

Determination of Nitrate Pollution in Both Natural Mineral Waters and Bottled/Packaging Waters in Iran

R. Norbakhsh, F. Ansari and K. Daneshmand Irani

Department of Food and Agriculture Research,
Institute of Standards and Industrial Research of Iran, Karaj, Iran

Abstract: Nitrate is an acute contaminant, which means a single exposure can affect health of persons. Potential source of nitrate include septic system, animal waste, commercial fertilizer and decaying organic matter. This study was conducted to investigate NO_3^- pollution in both natural mineral waters and bottled/packaging waters in Iran. The water samples were taken from 24 provinces of Iran. Nitrate concentration in the natural mineral waters and bottled/packaging waters varied from 0-15 with the average of 5.37 ppm and 0-25 with the average of 6.47 ppm, respectively. Results showed that all of the samples were in maximum safe NO_3^- concentration that was considered to be 50 ppm according to the World Health Organization. The most of both natural mineral water and bottled/packaging water (62 and 69% respectively) were in group 5-10. Based on the results of this study, only 4% of water samples were classified as having high risk to human health or environment.

Key words: Nitrate, pollution, natural mineral waters, bottled/packaging waters, Iran

INTRODUCTION

Drinking water high in nitrite is potentially harmful to human and animal health. Nitrate (NO_3^-) is a naturally occurring form of nitrogen (N) which is very mobile in water. It is essential for plant growth and is often added to soil to improve productivity. Nitrogenous fertilizer used on arable farmland can be a significant source of nitrate in ground water and surface water. Marked increase in fertilizer N rates applied to agricultural soils has caused N to be leached below the rooting zone (Hallberg, 1989).

Water moving it down through soil after rainfall or irrigation carries dissolved nitrate with it to ground water. In this way, nitrate enters the water supplies of many homeowners and then in all tap and bottled water.

While N provides large responses in crop yield and is an extremely valuable nutrient, it is the major nutrient of concern in water pollution (Davies, 2000).

The Iran drinking water standard, or maximum contaminant level (MCL), for nitrate is 50 mg L^{-1} (ISIRI, 2005, 2003). (Nitrate in water is commonly expressed as $\text{mg L}^{-1} \text{NO}_3^-$ or $\text{NO}_3\text{-N}$. The former expression is used throughout this study in order to be consistent with original data sources).

Jasa *et al.* (2006) reported adverse effects of high NO_3^- levels, most notably methemoglobinemia (sometimes referred to as "blue baby syndrome") stomach cancer and non-Hodgkin's Lymphoma.

The NO_3^- in water is international problem. Numerous international studies attest to agricultural sources being a predominant source for nitrate in groundwater. For example, Pacheco and Cabrera (1997) reported nitrate contamination in a karstic limestone aquifer beneath the Yucatan Peninsula of Mexico. They attributed the contamination to human and agricultural wastewater.

Strebel *et al.* (1989) and Fried (1991) reviewed nitrate pollution of groundwater in Europe (including Belgium, Denmark, France, Germany, The Netherlands and England). Their data showed a rising trend in nitrate concentrations over time.

In Europe, NO_3^- concentration exceeding the international (WHO, 1993) recommendations for drinking water (50 mg L^{-1}) have been found in ground water under 22% of cultivated land (Laegreid *et al.*, 1999).

Bernhard *et al.* (1992) also documented nitrate pollution in France, in alluvial deposits beneath the Asatian Plain. The problem followed conversion of land use from grasslands to intensive cultivation of grain corn. Similarly, Rivers *et al.* (1996) identified nitrate and ammonium in a sandstone aquifer beneath Nottingham, England.

The contamination originated from fertilizer and soil organic nitrogen. Oenema *et al.* (1998) attributed nitrate pollution of groundwater in The Netherlands to agricultural activity, mainly fertilizer and livestock manure. Sandy soils beneath concentrated dairy and pig/poultry farms were most severely impacted.

Nitrate pollution in 9 counties, all located in north-central and west-central Texas showed more than 50% of the observations exceeded the maximum contaminant level (MCL) of 44.27 mg L^{-1} (Hudak, 2000).

Zhang *et al.* (1996) studied nitrate pollution of groundwater in northern China. Over 50% of 69 locations investigated in the study area contained nitrate concentrations above 50 mg L^{-1} . High concentrations, up to 300 mg L^{-1} , were found in groundwater beneath vegetable-producing areas, small cities and towns and farmer's yards. Nitrogen fertilizer had been applied at all locations having high nitrate levels. The problem is expected to worsen in China, where increasing food demands require maximizing agricultural productivity. Zakutin *et al.* (1994) documented nitrate pollution in public water supplies within nine groundwater basins of the Commonwealth of Independent States (CIS) and neighboring countries.

In the Middle East, Kacaroglu and Gunay (1997) surveyed nitrate pollution in an alluvial aquifer beneath the urban complex of Eskisehir, Turkey. While irrigated agriculture is common in that area, the highest nitrate concentrations were beneath densely populated and unsewered parts of the study area. Septic tanks and contaminated water from the Porsuk River were principal nitrate sources. In the other study were investigated in Turkey, on the effects of anthropogenic activities on groundwater quality showed that the groundwater and Porsuk River water have high contents of nitrite (Yuce, 2007).

High nitrate levels in groundwater have also been found in southern Australia (Dillon *et al.*, 1991) and New Zealand. Principal nitrate sources in those countries include fertilizer applied to pastures and waste from livestock processing facilities.

These are but a few examples of past studies that attest to the international scope of nitrate contamination in groundwater.

In Iran, agricultural land may be considered to be the main source of NO_3^- , where intensification in the last 30 years has increased NO_3^- leaching from soils into both surface and ground waters. Iran, Egypt and Turkey account for 75% of the fertilizer-N consumption in the Near East (Bijay-Singh and Yadinde-Singh, 1995). During the last 3 decades, NO_3^- concentration of the groundwater has gradually increased and is reaching 50 mg L^{-1} NO_3^- in some parts of Iran.

Jalali (2005) studied nitrate pollution of groundwater in Hamadan, Iran. Results showed that of 311 wells, 63% had levels less than 50 mg L^{-1} NO_3^- and 37% had levels excess of the 50 mg L^{-1} NO_3^- .

Nitrate is very mobile once in groundwater-it tends not to adsorb or precipitate on aquifer solids. Moreover, Nitrate is not routinely removed from well water. High nitrate concentrations can adversely affect consumers of both public and rural water supplies. The purpose of this study was to: determination of nitrate pollution in both natural mineral waters and bottled/package waters offered for sale as food, in Iran.

MATERIALS AND METHODS

Natural mineral water and bottled/package water samples from the 24 provinces of Iran were brought to the Food and Agriculture Department, Institute of Standard and Industrial Research.

In order to avoid contamination, clean plastic containers were used for bringing samples. The samples were stored in polyethylene containers, adequately labeled and preserved in the refrigerator until they were taken to the laboratory.

The study was then carried out at Water Science laboratory. About one hundred samples of each group (natural mineral waters and bottled/package waters) were examined. Water samples were measured for their NO_3^- analysis during summer 2007. Therefore, there was no seasonal variation in NO_3^- content in samples.

NO_3^- contents were determined by preserving specimens with $40 \text{ mg HgCl}_2 \text{ L}^{-1}$ and was stored at 4°C . Then it was adjusted to pH with ca and CH_3COOH (1 + 3) and was filtered through $0.45 \mu\text{m}$ filter. Set of matched tubes for blanks, standards and specimens were prepared. Ten mL of specimen, or aliquot diluted to 10 mL, was pipetted in to specimen tubes. Tubes were swirled and placed in $0-10^\circ\text{C}$ bath and then pipetted 10 mL $6.5\text{M H}_2\text{SO}_4$ into each tube and swirled. Let all tubes were come to thermal equilibrium About. 0.5 mL brucine reagents were added to all tubes and were swirled. Then tubes were transferred to boiling water-bath for exactly 25 min and then cooled to $20-25^\circ\text{C}$. The analysis was determined by UV-vis spectrophotometer Varian 1E instrument in 410 nm wavelength against reagent blank. Also, calibration curve of nitrate was drawn with set of standards solutions containing $0.1-2 \text{ mg N L}^{-1}$ (AOAC, 2000).

On the basis of NO_3^- concentrations the samples were grouped into one of five classes (Table 1) (Daniels and Mesner, 2005). Nitrate concentrations in groups, 4 and 5 exceed the international (WHO, 1993) and ISIRI recommendations for drinking water.

Statistical analysis: Statistical analysis of the obtained results was performed according to paired-samples t-test

Table 1: Interpretation of nitrate level in water

Nitrate Level (ppm)*	Interpretation
Group 1 (0-10)	Safe for humans and livestock. However, concentrations of more than 4 ppm are an indicator of possible pollution sources and could cause environmental problems.
Group 2 (11-20)	Generally safe for human adults and livestock. Not safe for infants because their digestive systems cannot absorb and excrete nitrate.
Group 3 (21-40)	Should not be used as a drinking water source but short-term use acceptable for adults and livestock unless food or feed sources are very high in nitrates.
Group 4 (41-100)	Risky for adults and young livestock. Probably acceptable for mature and livestock if feed is low in nitrates.
Group 5 (Over 100)	Should not be used

*parts per million

employing the SPSS statistical program. Means of duplicate analysis from 100 samples of each region were reported for the studied parameters.

RESULTS

As shown in Fig. 1 the frequency distribution of nitrate concentration are presented for natural mineral water. It should be noted that the concentration of nitrate in groups over the (21-40) were not in the detectable range. It should be noted that the frequency distribution of nitrate concentration in group (5-10) was determined as 62% which appear to be quite high and in group (0-4) was 35%. The frequency distribution of nitrate concentration for bottled/packaging water samples are presented in Fig. 2. Similar to what was mentioned for natural mineral water earlier, almost the frequency distributions of nitrate concentrations for bottled/packaging water were not in the detectable range and in group (5-10) was determined as 69% which is similar to another group and 26% for group (0-4).

In Table 2 absolute and relative frequency distribution of nitrate values in all samples show that over the 50% of samples (65.5%) were in group 5-10.

In Table 3 the result of water analysis for NO_3^- concentration are shown. Nitrate concentration varied from 0-25 ppm with an average of 5.92 ppm. The median of all samples were in 5 ppm.

Table 2: Absolute and relative frequency distribution of nitrate value in natural mineral and bottle/packing waters in Iran

Nitrate Level (ppm)*	No. (n = 200)	(%)
0-4	61	30.5
5-10	131	65.5
11-20	7	3.5
21-40	1	0.5
41-100	0	0
>100	0	0

* parts per million

Table 3: Statistical analysis of nitrate value in natural mineral and bottle/packing waters in Iran

Statistical analysis	Natural mineral waters (n = 100)	Bottled/packaging waters (n = 100)	Natural mineral and bottled/packaging waters
Max	15	25	25
Min	0	0	0
Mean	5.37	6.47	5.92
SD	2.90	3.74	3.38
Median	5	5	5

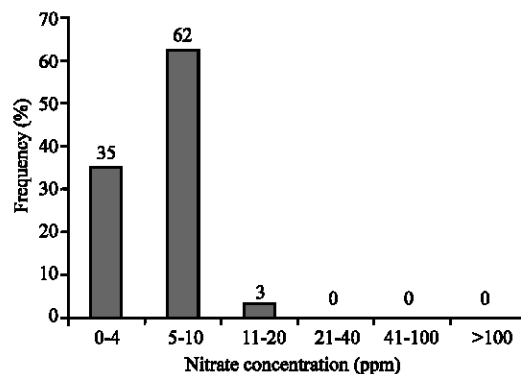


Fig. 1: Frequency distribution for nitrate concentration in natural mineral water samples from parts of Iran

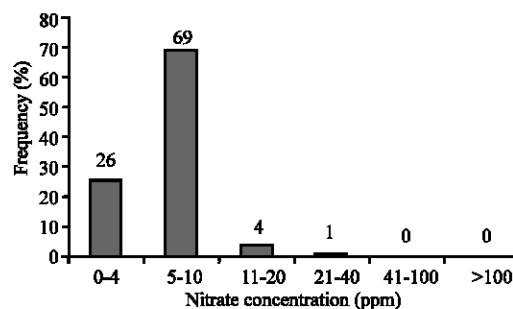


Fig. 2: Frequency distribution for nitrate concentration in bottle/packaging water samples

DISCUSSION

The results of NO_3^- concentration of samples in both natural mineral water and bottled/packaging water show that all of them were in maximum safe NO_3^- concentration that was considered to be 50 ppm according to the World Health Organization (WHO, 1993). Also, in 1999, 99.94% of tests for nitrate on samples taken from public water supplies in England and Wales met the nitrate standard too (AET, 2007).

The U.S. Environmental Protection Agency (USEPA) has set the primary drinking water standard (from public water supplies) for nitrate at 10 ppm (Daniels and Mesner, 2005).

The average value of nitrate in natural mineral water and bottled/package water were 5.37 and 6.47 ppm and their concentrations varied from 0-15 and 0-25 ppm, respectively. Furthermore, it has been noted that the median of all samples were in 5 ppm (Table 3).

The most of both natural mineral water and bottled/package water (62 and 69%, respectively) were in group 5-10. According to the interpretation of nitrate level in water (Table 1) this amount is safe for human adults and livestock and concentrations of more than 4 ppm are an indicator of possible pollution sources and could cause environmental problems. The results of our study indicated that, remedial action should not be taken for waters that consume by human adults and livestock. But possible pollution sources may be exist.

Although, based on the results of this study, the data regarding relative frequency of samples in both natural mineral water and bottled/package water was 30.5% in group one (Table 2), which based on interpretation of nitrate level at the range of 0-10 ppm is in Table 1. this amount is safe for human adults and livestock.

Only in 4% of samples NO_3^- concentration was above 11 ppm (Table 2). Therefore, it should be noted as a risk for infant because their digestive systems cannot absorb and excrete nitrate (Daniels and Mesner, 2005).

CONCLUSION

The production of adequate and safe drinking water is a high priority issue for safeguarding the health and well-being of humans all over the world. Natural mineral water and bottled/package water are important for water supply to meet human needs in many parts of Iran especially in warm regions. Based on the results of this study, only 4% of water samples were classified as having high risk to human health or environment.

Due to the lack of information specifying the source of each sample obviously, the further studies need to consider in Iran.

ACKNOWLEDGEMENT

This work has been funded by a grant provided by "Institute of Standard and Industrial Research of Iran, Department of Food and Agriculture, Karaj, Iran". Gratitude is expressed to "Research Council of the University of Tehran" for the partial support of the work.

REFERENCES

Advanced Environmental Technology, 2007. Nitrate in drinking water. http://www.accepta.com/industry_water_treatment/nitrate_drinking_water.asp.

- AOAC, 2000. Nitrogen (nitrate) in water. Official method 973.50, Chapter 11, pp: 11.
- Bernhard, C., R. Carbiener and A.R. Cloots, 1992. Nitrate pollution of groundwater in the Asatian Plain (France)-a multidisciplinary study of an agricultural area: The Central Ried of the Ill River. *Environ. Geol. Water Sci.*, 20 (2): 125-137.
- Bijay-Singh and G.S. Yadvinder-Singh, 1995. Fertilizer- N use efficiency and nitrate pollution of groundwater in developing countries. *J. Contamin. Hydrol.*, 20: 167-184.
- Daniels, B. and N. Mesner, 2005. Safe drinking water in Utah, nitrate. <http://thomsonscientific.com/cgi-bin/jmlst/jlresults.cgi?PC=MASTER&ISSN=1895-1053>.
- Davies, D.B., 2000. The nitrate issue in England and Wales. *Soil Use Manage.*, 16: 142-144.
- Dillon, P.J., S.R. Ragusa and S.B. Richardson, 1991. Biochemistry of a plume of nitrate-contaminated groundwater. In: Bogardi, I. and R.D. Kuzelka (Eds.). Nitrate Contamination: Exposure, Consequence and Control NATO ASI Serial G: Ecological Sciences 309 Springer, Berlin, pp: 173-180.
- Fried, J.J., 1991. Nitrates and Their Control in the EEC Aquatic Environment. In: Bogardi, I. and R.D. Kuzelka (Eds.), 1991. Nitrate Contamination: Exposure, Consequence and Control NATO ASI Serial G: Ecological Sciences 309 Springer, Berlin, pp: 3-11.
- Hallberg, G.R., 1989. Nitrate in Groundwater in the United States. In: Follee, R.F. (Ed.), Nitrogen Management and Groundwater Protection. Elsevier, Amsterdam, Netherlands, pp: 35-138.
- Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water. United States Geological Survey Water-Supply Paper, 2254: 1-263.
- Hudak, P.F., 2000. Regional trends in nitrate content of Texas groundwater. *J. Hydrol.*, 228 (1-2): 37-47.
- ISIRI 2441, 2005. Natural mineral water-Specifications. Institute of Standard and Industrial Research of Iran. First revision.
- ISIRI 6694, 2003. Water-Pakaged (bottled) drinking waters-Specifications. Institute of Standard and Industrial Research of Iran. First revision.
- Jalali, M., 2005. Nitrates leaching from agricultural land in Hamadan, western Iran. *Agric. Ecosyst. Environ.*, 110: 210-218.
- Jasa, P., S. Skipton, D. Varner and D. Hay, 2006. Drinking water: Nitrate-nitrogen. Published by university of Nebraska-Lincoln extension. Institute of agriculture and natural resources, G1279.
- Kacaroglu, F. and G. Gunay, 1997. Groundwater nitrate pollution in an alluvium aquifer, Eskisehir urban area in its vicinity, Turkey. *Environ. Geol.*, 31 (3/4): 178-184.

- Laegreid, M., O.C. Bockman and O. Kaarstad, 1999. Agriculture, fertilizers and environment. CAB International. Wallingford and Norsk Hydro, ASA, Oslo.
- Oenema, O., P.C.M. Boers and W.J. Willems, 1998. Leaching of nitrate from agriculture to groundwater: The effect of policies and measures in the Netherlands. *Environ. Pollut.*, 102: 471-478.
- Pacheco, J. and S. Cabrera, 1997. Groundwater contamination by nitrates in the Yucatan Peninsula, Mexico. *Hydrogeol. J.*, 5 (2): 47-53.
- Rivers, C.N., K.M. Hiscock, N.A. Feast, M.H. Barrett and P.F. Dennis, 1996. Use of nitrogen isotopes to identify nitrogen contamination of the Sherwood sandstone aquifer beneath the City of Nottingham, UK. *Hydrogeol. J.*, 4 (1): 90-102.
- Strebel, O., W.H.M. Duynisveld and J. Bottcher, 1989. Nitrate pollution of groundwater in Western Europe. *Agric. Ecosyst. Environ.*, 26: 189-214.
- WHO, 1993. Guidelines for Drinking Water Quality. 1. Recommendation. 2nd Edn. World Health Organization, Geneva.
- Yuce, G., 2007. Spatial distribution of groundwater pollution in the Porsuk River Basin (PRB), Turkey. *Int. J. Environ. Pollut.*, 30 (3/4): 529-547.
- Zakutin, V.P., D.A. Fetisenko, Z.N. Panteleeva, A.A. Bogomolova and N.N. Chugonova, 1994. Nitrate pollution of ground water in the area of the CIS and adjacent countries. *Water Resour.*, 21 (3): 346-352.
- Zhang, W.L., Z.X. Tian and X.Q. Li, 1996. Nitrate pollution of groundwater in northern China. *Agric. Ecosyst. Environ.*, 59 (3): 223-231.