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REMOVAL OF NITRATES FROM DRINKING-WATER

Report on a WHO Working Group

Budapest, Hungary 2-5 September 1986

LIPPARY INTELECTIONAL REFERENCE DETERS THE CLEAR OF WATER SUPPLY AND SANELVION (JRC)

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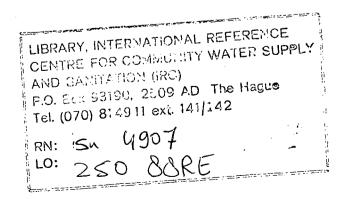
By 1990, all people of the Region should have adequate supplies of safe drinking-water, and by the year 1995 pollution of rivers, lakes and seas should no longer pose a threat to human health.

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1. Introduction

The continuous increase of nitrates in groundwater and in surface water resources represents a potential danger to water supplies. Although several promising attempts have been made by researchers to remove nitrates from drinking-water, most of the possible treatment methods need further investigation. Moreover, some of the techniques available at present have shown that they may induce secondary water quality problems.

The World Health Organization Regional Office for Europe, in cooperation with its Hungarian collaborating centre, the Research Centre for Water Resources Development (VITUKI), therefore decided to organize a working group to discuss the alternative methods available in the countries of the European Region to reduce and prevent excessive nitrate concentrations in drinking-water.

Twenty-four experts from 13 countries, including representatives of seven international institutions and organizations, attended the meeting, and some of them presented country reports or reviewed some specific aspect of the topic. Alternative nitrate removal techniques, as used in the various countries represented, were discussed in the light of the experience gained. The possibility of exploring the concomitant use of two or more nitrate removal techniques was looked into. The practicability of nitrate removal *in situ* was also explored to ascertain the potential of groundwater to be rehabilitated once it has been severely affected by excessive nitrate levels. The financial aspects of the various options were given serious consideration as important factors governing their implementation.

The Working Group divided itself into two discussion groups: group 1 discussed biological, physical and physicochemical methods of nitrate removal, and group 2 discussed the prevention of groundwater pollution with nitrates, including *in situ* removal, pollution control and the health and legal implications of these options.

2. Background information

Considering that drinking-water resources, especially aquifers near to the ground surface, are being reduced by the presence of nitrates originating mainly from agricultural production and improper disposal of municipal and industrial waste, the responsible organs of the Member States of the European Region together with WHO expressed their concern about the possible hazards represented by the presence of a high concentration of nitrates in drinking-water. Several expert meetings have discussed the possible health effects of consuming food and drinking-water containing a high concentration of nitrates and nitrogen compounds. It was recommended that this problem should be investigated to find an appropriate technical solution, permitting the recovery of contaminated water by making use of appropriate nitrate removal techniques. However, as water resources are becoming scarce, emphasis should be placed on the prevention of all kinds of pollution.

3. Presentations, by country

3.1 Austria

In Austria, the situation of nitrate contamination of water started in 1950 with a rise in the use of fertilizers of mineral origin containing

nitrogen (the amount of fertilizer used today is four times larger than that used in 1950).

The main guidance given to achieve a low nitrate content in subsoil water is to decrease nitrate contamination in the concerned catchment areas by a rational application of agrochemicals.

The exploitation of new uncontaminated sources is being intensified, and efforts are being made to decrease the nitrate content by mixing contaminated water with water of satisfactory quality.

In case the proposed precautions cannot be implemented, any technical possibility of physicochemical or biological water treatment technology has to be considered.

Nitrate removal from drinking-water by means of ion exchange or reversed osmotic processes is applied on a reduced scale. Owing to the high investment and operating costs of such systems, application is limited to special situations. General use in public water networks proved unavailing at the time, primarily for the reasons mentioned above. Furthermore, some of these procedures may result in additional environmental difficulties by raising new problems of decontamination of the chemical by-products resulting from these techniques.

At present, biological water purification techniques to reduce nitrate content in drinking-water is limited to experiments carried out by research teams of producers and distributors of water treatment equipment.

3.2 Czechoslovakia

In Czechoslovakia, the highest priority is given to protection of drinking-water resources by means of establishing protection zones. However, partly because of the increased use in agriculture of fertilizers and municipal and industrial waste and partly because of the presence of natural sources of nitrates, levels in groundwater have begun to rise.

During the past 13 years (1973-1986), nitrate levels in drinking-water have increased above $10.00 \text{ mg N-NO}_3/1$ at 1% of water produced. The level is expected to increase by much as 6-12% per year. This situation has forced national water authorities to conduct research into nitrate problems and to build up treatment plants for nitrate removal.

The denitrification of water has been solved at three levels: denitrification of water in the place of its use in homes; denitrification of water for public supply by means of de-ionization and demineralization by ion exchange and membrane processes, equipment for electrodialysis and reverse osmosis; and specific methods of chemical, biological and microbiological denitrification.

Two different types of equipment for ion exchange in private homes have been developed: BLEXPUR filter and NITROPUR filtration equipment, according to the Czechoslovak Patent AO 200 907. Its lifetime is only three days.

Specific methods of chemical, heterotrophic and autotrophic denitrification were tested in 1975-1986 with the following results.

Chemical reduction of nitrates to ammonia using reductants such as iron (Fe), iron sulfate (FeS), magnesium (Mg), aluminium (Al), zinc (Zn) and catalysers (copper (Cu) is not too satisfactory for water treatment, as the water hardness increases disproportionately). The ammonia (NH_3) produced is removed by aeration of the water in alkaline medium, and the NH_3 residue after aeration is precipitated in a magnesium phosphate precipitate.

Chemical reduction of nitrates in filtration equipment, according to the Czechoslovak Patent 114602 covering the filter material (mixed-bed metal showings Fe and Cu) and sand filter, is still being investigated for denitrification of water.

Autotrophic denitrification using green organisms (macrophyta and algae) is in the research stage. Autotrophic microbiological denitrification using hydrogen as an energy source has not yet been tested.

Heterotrophic denitrification has been tested on models and pilot plants and is now applied in routine operations. The carbon (C) source is ethanol at the ratio of $C:NO_3 = 5:1$ or less, the pH ranks from 7.3 to 8.3, and the optimal temperature is up to 8°C. Denitrification is followed by clarification, sand filtration and disinfection of the water.

Denitrification in reactors has been investigated since 1981 and is being implemented in a pilot plant with a capacity of 45 1/s in Breclav, according to the Czechoslovak invention PV 4634-84 making use of a biocatalyser.

The biocatalyser is used in the form of compacted granules (3 mm) of chemically immobilized cells of mixed or pure bacterial cultures exhibiting denitrification activity. Immobilized cells are dead, incapable of growth and multiplication but retaining the required enzymatic activities.

Water purified by denitrification is not suitable because of the oxygen content, the presence of bacteriological indicators, and eventually because of the levels of turbidity. Elimination of turbidity, which is caused by the presence of a great number of denitrified bacteria, can be reached by standard coagulation methods.

3.2.1 Biological denitrification in situ

The principle of biological denitrification is based on the injection into the subsoil of a biological agent that is infiltrated through bore holes. The biological agent is dispersed in the ground owing to the influence of diffusion and of the water flow. The presence of a biological agent increases the number of denitrifying bacteria to the required level. When a sufficient quantity of a biological agent is present and when other conditions are fulfilled, effective denitrification of water begins.

3.3 Finland

In Finland, 75% of the population are served by public water supplies that are under the health authorities' regular control.

Elevated nitrate concentrations in private wells outside the organized water supply have shown to be a growing problem. The results of investigations show that, roughly estimated, in 10% of all the samples taken from private wells in rural areas, the nitrate concentration exceeds 50 mg/l.

Concentrations higher than 100 mg/l are not very common. A few wells with a concentration of 200-400 mg/l have been found recently.

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No cases of methaemoglobinaemia have been reported.

In Finland, where a lot of unpolluted water is still available, the methods adopted to solve the problems caused by nitrates in drinking-water have been the following: using water from another source or using bottled water for baby-feeding; and closure of the water source and replacement with a lower nitrate supply, such as digging a new well, extending the public water system to the area, and transporting water from the public water supply to consumers.

3.4 France

In France, in the light of current techniques, nitrates can be removed by reverse osmosis, ion exchange or biological denitrification. DEGREMONT obtained official approval in July 1981 for a biological nitrate removal process using acetic acid, in May 1982 for a biological nitrate removal process using ethanol, and in May 1985 for an ion exchange process. Each of these official approvals was granted in the light of pilot tests carried out at the Elisabethville site (Paris region) for the biological processes or at the Plouenan site (Brittany) for the ion exchange process. DEGREMONT has built two industrial-scale plants since approval was granted.

The two plants at Chateau Landon and Champfleur have now been in service for one and two years respectively. It has been possible to draw comprehensive conclusions in relation to the operational problems encountered by comparing the use of the two different sources of carbonaceous nutrient and the effective size of the filtering media. It has been concluded from the results obtained that heterotrophic biological removal is a reliable process which can be used to produce drinking-water for distribution, which complies with official standards and which is at a cost comparable to other treatment processes.

For the ion exchange process, a pilot plant was set up near a well, located in the Ile de France region (township of Elisabethville). The pilot plant could treat 300-500 l/h. The water used in testing contained between 100 mg/l and 120 mg/l nitrates.

Testing done on two types of water (well water and stream water) demonstrated that the denitrification process using a resin ion exchanger can produce water of high quality from every point of view.

Tests revealed that the treatment is reliable. This was demonstrated by carrying out a series of shutdowns of variable lengths of time.

The resin used revealed a net capacity corresponding to a cycle of 6-12 hours in testing conditions for the treatment of water containing up to 170 mg/l NO_3 and 120 mg/l SO_4 .

There is no doubt that the primary limiting conditions for the use of resin ion exchanges is that regeneration produces eluates, heavily loaded with nitrates, sulfates, chlorides and sodium. The process can, however, be used at low temperatures (less than 8°C) when the biological process is not working perfectly.

3.5 German Democratic Republic

In the German Democratic Republic, the increasing nitrate content in drinking-water resources has necessitated the development of economically feasible nitrate removal techniques. Research was primarily directed towards the well known ion exchange process.

The ion exchange technique is a widely used procedure to reduce nitrate levels in drinking-water. The complex nature of the resins, the exchange process and technique have resulted in some concern about the concomitant water quality changes and potential health problems, such as removal of iodine as a side effect, replacement of bicarbonate (HCO_3^-) by chloride, bacterial growth on the resin surface, and release of organic and inorganic compounds from the resin. Thus, several precautions must be taken if denitrified water is to be supplied to the consumer.

The resin-treated water has to be disinfected before delivery in the drinking-water supply system, but this has to be done after resin treatment. This is necessary to prevent bacterial aftergrowth.

Resin-treated water should be blended with other drinking-water as much as possible. In this way, the risk caused by the changed ionic balance, by removal of ions other than nitrates, and by contaminants originating from the resin can be mitigated. Therefore, the nitrate concentration that remains in the treated water should be as low as possible. From the same point of view, the delivery of treated water should be stopped in the earliest point of breakthrough. It has to be ensured that a temporary increase in the nitrate concentration above the primary level is not possible.

In the hands of a well trained operational staff, the use of strongly basic-type ion exchange resins is an acceptable method for nitrate removal from drinking-water provided that there is no possibility of blocking the sources of nitrate contamination. The concomitant potential health risks of nitrate removal by ion exchange resins have to be measured by the degree of health protection that is achieved by the mitigated nitrate exposition.

3.6 Federal Republic of Germany

According to the official statistics of 1982 in the Federal Republic of Germany, the nitrate concentration in groundwater shows limits above 50 mg/l while for other water sources the nitrate concentration is below 50 mg/l.

In the different regions of the Federal Republic, from 1% up to nearly 10% of the water distributed by public water supplies show nitrate concentrations over 50 mg/1. Private supplies have bigger problems, up to 50% of them distributing water with an excess of nitrates.

Until now, no routine denitrification treatment has been carried out. All existing treatment plans are still in an experimental stage. In general, the following treatment variations are tested:

 biological denitrification: heterotrophic denitrification with ethanol (Verbandswasserwerk Langenfeld-Monheim, 300 m³/h); autotrophic denitrification with hydrogen (Stadtwerke Mönchengladbach, 50 m³/h); subterrestrial denitrification (Stadtwerke Neuss, Wasserwerk Briochdorf); and denitrification by a plant/soil filter (reed, rush) (Stadtwerke Viersen);

- ion exchange: anion exchange (regeneration with chloride or hydrogen carbonate) and complete de-ionizing methods (regeneration with NaOH/HCl); and complete de-ionizing, the CARIX method (regeneration with carbon dioxide (CO₂)) (Stadtwerke Bad Rappenau);
- reverse osmosis: reverse osmosis coupled with a concentrate treatment in three steps - softening, electrodialysis and evaporation (Stadtwerke Mönchengladbach, Wasserwerk Gatzweiler).

It is accepted that reducing the input of nitrates should have first priority to any other technical control step.

Biological methods are of special interest because of their acceptance by the population and, probably, because of their low cost range if performed on a large scale. In addition, health risks are not expected. In general, there are two different procedures available: denitrification in water processing plants using bioreactors, and *in situ* removal of nitrates in the aquifer.

Most of the experience available is related to the use of bioreactor technology. Two methods are used: NITRAZUR and DENIPOR. Both use acetic acid and activated carbon denitrification with ethanol. These are well investigated methods that work quite satisfactorily. There are difficulties, however, in the discharge of the biomasses produced and in the increase of HCO_3^- in the treated water.

In the case of heterotrophic denitrification on activated carbon at Neuss, the process is followed by aeration of the effluent and by a reinfiltration step. The DENITROPOR method, working on a greater scale at Langenfeld (50 m³/h), will provide water suited for immediate distribution.

Denitrification by means of water plants should be effective theoretically. The project implemented at Viersen is a relatively small pilot plant. The autotrophic DENITROPUR process at Mönchengladbach is very satisfactory and operates at a larger scale (50 m³/h). Hydrogen gas is used as a source of energy, while CO_2 is converted to organic carbon. The capacity could be doubled without difficulty. There is a small production of biomass by autotrophic bacteria that facilitates the handling of the sludge produced. Besides H₂, CO_2 and PO_4^{3-} must be added.

In situ denitrification is tested at Bochold. Processed sewage effluent is used as a carbon source as well as methane (CH₄). Use of CH₄ is connected with a loss of nitrates and a production of N₂ gas and of CO₂. Although there are some difficulties in keeping the infiltration wells clean, the method seems to be promising. The use of pyrites for denitrification must also be considered. The cost is relatively low in the NITRAZUR and DENIPOR methods, while the use of hydrogen gas is at present the most expensive one. Nevertheless, when technically developed, methanotrophic denitrification will be the most cost-saving procedure.

3.7 Hungary

VITUKI presented a state-of-the-art review of nitrate removal techniques and of nitrate contamination of groundwater resources in Hungary.

The main problems with nitrate contamination occur in areas of the country where the population has no access to public water supplies and where shallow wells taking water from near-surface aquifers are used. The high nitrate concentration of these water resources does not allow the use of water for consumption. Bottled water is distributed to these settlements to prevent health consequences.

The state-of-the-art review dealt with possible techniques of nitrate removal.

Reverse osmosis, electrodialysis, chemical nitrate reduction, ion exchange and various biological denitrification processes were evaluated, together with possible methods of source control.

It was found that at present ion exchange and bacterial denitrification are applied at water treatment plants producing drinking-water. Even these methods, although under operation, have disadvantages.

The growing tendency to find nitrate concentrations in water resources has become one of the most serious problems to be solved in water supply. Source control is a feasible way of reducing nitrate content, but it is evident that, because of growing expectations for increased agricultural production by spreading nitrates on soils and because of the limited funds available for municipal wastewater treatment, it is not foreseeable that there will be any drastic decrease of nitrate concentrations in water sources.

It is therefore essential to find the most appropriate method or methods of nitrate removal from water sources and to promote the use of several new and promising achievements in the field of treatment techniques. Some of the new methods may be competitive to ion exchange and biological denitrification, but it is expected that they will find practical application in the near future.

Most of these methods are still in the research phase, and some of them are being operated on a pilot-scale basis.

3.7.1 Twin-type fluidized-bed bioreactor for nitrate removal

The phase of nitrate degradation and substrate uptake of bacteria can be separated in space and time, as it is verified by the patented BIONIT denitrification system of VITUKI and the Water Works of Budapest. Thus, man-made pollution during nitrate removal can be avoided, which makes the process economical when compared with other treatment alternatives.

The most important conclusions drawn from the experiment are that denitrifying bacteria are able to work periodically, i.e. nitrate degradation and substrate uptake can be accomplished in sequential stages; the retention times necessary for nitrate removal and substrate uptake are similar; and the expected rate of nitrogen removal is $2-4 \text{ kg/m}^3/\text{d}$ when using saccharose as a source of organic carbon.

Results of the cost-benefit analysis show that the BIONIT method is competitive to other conventional systems of nitrate removal, especially in medium-capacity and large-capacity ranges.

3.7.2 Nitrate removal by apathogenic fungi (AZOTEX-B)

The principle underlying the method AZOTEX-B is that, in their biological activity, fungi use nitrates, reducing them within their cell substance. Aerobic conditions are essential for the metabolism of fungi. Since the organic content of drinking-water is low, organic matter must be added to the raw water for achieving effective nitrate removal. The unused part of this organic matter is then removed from the treated water in stages during the secondary treatment that is always unavoidable when using biological methods. A pilot plant with a capacity of 50 1/h was built and operated with promising results.

3.7.3 Combined chemical and physicochemical method of nitrate removal

Nitrates dissolved in water can be decomposed, and nitrate nitrogen can be eliminated with different organic compounds by ultraviolet irradiation of 185 nm wavelength.

The daily output of a pilot scale ultraviolet reactor of 40 W power is 3-4 litres nitrate-free water.

The main advantages of ultraviolet-promoted nitrate removal are that no special chemicals and microorganisms need to be added to the water; sterilization of water is also performed simultaneously with denitrification; and, owing to its simplicity, the method can be used in a simple device for domestic use.

It is important to mention that the capacity of the process can be considerably increased by the application of an ultraviolet reactor of large power.

3.7.4 Hygiene aspects of nitrate removal processes

Biological denitrification processes are still under investigation. The by-products of bacteria used and the remaining organic materials may cause no direct harm to human health, but they may perhaps cause or promote secondary biological or bacteriological pollution in the distribution system. More data are needed to evaluate these processes, and more knowledge is required to overcome these problems. However, more work has been implemented, and more experience has been gained by using the ion exchange method than any other method for the removal of nitrates.

The hygiene problems of ion exchange processes that have to be investigated are (a) the possible instability of the resin; (b) the need for better operational control owing to the breakthrough phenomena; (c) microbiological/bacteriological production on the surface of the resin; and (d) waste problems associated with the regeneration of the resin.

Other methods are still under small-scale investigation. Thus, hygiene evaluation of these methods is the task of the future.

3.8 Malta

In Malta, nitrate levels show an upward trend. This is particularly the case with water extracted from the perched aquifer. The origin of these high

nitrate levels is probably because of indiscriminate use of nitrogenous fertilizers in agriculture, coupled with the permeable nature of the local geology and the relatively heavy rainfall spells during the rainy season.

Blending high nitrate sources with low nitrate sources before distribution has been the traditional way of maintaining nitrate levels within acceptable standards. This method has been found very suitable under local conditions. It is not expensive, is simple to carry out and does not require expert supervision. Blending, however, may not be the solution in all situations.

During this decade, an attempt was made to introduce nitrate removal technology. An ion exchange unit was set up at Mgrarr, an area supplied from the perched aquifer. However, the plant has still to be commissioned; the main reasons for delay are lack of qualified personnel to run the plant and the prohibitive cost of resin regeneration.

Attention has also been focused in microbiological methods of nitrate reduction. Laboratory-scale experiments based on microbiological denitrification have been carried out. The aim of these experiments was to study the feasibility of nitrate removal using naturally occurring microorganisms. Methanol and sucrose served as a carbon source in these experiments. The results and experience gained in these trials are currently being evaluated.

3.9 Netherlands

In the Netherlands, the increasing nitrate load of groundwater used for drinking-water supplies called for the testing of new appropriate and economically feasible nitrate removal methods. Besides the conventional processes, two promising methods have been tested.

A new process is described for nitrate removal from groundwater: biological/physicochemical nitrate removal. This technique is a combination of biological denitrification and ion exchange, by which the disadvantages of the separate techniques can be avoided. Nitrates are removed from the groundwater by ion exchange, but the resin is regenerated in a closed circuit with the use of a denitrification reactor. Direct contact between groundwater and denitrifying bacteria is prevented, and brine production and salt requirements for regeneration are minimal.

Compared with direct biological denitrification of groundwater, the production of bacteriologically reliable drinking-water seems possible by means of simple measures. Also, groundwater with a high sulfate concentration can be treated with this technique when a nitrate-selective resin is used, such as Amberlite IRA996.

Another method is the denitrification of groundwater with the sulfur/limestone process, which is designed in the form of a slow sand filter where denitrification is induced by the *Thiobacillus denitrificans* settling on the filter media. Good results were obtained (about 70% removal capacity). However, post-treatment is necessary owing to the presence of sulfur particles, high bacteria count, assimilative organic compounds, and nitrates in the water.

3.10 Poland

In Poland, nitrates do not present major problems in drinking-water supplies, but owing to the slight increase of nitrates in water resources, a project has been started to investigate possible nitrate removal techniques.

3.11 United Kingdom

In the United Kingdom, rising concentrations of nitrates in surface waters and groundwaters have led to the development of treatment processes for nitrate removal. Both ion exchange and biological denitrification plants have been operated at full-scale.

It is estimated that about 7% of the population is periodically exposed to nitrate levels above 11.3 mg NO₃ N/1 and about 36\% to levels above 5.6 mg NO₃ N/1.

Research into methods for controlling nitrates in water supplies has been carried out by the Water Research Centre and the water authorities, particularly the Anglian Water Authorities, who have by far the greatest share of the nitrate problem in the United Kingdom.

Available options for reducing the nitrate level in public water supplies are blending with low nitrate water prior to supply; denitrification treatment; storage of raw water to allow natural denitrification to occur; and closure of the source and replacement with a lower nitrate supply.

Blending with low nitrate water prior to supply is currently the most widely applied strategy to limit nitrate concentration in public supplies in the United Kingdom. However, this option can be expensive if low nitrate water has to be piped over long distances and is limited by the availability of low nitrate water.

Storage of high nitrate raw water over lengthy periods has considerable benefits owing to denitrification in the reservoir. However, the construction of new reservoirs is expensive and could not be justified if the reservoir is provided solely for the control of nitrates. Hence, in many cases, treatment will be the only viable economic option for controlling nitrate concentrations in public supplies.

Several treatment processes have been considered for the removal of nitrates from water supplies. The two processes that show the greatest potential for application in the United Kingdom are continuous fluidized-bed biological denitrification and single-bed strong-base anion exchange.

4. Discussion

The presentations were followed by informal discussion. Questions and comments from delegates were focused on a better understanding of technical and administrative problems associated with the operation of different removal techniques.

Thereafter, the Working Group divided itself into two discussion groups: group 1 discussed biological, physical and physicochemical methods of nitrate removal and Group 2 discussed the prevention of groundwater pollution, including *in situ* removal, pollution control and the health and legal implications of these options.

The group discussions resulted in the production of an analysis of the present situation of nitrates in water supplies and of the control measures supplemented or proposed (Table 1). In addition, a list of nitrate removal techniques, used or investigated in some European countries, is given in Tables 2-4. A comparison of these techniques is presented in Table 5.

At a plenary session, the recommendations were discussed and adopted.

5. Conclusions and recommendations

(1) The continued increase of nitrates in groundwater and surface water sources is a potential danger to the water supplies in the Region, and measures to control nitrate concentrations are necessary. Although researchers have made several promising attempts to remove nitrates from drinking-water, preventive measures need to be adopted not only because it is important to protect the environment but also because suitable treatment processes have not been developed and preventive measures might, in the long term, cost less than treatment.

(2) Measures to prevent nitrate pollution offer long-term advantages for control of the problem. To implement such preventive measures, it will be necessary to gather information on the physical nature of the problem, existing legislation and current codes of practice for drinking-water. A review of legislation and land-use practices in individual countries will require cooperation among authorities involved in agriculture, water management, industries, environment and public health.

(3) A wide range of biological and physicochemical treatment processes for removing nitrates from drinking-water has been investigated. A list of installations operating in the countries represented at the meeting has been prepared. The list indicates that only a limited number of treatment plants have been operating and for relatively short periods. Results to date are insufficient to establish the long-term feasibility of any of the processes.

(4) The selection of suitable processes for a particular application is governed by the following criteria: stage of development, cost, raw water quality, the post-treatment required, waste production, chemical and technical hazards, and flexibility of operation.

Based on these criteria, seven basic process techniques were described and compared by the Working Group. They fell into three categories: heterotrophic and autotrophic biological denitrification, electrodialysis, and photochemical and chemical reduction. No simple, reliable and cheap process has yet been found for long-term and full-scale application.

(5) The nitrate removal processes most widely investigated are ion exchange, biological denitrification and reverse osmosis, all of which are commercially available but complex and expensive. The combined use of different kinds of technique may have advantages, especially in the disposal of waste produced by these processes.

(6) At present, methods available for the *in situ* removal of nitrates from groundwater have not yet shown satisfactory results. However, such methods offer potential advantages, particularly in terms of cost, and further research should be encouraged.

(7) To supply small settlements with safe drinking-water, especially in rural districts, methods and techniques should be elaborated that afford technical reliability and require low cost and a minimum of maintenance and technically skilled personnel.

(8) The Working Group, although recognizing the importance of introducing preventive measures, wishes to draw attention to the fact that, in many countries, the concentration of nitrates in groundwater sources will not be reduced for many years to come, even if preventive measures are introduced, owing to the present levels of nitrates in soil. Therefore, considering the results achieved so far in the development of reliable denitrification methods, Member States should continue their investigations in this field.

(9) The Working Group wishes to draw attention to the fact that the removal of nitrates from water may in certain cases involve the introduction of harmful substances into water sources or may remove other substances essential for maintaining health.

(10) The effects on health, other than methaemoglobinaemia, of nitrates in drinking-water need further investigation, since it has long been suspected that a high nitrate concentration may have other adverse consequences. In the mean time, drinking-water with a low nitrate concentration should be supplied to the whole population.

(11) Member States of the Region should organize interdisciplinary working groups to develop better coordination among the relevant national authorities, so as to harmonize legislation and submit reports to the Regional Office for Europe on legislative measures with special regard to legal protection against nitrate pollution.

(12) The coordination of research efforts at international level offers many benefits, and WHO should play a major role in promoting and disseminating information in this area. A review of existing legislation in this field should be prepared, with the basic aims of highlighting possible links and gaps and preparing proposals for improving legislation.

Protection measures in force. Removal Removal around deep (low NO3) wells proposed legislation. Removal processes and Bottled water. Closure of source Centralization of water treatment Control measures proposed Treatment processes investigated Treatment processes investigated Protection measures implemented. processes and in situ treatment processes and in situ treatment Protection measures imposed by in situ treatment investigated Protection measures in effect. Protection measures proposed. Removal processes and in situ Protection measures proposed. or implemented Ion exchange investigated Treatment investigated treatment investigated investigated Investigated 7% of public supplies 40 mg/l. Severe problems (levels up to 200 mg N03/l) in private wells Levels high only in groundwater. 1.5% of public supplies and 50% of private wells $^550\ mg\ NO_3/1$ Levels high only in groundwater. 1.5% of public Highly variable from region to region. 15% of public supplies exceed 50 mg/l in lower Austria European Community directive With current application of manure, 10% of public supplies will exceed 50 mg N03/1 within Up to 7% of public supplies exceed 50 mg NO3/1 on occasion Less than 1% of public supplies 30 mg/l. 10% of private wells 50 mg/l (private wells serve 25% of the population) (private wells serve 25% of the population) supplies 45 mg/l. More severe problem in 5% of public supplies and 50% of private supplies exceed 50 mg $\rm N0_3/I$ Up to 4% of public supplies 50 mg NO $_3/1$ Levels up to 300 mg NO₃/1 in groundwater Compliance with standard private wells 10 years European Community directive European Community directive European Community directive 30 mg NO $_3/1$ warning level 50 mg NO $_3/1$ action level 50 mg NO₃/l recommended 100 mg NO₃/l maximum Standard for nitrate mg NO3/1 guide level 100 mg NO₃/l maximum concentration mg NO₃/l maximum None quoted None quoted 60 45 Czechoslovakia United Kingdom Republic of Nether lands Country Germany, llungary Austria Finland Federal France Poland Malta

Table 1. Nitrates in water supplies in some European countries represented at the Working Group

Table 2. Biological denitrification demonstration scale plant

Country	Organization	Location	Rav vater	Plant size	Period of operation	Process type	Post-treatment
Czechoslovakia		Breclav	Groundwater	160 m ³ /h	Present	Immobilized cells on granular support in fluidized bed. Biocatalysis. No carbon source added. System regenerated every six months	None provided y
France	Degrémont	Chateau Landon Champfleur	Groundwater Groundwater	50 m ³ /h 70 m ³ /h	1984-present 1983-present	Fixed bed (Biolite), hetero- trophic with acetic acid. Fixed bed (Biolite) with heterotrophic ethanol	Aeration, GAC filtration
Germany, Federal Republic of	Preussag AG and the Hygiene- Institut, Bonn	Langenfeld	Groundwater	50 ш ³ /h	Present	Fixed bed (Styropur), hetero- trophic with ethanol	Aeration, sand filtration
	Buro Lahmeyer, Karlsruhe University	Neuss	Groundwater	I	Present	Activated carbon fixed bed, heterotrophic with acetic acid	Aeration, groundwater recharge
	Karlsruhe University	Karlsruhe	Groundwater	ı	Present	Biolite fixed bed, hetero- trophic with acetic acid	Aeration, coagulation, GAC filtration
	Sulzer Bros	Mönchengladbach Groundwater	ı Groundwater	50 ш ³ /h	From 1986	Fixed bed, autotrophic with hydrogen	Aeriation, sand filtration
Hungary	VITUKI	Budapest	Groundwater	4 m ³ /h	1985-present	Twin-fluidized bed, hetero- trophic with sugar	None provided
Netherlands	KIWA	Montferland	Groundwater	35 ш ³ /ћ	1986	Autotrophic sulfur/limestone. Fixed-bed low-rate upflow filtration	Aeration, groundwater recharge
United Kingdom	Water Research Centre Anglian Water Authorities Department of the Environment	Bucklesham nt	Surface water	100 ш ³ /ћ	1982-1984	Fluidized sand, hetero- trophic with methanol, ethanol or acetic acid	Aeration, coagulation, sedimentation, sand filtration

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Table 3. Ion exchange demonstration scale plant

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Country	Organization	Location	Raw water	Plant stze	Period of operation	Requírement	Сотаеnts
France	Degrémont	Brittany	Surface water and groundwater	1 m ³ /h	1985-present Chloride	Chloride	Prime objective to demonstrate automation of the process
Germany, Federal Republic of	Kernforschings- zentum, Karlsruhe	Mobile pilot plant	Groundwater	5 m ³ /h	1982-present	C0 ₂	CARIX process for demineral- ization. Mixed anion/cation exchange resin bed
Hungary	VITUKI	Baranya	Groundwater	2.8 m ³ /h 2.7 _3/h	1	Chloride)	Fixed-bed process
				2.7 m3/h 1.2 m3/h 0.2 m3/h		ci /HcO3) Chloride) C1 ⁻ /HCO ₃)	Cartridge-type for offsite regeneration
Netherlands	Wageningen	Doetinchem, Montferland	Groundwater	14 m ³ /h	From 1986	HCO 3	Combined process with biological denitrification of regenerant and recycle
United Kingdom	United Kingdom Anglian Water Authorities	Waneham Bridge	Groundwater	75 ш ³ /h	1976-1978	Chloride	Continuous loop process
		Dorking	Groundwater	96 m ³ /h	1978-1988	Chloride	Fixed-bed process

Table 4. Other processes and plants

Country	Type	Feed water	Size	Comments
Austria	Reserve osmosis and ion exchange	1	Small scale	Temporary measures for special situations
Czechoslovakia	Ion exchange	Mains supply	Single dwellings	Point-of-use, non-regenerative cartridge
	Chemical reduction	I	Pilot scale	Fe/Cu bed plus sand filtration
Germany, Federal	Reverse osmosis	I	,	At two sites with treatment of permeate
Republic of	Reed bed	Groundwater	Pilot scale	Groundwater recharge
Hungary	Photochemical reduction	Mains supply	Laboratory scale	Aimed at point-of-use application. Uses ultraviolet light, so provides disinfection
	Fungal biological denitrification	Groundwater	Pilot scale 0,1 m ³ /h	Aerobic nitrate assimilation by apathogenic fungi in fixed-bed reactor

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Process type	Stage of development	Relative cost ^a	Raw/feed water quality	Post- treatment requirements	waste production ·	Classical /technical hazards	Suftability/ flexibility of operation
Autotrophic biological denitrification	Demonstration scale trials in progress. H2 process commer- cially available	-4	No special needs for H2 process. Sulfur/limestone process needs low turbidity	Re-aeration and filtration	Small amounts of Surplus biomass that can be thickened to high concentration and low volume	Storage of hydrogen. Produc- tion of nitrate. Production of H ₂ S from sulfur process	Long start-up. Continuous operation preferable. Use of S process limited by sulfate concentra- tion of raw water
Heterotrophic biological denitrification	Tested at demon- stration scale. Commercially available	4	No special needs	Re-aeration and filtration	Small amounts of surplus biomass that can be thickened to high concentration and low volume	Carbon source residual. Nitrite production	Long start-up. Continuous operation preferable. Use of S process limited by sulfate concentra- tion of raw water
Ion exchange	Tested at demon- stration scale. Commercially available	m	Needs low turbidity, low organics and low iron/manganese	Blending	Large volumes of used regenerant for disposal. Possible reluc- tion in waste volume by treatwent/recycle	Leaching of trace organics from resin. Increased corrosivity of treated water	Rapid start-up. Suitable for intermittent opera- tion. Use limited by raw water sulfate and chloride
Membrane processes (reverse osmosis and electrodialysis	Tested at demon- stration scale. Commercially available	8	Membrane suscep- tible to fouling by solids, organics, silica and bacteria	Blending/ mínerali- zation	Large volumes of low-strength waste	None .	Rapid start-up
Photochemical reduction	Laboratory testing only using ultraviolet	1	Needs low turbidity and colour		None	Increased organic carbon, NH3 and NO2 possible	Most likely applica- tion as point-of-use treatment method
Chemical reduction	Pilot plant tests	7	No special needs	Aeration for NH3 removal under high pH conditions	Large volumes of Fe sludge S	None	Reaction rates low. Not practical on a large scale

<u>Annex 1</u>

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