and river water enter public piped water supplies which is therefore affected by agricultural practice.

Piped water supply, as opposed to untreated domestic well-water, has been the principle form of water supply in Western Europe for the last 30 years and about 98% of the population now receive piped-water. Local legislation has controlled the quality of these supplies since the mid 19th century. More recently controls have been based on an EC Directive (EEC, 1980). Of the 62 parameters, nitrate is listed within a group of non-toxic substances the concentration of which may exceed that stated in the Directive at the discretion of individual Member States, provided there is no danger to public health. The Directive specifies a "maximum admissible concentration" for nitrate of 50 mg NO_3^- l^{-1}, in line with the "recommended" concentration specified by WHO (1970); it also defined a target guide level of 25 mg l^{-1} without defining the criteria by which this level was agreed.

Until 1984 the WHO standard for drinking water, whilst recommending a concentration below 50 mg NO_3^- l^{-1}, classified concentrations between 50 and 100 mg l^{-1} as conditionally acceptable. Concentrations in excess of 100 mg l^{-1} were not recommended. Subsequently WHO (1984) reduced the recommended standard to 10 mg NO_3-N l^{-1} (45 mg NO_3 l^{-1}) and dispensed with the earlier defined acceptable range largely on the basis of an assumed risk of occurrence of infantile methaemoglobinaemia.

Current views on nitrate toxicity are not settled and ECETOC considered that a critical and comprehensive literature review might serve to clarify the situation and identify inconsistencies and possible mistakes in the earlier work and indicate areas where further research is desirable.

This report reviews the significance of nitrate in Western European water supplies, the role of agriculture, how nitrate reaches the water supply, nitrate intake by the human population, and its possible effect upon the man have been examined.

The terms of reference of the Task Force were to :

- establish the main sources of nitrate and quantify the nitrate content of ground and drinking water in Western Europe.

- define the main sources of nitrate intake by the Western European Consumer and the total daily nitrate intake.

- review the evidence that nitrate intake effects the health status of either individuals or populations.

- review critical evidence in relation to WHO recommendations on nitrate in drinking water, and if appropriate explain why conclusions differ.

Units

The units used to express nitrate concentration are a source of confusion. Concentration has been expressed in moles, mg NO_3^- l^{-1} or mg NO_3-N l^{-1}. WHO (1985) adopted the latter. We have chosen the conventional mg NO_3^- l^{-1} as it is employed in most of the original papers and reflects the established usage in European Water Quality

Regulations. The disadvantage is that concentrations of NO_3 and NO_2 are not immediately comparable on a molar basis.

For conversion from one system to another the following factors can be used:

1 mg NO_3^- l^{-1}	=	0.226 mg NO_3^- - N l^{-1}		
1 mg NO_3-N l^{-1}	=	4.429 mg NO_3^- l^{-1}		
1 m mole l^{-1}	=	62 mg NO_3^- l^{-1}	=	46 mg NO_2^- l^{-1}
	=	14 mg NO_3 - N l^{-1}	=	14 mg NO_2^- N l^{-1}

Glossary

Some of the agricultural, medical and chemical terms used in this document are not in every day use and are defined in the glossary (Appendix 1) to assist readers.

Literature

Much of the medical evidence cited in this and other documents (eg WHO 1970, 1985) has not been peer reviewed. Many of the reports are based on evidence as seen by the clinical investigators conducting the work at the time which with the benefit of hindsight, is often lacking in important material evidence.

The literature up to the end of 1986 should be well covered. Later papers (up to the autumn of 1987) are also included but the coverage may not be complete.

2. NITRATE CONTENT OF EUROPEAN WATER.

2.1 Background

Although this is a well investigated topic the information published in the scientific literature is inadequate and incomplete. Most information has been generated by the public water undertakings and supplied routinely to Government Departments. Summarized data for a number of European countries is given in Appendix 2.

A recent UK Government report (UK-DOE, 1986) has examined nitrate concentrations in public water supplies, current trends and future predictions. All UK public water supplies comply with a rolling 3-monthly mean nitrate concentration not exceeding 80 mg NO_3^- l^{-1}, with no individual sample exceeding 100 mg NO_3^- l^{-1}. Rivers show a seasonal pattern of nitrate levels; these are highest in the winter when drainage from the land occurs during autumn and winter rains. Fig 1 shows a long term rise and the annual variation in nitrate levels for a UK river showing high concentrations of nitrate. It will be seen that peak winter levels can exceed 100 mg NO_3^- l^{-1} and during such periods it is necessary to restrict supply to waterworks which draw water directly from the river and to provide alternative supplies.

In underground waters elevated nitrate levels are found where arable land overlies the water-bearing rock (aquifer) and there is no intervening clay barrier. High nitrate water percolates downwards and, depending on the thickness of the overlying rock takes between 5 and 40 years to reach the water table.

The extent of nitrate accumulation depends on climatic and geological conditions. Mathematical models predict that for the most severely affected area in UK levels may eventually reach about 150 mg NO_3^- l^{-1} ; this assumes a continuation of present agricultural practice (Foster *et al*, 1986). Over the last 50 years the level of nitrate in rivers and in water pumped from deep wells has risen greatly. The extent of the rise is highly variable and depends on a range of factors. There is some evidence that this trend is changing; data from monitoring at 149 stations on rivers in England, Wales and Scotland shows no significant change in the average nitrate content of river water from 1977 to 1984 although regional variations exist (UK, DOE, 1986). This apparent plateau has occurred even though fertilizer use (nitrogen/hectare) has increased considerably especially in the arable farming areas. Evidence showing a similar trend is available from some rivers in the Federal Republic of Germany (Appendix 2).

Practical and financial constraints limit the actions that may be taken by authorities in providing water to the EEC standard. Possible actions are :

1. replacement of high nitrate sources, by diverting water from low nitrate supplies by means of trunk mains.

2. controlled blending of low and high nitrate waters; this has been practised by several water authorities, however, this can only be a relatively short term measure if the general levels of nitrate in water continue to rise.

3. maximise natural denitrification by long storage in large reservoirs.

4. provide additional water treatment processes, e.g. ion exchange processes (Greene, 1980), or microbiological denitrification (Wilkinson et al, 1982). The long term health implications of such processes are unknown, so they need to be implemented with care.

5. provision of bottled water to populations identified at risk, particularly to infants under 6 months of age.

Competent authorities have to assess the effectiveness and costs of the various actions they might take to limit nitrate intake. Apparent risks (cf sections 6, 7 and 8) and the sources of contamination have to be taken into account. Closure of high nitrate sources and their replacement by low nitrate sources implies provision of new trunk water mains and the availability of low nitrate supplies. Blending also calls for alternative sources and facilities which operate seasonally.

Biological denitrification processes occur naturally within the muds when water is stored in reservoirs (Vollenweider, 1968). Both ion exchange and denitrification processes are feasible, but the costs substantial, the former is suitable for both ground and surface waters supplies and is preferred for small installations for operational reasons; the process is complicated by the need to dispose of spent regenerant brine and to maintain the final water quality. Microbiological denitrification is an alternative for surface derived waters, particularly for larger plants. Start-up is slower than for ion exchange and further physico-chemical treatment of the denitrified water is necessary. Operation and maintenance are more onerous, requiring the strict monitoring of residual methanol levels in the water. Operating experience has indicated a need for careful maintenance; this restricts such processes to manned water treatment works. Operational experience has demonstrated problems associated with intermittent high nitrite levels in the water to be treated and poor performance of monitoring equipment.

2.2 Factors influencing water Nitrate Levels

As will be described in section 7, the main public health concern arises from water derived from private wells, which supply 2% of the EEC population (based on a European Community of 10 States, excluding Spain and Portugal, for which information is not easily available).

The alternative to removal of nitrate during water treatment is reduction of the input of nitrate into the environment. This is linked inevitably to agricultural productivity and land use. A reduction of fertilizer usage would probably have minor effects on nitrate levels for the following reasons :

a. The organic nitrogen reservoir in the soil is large, and in highly productive soil systems is bound to organic material that would take many years to diminish.

b. An arable agriculture even with reduced fertilizer usage and crop yields could still produce nitrate levels in excess of 80 mg NO_3^- l^{-1}.