Bull. Chem. Soc. Ethiop. 2005, 19(1), 35-44.
Printed in Ethiopia
ISSN 1011-3924

ANALYSIS OF NITRATES AND NITRITES IN SOME WATER AND FACTORY EFFLUENT SAMPLES FROM SOME CITIES IN SWAZILAND

A.O. Fadiran* and S.M. Mamba

Chemistry Department, University of Swaziland, P/Bag 4 Kwaluseni, Swaziland

(Received August 8, 2004; revised October 4, 2004)

ABSTRACT. The levels of nitrates and nitrites in drinking water, river water and factory effluents from three major cities in Swaziland were determined by a pre-calibrated colorimetric method. The pooled mean concentration range for the nitrates in the river water samples is 1.74±0.13 – 115±3.27 mg/L as NO_3–N and for nitrites is 1.50 ± 1.70 – 2.90 ± 2.77 mg/L as NO_2–N. For the factory effluents, nitrate levels varied between 72.3 ± 6.81 mg/L and 75.7 ± 3.21 mg/L, giving a pooled mean of 74.0 ± 3.76 mg/L, while the concentration range for nitrites is 0.16 ± 0.02 – 0.21 ± 0.07 mg/L, giving a pooled mean of 0.18 ± 0.03 mg/L as NO_2–N. Nitrate levels in the drinking water samples ranged between 0.70 ± 0.10 – 1.6 ± 0.07 mg/L, giving a pooled mean concentration of 1.3 ± 0.26 mg/L as NO_3–N, while levels of the nitrites vary from $1.1 \times 10^{-3} \pm 1.2 \times 10^{-4}$ – $7.93 \times 10^{-3} \pm 8.1 \times 10^{-4}$ mg/L, yielding a pooled mean of $3.4 \times 10^{-3} \pm 3.0 \times 10^{-4}$ mg/L as NO_2–N. The observed mean as well as the highest single-point values for both nitrates and nitrites in drinking water are well below WHO's maximum acceptable concentration (MAC), of 10.0 mg/L nitrate as NO_3–N and 3.0 mg/L nitrite as NO_2–N. However, the levels of both species in the river water and factory effluents are high enough to necessitate the monitoring of their respective levels.

KEY WORDS: Leaching, Runoff, Methemoglobinemia, Nitrate fertilizer, Nitrogenous-waste, Water quality assessment

INTRODUCTION

The determination of the levels of nitrate as nitrogen (mg/L NO_3–N) and nitrite as nitrogen (mg/L NO_2–N) in surface waters is usually an integral part of basic water quality assessment or background monitoring programs because their concentrations are general indicators of the nutrient status and the degree of organic pollution of the affected water body. Nitrate is also recommended for regular monitoring in drinking water because of the potential health risks associated with its elevated levels in drinking water, especially for infants less than six months old and animals [1-12].

The major sources of accumulated nitrates and nitrites in drinking water, surface water and the environment at large are non-point source from excessive use of nitrate based fertilizers or from inadequately treated or untreated sewage [1, 2]. Other sources of nitrate and nitrite include wastes produced by certain industrial processes such as paper and munitions manufacturing, point source runoff from human and animal wastes septic/solid disposal, landfills [3-6]. Besides the listed artificial sources of nitrate and nitrite, both species are released into the soil and water as a result of the breakdown of naturally occurring organic nitrogen compounds through mineralization, hydrolysis and bacterially activated reactions [7, 8]. According to Speiran [8], urea, like a number of other forms of organic nitrogen in soil and natural waters is converted to ammonia under aerobic and anaerobic microbial processes. The ammonia is subsequently converted to nitrate and nitrite. Additionally, ammonia may be added to water during treatment to convert free residual chlorine to chloramine and any excess ammonia from this process can be oxidized to nitrite [2]. Both nitrate and nitrite are highly soluble in water. They do not bind to

*Corresponding author. E-mail: fadiran@uniswacc.uniswa.sz

soil, thus they have a high migration potential through soil. Consequently both species can be easily washed into surface waters by rain or leached through soil into ground water most especially shallow ones, from sources listed above. Factors that influence the leaching of both nitrate and nitrite into water bodies and hence their levels in them include plant cover, land use, fertilizer usage, soil type, rainfall pattern, irrigation, climatic condition and depth of ground water below land surface [1, 2, 9]. Elevated nitrate concentrations have been associated with minor, occasional, marked or severe deterioration requiring major treatment or excluding desired use on drinking water, surface waters, aquatic wildlife and fisheries [1, 2]. Consumption of drinking water containing high nitrate concentrations by infants less than six months old and certain young animals can cause oxygen deficiency in the blood, a potentially fatal condition known as methemoglobinemia or "blue baby syndrome" [1, 2, 11-14]. Also nitrite (from ingested nitrate) can react with amines and amides in human stomach to produce the highly carcinogenic N–nitroso compounds in the body. [1, 2, 11-14]. Cattle, sheep, baby pigs, baby chickens as well as horses are also susceptible to nitrate poisoning [15, 16]. Oxidation of nitrite to nitrate by dissolved oxygen in water results in a depletion of the oxygen level in water [2, 17, 18]. Nitrate is also considered with phosphorus to be a major cause of eutrophication in waters For instance, the U.S. Environmental Protection Agency (USEPA) fixed a MCL of 10 mg/L NO_3–N and 3 mg/L NO_2–N [1, 2, 11, 18, 19, 20]. According to USEPA, "only two substances for which standards have been set pose an immediate threat to health whenever they are exceeded: bacteria and nitrate" [21]. Indeed, it has been recommended that nitrate/nitrite levels should be monitored at intervals of three years minimum [21].

Several methods are now available for the analysis of both nitrates and nitrites in water samples [2, 12, 17, 22-27]. However, the automated colorimetric method is very sensitive and convenient. Majority of Swazi population dwell in sub-urban and rural communities and depend on surface waters for most of their domestic activities. Livestock practices are the free-range type and the animals drink from available surface waters, hence the need for continuous monitoring of the nitrate/nitrite levels in aquatic bodies in the country.

Moreover, major analysis of nitrates and nitrites in Swaziland waters (surface and groundwater) was carried out between 1986 and1991 [28], hence a study of this nature at a nation-wide level is long overdue. We report here the levels of NO_3–N and NO_2–N in drinking water, surface water and some factory effluents from selected cities of Swaziland, using the automated spectrophotometric method.

EXPERIMENTAL

Apparatus

The advanced water quality laboratory series HATCH-DR 2010 datalogging spectrophotometer was used. It is a microprocessor-controlled, LED sourced filter photometer with in-built programs for measurements of various parameters in water including NO_3–N and NO_2–N at programmed wavelengths and reaction times.

Reagents

Sodium nitrite (AR) was dried in an oven at 110 °C for 1 h, and then cooled in a desiccator before being weighed accurately. NitraVer 5 nitrate reagent powder pillow – which contains cadmium, gentisic acid, magnesium sulphate, potassium phosphate and monobasic sulfanilic acid, which on reaction with the sample produces the amber-coloured nitrate complex; NitriVer 3 nitrite reagent powder pillow – which contains 1,2-cyclohexanediamine tetraacetic acid,

trisodium salt, chromotrophic acid, potassium phosphate, monobasic potassium pyrosulphate, and sodium sulfanilate, and upon reaction with the sample produces the pink coloured nitrite complex; nitrate and nitrite standards (HACH Chemical Company U.S.A.); bromine water and phenol were used. Distilled, de-ionised water was used for preparation of all the reagent solutions.

Surface water samples were collected from major rivers that run through selected main cities in the country or those receiving effluents from some manufacturing industries namely Mzimnene in Manzini, Lusushwana in Matsapha, and Mbabane in Mbabane. Samples were collected from each of the selected river before and after the respective cities or industrial/agricultural set up through which they pass. Drinking water samples were collected from Manzini (the largest city in the country), Mbabane (the capital city), and Matsapha (Kwaluseni Campus of the University). Industrial effluents were collected from one food manufacturing industry and one paper/pulp industry.

Samples were collected in scrupulously cleaned 2.5 L brown, resistant borosilicate Winchester bottles, filled to the brim and then sealed with Teflon lined caps. The bottles were transferred to the laboratory in a big plastic cooler and subsequently stored in a refrigerator at 4 °C immediately on reaching the laboratory. These steps help in substantially retarding biological activity as well as the rates of possible physical and chemical reactions [5, 24, 29]. Samples were filtered and analyzed soon within 48 h of refrigeration at 4 °C [5, 24, 29, 30]. Three samples were collected from each sampling point and sampling and analysis were carried out over a period of five months (between November 2000 and March 2001) – at an average interval of four weeks.

Principles

The spectrophotometric method employed utilizes the quantitative reduction of nitrate in the sample to nitrite by cadmium and the subsequent production of the amber coloured product (through the reaction of the nitrite with sulfuric acid and the coupling of the formed diazonium salt with gentisic acid), whose intensity is proportional to the original [NO_3–N] in the sample and obeys Beer's law. Interference by nitrite is compensated for by addition of bromine water followed by phenol – as described under analysis below.

For nitrite measurement, the diazonium salt resulting from the reaction of the sample nitrite with sulfuric acid couples with chromotropic acid to produce a pink coloured complex directly proportional to the [NO_2–N] in sample and obeys Beer's law.

Procedure

NO_3–N. The program for the nitrate determination was entered and the wavelength set at 500 nm. A 25 mL sample cell was filled with the sample. Bromine water was added in drops until the developed yellow colour stayed, followed by a drop of phenol solution to produce a colourless solution. A NitraVer 5 nitrate reagent powder pillow was added and the cell stoppered. It was shaken vigorously for 1 min and then allowed to stand for five minutes to complete the reaction. Another cell was filled with 25 mL sample (but without addition of the NitraVer 5 nitrate reagents), placed in the cell compartment and used to zero the instrument (nitrate in the untreated sample is not detectable). The prepared sample was then placed in the cell compartment and the concentration of the nitrate read in mg/L NO_3–N [31].

NO_2–N. The program for nitrite measurement was selected and the wavelength set at 507 nm. A 10 mL sample cell was filled with 10 mL sample and the contents of a NitriVer 3 nitrite reagent pillow was emptied into the cell. The cell was capped, properly shaken for 1 min and then

allowed to stand for 20 min for completion of reaction. Another 10 mL cell was filled with the sample (without adding the NitriVer 3 nitrite reagents), and then used to zero the instrument. It was then replaced with the treated sample (after the 20 min reaction time) and the nitrite concentration read in mg/L NO_3–N [31].

Reagent blanks were estimated/measured for each set of the NitraVer 5 nitrate and NitriVer 3 nitrate reagent pillows. The reagent blank values were deducted from the respective results for samples.

RESULTS AND DISCUSSION

River water

Generally, levels of nitrate and nitrite (and indeed other water quality parameters) obtained in river water samples are subject to undergo variability because they are governed by factors such as speed of the river, seasonal/climatic variations, soil over which it flows, nature and rate of sewage and factory effluent discharges into it and the sampling point [1, 2, 11, 12, 14, 15].

The estimated ranged mean monthly mg/L NO_3–N and mg/L NO_2–N levels in the investigated rivers are summarized in Tables 1 and 2.

Table 1. Ranged monthly averages of mg/L NO_3–N in rivers* passing through the selected cities and industrial/agricultural areas.

Month/parameter	Nov	Jan	Feb	Mar	Overall range (mg/L NO_3–N)
Ranged averages** (mg/L NO_3–N)	1.25 ± 0.12 - 2.70 ± 0.20	100 ± 4.80 - 140 ± 5.0	24.0 ± 4.18 - 44.0 ± 3.54	18.0 ± 2.10 - 36.0 ± 1.89	1.25 ± 0.12 - 140 ± 5.0
Pooled Mean $X_p + s_p$	1.74 ± 0.13	115.0 ± 3.25	42.2 ± 2.20	28.5 ± 1.61	1.74 ± 0.13 - 115.0 ± 3.25
Point with highest value	MAMT	MAMT	MAMT	MAMC	–
Point with lowest value	MBMC	MBMT	LBMIA	LBMIA	–

*Sampling points from the rivers are abbreviated as MBMC: Mzimnene before Manzini city, MAMC: Mzimnene after Manzini city, LBMIA: Lusushwana before Matsapha Industrial Area, LAMIA: Lusushwana after Matsapha Industrial Area, MBMT: Mbabane before Mbabane town, MAMT: Mbabane after Mbabane town. **Mean of three replicates.

Table 2. Ranged monthly averages of mg/L NO_2–N in rivers* passing through the selected cities and industrial/agricultural areas.

Month/parameter	Nov	Jan	Feb	March	Overall range (mg/L NO_2–N)
Ranged averages** (mg/L NO_2–N)	1.0×10^{-3} – $(2.0 \pm 0.17) \times 10^{-3}$	1.0×10^{-3} – $(4.0 \pm 0.10) \times 10^{-3}$	1.0×10^{-3} – $(6.40 \pm 0.47) \times 10^{-3}$	1.0×10^{-3} – $(6.0 \pm 0.100) \times 10^{-3}$	1.0×10^{-3} – $(6.40 \pm 0.47) \times 10^{-3}$
Pooled mean $X_p + s_p$	$(1.50 \pm 0.17) \times 10^{-3}$	$(2.45 \pm 0.125) \times 10^{-3}$	$(2.90 \pm 0.28) \times 10^{-3}$	$(2.57 \pm 0.15) \times 10^{-3}$	$(1.50 \pm 0.17) \times 10^{-3}$ – $(2.90 \pm 0.28) \times 10^{-3}$
Point with highest value	MAMC	MAMC	MBMC	MBMC	–
Point with lowest value	MAMT	MAMT	LBMIA MBMT	MBMT	–

*As interpreted under Table 1. **Mean of three replicates.

An overall monthly variation pattern for all the sources has been considered here in order to give a general picture of the periodic variation in the levels of these species in all the rivers under consideration. However sampling points with only the highest and lowest nitrate/nitrite levels for each month are indicated. Table 3 depicts the highest, the lowest and the pooled mean over the five month period for each of the rivers. From these tables, nitrate levels for all the sampling points and over the sampling period vary between $1.25 \pm 0.12 - 140 \pm 5.0$ mg/L NO_3–N while the pooled mean for the same data set varies from $1.74 \pm 0.130 - 115 \pm 3.25$ mg/L NO_3–N. The corresponding values for the nitrite in these samples are $1.0 \times 10^{-3} - (2.9 \pm 0.28) \times 10^{-3}$ mg/L NO_2–N, respectively. The variation patterns for the two species over the sampling period manifest some structural similarity as they both have their peak pooled means between January and February and their lowest in November. This picture is depicted when sampling points are considered on individual basis (Table 3). The observed variation in the mg/L NO_3–N and mg/L NO_2–N follows, to a reasonable extent, the rainfall pattern for the country. Usually, the main raining season stretches between November and March/April with the heaviest downpour in January/February. This is also the planting season nationwide with the corresponding maximal application of nitrate-based fertilizers and animal manure for the enhancement of crop growth and yield. Any excess nitrate from these non-point sources are either washed into the rivers by rain or leached into them through the soil, resulting in the observed high levels of nitrate in the rivers. [1-11, 14]. This observation is supported by the claim that agricultural practices, with the usual attendant excessive use of nitrate fertilizers and animal manure, constitute the most important source of elevated concentrations of nitrate and nitrite in aquatic bodies [1-3, 5-11, 14, 15, 22, 23]. Additionally increased soil aeration resulting from clearing and ploughing for planting inadvertently enhance the action of nitrifying bacteria with a consequent increase in soil nitrate [5]. Similar patterns have been observed in the monitored mg/L NO_3–N levels of some UK rivers with autumn and winter peaks in excess of 100 mg/L NO_3–N and levels often higher than the MCL/MAC in areas of intensive agricultural activities [1].

Table 3. Highest and lowest mg/L NO_3–N and mg/L NO_2–N for samples taken at fixed points in the rivers.

Sampling point on river	mg/L NO_3–N			mg/L NO_2–N x 10^{-3}		
	Highest	Lowest	$(X_p + s_p)^*$	Highest	Lowest	$(X_p + s_p)^*$
Mzimnene, before city	50.0 ± 3.54 (Feb)**	1.25 ± 0.12 (Nov)	27.8 ± 2.42	6.4 ± 0.47 (Feb)**	1.3 ± 0.23 (Nov)	4.6 ± 0.31
Mzimnene, after city	110 ± 3.5 (Jan)	1.30 ± 0.13 (Nov)	50.3 ± 2.28	5.8 ± 0.45 (Feb)	2.0 ± 0.17 (Nov)	4.1 ± 0.14
Lusushwana, before industries	110.0 (Jan)	1.25 ± 0.25 (Nov)	44.6 ± 3.42	1.8 ± 0.26 (Jan)	1.0 (Feb)	1.4 ± 0.29
Lusushwana, after industries	31.0 ± 2.24 (Feb)**	1.40 ± 0.11 (Nov)	18.2 ± 1.72	1.4 ± 0.55 (Feb)	1.2 ± 0.18 (Mar)	1.3 ± 0 12
Mbabane, before town	100 ± 4.80 (Jan)	2.51 ± 0.21 (Nov)	42.9 ± 2.65	3.0 ± 2.2 (Jan)	1.0 (Feb/Mar)	1.7 ± 0.02
Mbabane, after town	140 ± 5.0 (Jan)	2.70 ± 0.20 (Nov)	57.6 ± 3.46	1.80 ± 0.45 (Feb)	1.0 (Nov/Jan)	1.4 ± 0.08

*$X_p + s_p$ = Pooled mean for five months.
**Jan, which usually records highest level not included due to sampling problem.

In unpolluted surface waters nitrate levels are usually less than 1.0 mg/L, and rarely exceeding 5.0 mg/L NO_3–N, while nitrite levels are usually less than 0.30 mg/L NO_2–N. Hence levels in excess of these values are indicative of artificial pollution of which agricultural practice

ranks highest. It then follows that the degree of nitrate/nitrite pollution of these rivers indicates the extent of agricultural practices going around the river. This reasoning is also in agreement with our results. Nitrate and nitrite levels from similar points on the Mzimnene and Mbabane rivers are relatively higher than those obtained for similar points on the Lusushwana river, around which less intensive agricultural activities than the former two are going on.

The mg/L NO_2–N obtained in all the rivers investigated are quite low, with a pooled mean range of 1.0×10^{-3} – $(6.4 \pm 0.4) \times 10^{-3}$ mg/L NO_2–N. These levels fulfill the MCL's recommendations of 0.06 mg/L NO_2^- (~0.02 mg/L NO_2–N) by Canada, 0.08 mg/L NO_2^- (0.024 mg/L NO_2–N) by USSR and 0.01 – 0.03 mg/L NO_2^- (0.003 – 0.009 mg/L NO_2–N) by EC for fisheries and aquatic life [1]. Also they are all lower than the MCL's of between 1.0 – 3.0 mg/L 0.06 mg/L NO_2–N for drinking water recommended by most of the international organizations [1, 2, 11, 19, 20]. This implies that microbial activities leading to the formation of nitrite, as an intermediate product in the oxidation of ammonia to nitrate [1, 2, 7-9], are low in all these sampling points on the rivers. The relatively high levels of nitrate in the river water samples and the fact that all the points with the highest mg/L NO_3–N for all the months are located after the river concerned has passed through the city or industrial area indicate that leachates and run-off from domestic activities (pit-latrines, sewage treatment, etc) and industrial effluents have also contributed to the elevated nitrate concentrations in all these rivers (Tables 1 and 2). Although water from these rivers may not, in most instances, be used for drinking by human, they are the sources of water for the free grazing animals including cattle, sheep, goat and pigs owned by farmers throughout the country. Considering the assertion that nitrate levels greater than 25 mg/L NO_3–N can be hazardous to animals [15] and the MCL of 40.0 mg/L NO_3^- (i.e. 9.04 mg/L NO_3–N) recommended by USSR for fisheries and aquatic life [5], these rivers can be considered as polluted by nitrate to levels that are dangerous even for animal consumption because all the monthly pooled means, with the exception of November and the pooled mean for each river are greater than these values..

Mtetwa [32] obtained an average value of 2.79 mg/L NO_3–N for samples from the Lusushwana river in 1991-92, which is generally significantly lower than our values. These sharp increases in the nitrate levels, which are some nine to sixteen times greater within a ten-year interval, are consequences of the rapidly increasing population, industrial activities and agricultural practices with the fast replacement of the traditional farming methods by the modern mechanized and highly commercialized processes. The observed high levels of nitrate in these rivers in conjunction with phosphates, (both of them being plant nutrients), are most likely to enhance a rapid growth of aquatic plants and thereby serve as potential causes of aquatic algal bloom and eutrophication [18].

Drinking water

The mg/L NO_3–N and mg/L NO_2–N in drinking (tap) water samples from three major cities in the country are summarized in Table 4. The readings were not extended over time. The levels of nitrate and nitrite in drinking water samples varied from 0.70 ± 0.10 – 1.58 ± 0.07 mg/L NO_3–N and $(1.07 \pm 0.12) \times 10^{-3}$ – $(7.93 \pm 0.81) \times 10^{-3}$ mg/L NO_2–N, respectively. And, for all these drinking water samples, the pooled means are 1.25 ± 0.16 mg/L NO_3–N and $(3.35 \pm 0.30) \times 10^{-3}$ mg/L NO_3–N, respectively. Considering the fact that the water has been treated prior to distribution for public consumption, it is expected that the levels of these species in them should be less than their natural levels of 0.1 – 1.0 mg/L NO_3–N and 0.001 – 0.1 mg/L NO_2–N in fresh and surface waters [1, 2, 5]. For nitrite, this expectation is met to a good extent, however, in the case of nitrate both the pooled mean value and all but one point source failed to meet this expectation. The most likely reason for this is the already very high levels of nitrate in the raw river water sources being treated for public distribution. Another important factor that is

probably responsible for the observed nitrate/nitrite levels in these drinking water samples and the slight variations between them is the quantity and effect of ammonia added to convert free residual chlorine to chloramine during water treatment. Thereafter, any excess ammonia can be oxidized to nitrite and nitrate through aerobic/anaerobic bacterial activities [1, 2, 7, 8]. The random nature of this factor and others that can influence it, such as temperature and bacterial population, could in addition account for the observed variation in the nitrate and nitrite levels in the drinking (tap) water samples analyzed. However all the individual drinking water samples as well as the pooled means have nitrate levels much lower than the MCL/MAC of 10 mg/L NO_3–N recommended by WHO and USEPA and other international bodies, and nitrite levels are also far below the MCL/MAC of 1.0 NO_2–N mg/L recommended by the same bodies for drinking water [1, 2, 5, 15, 16, 18-23] (Table 5). Fatoki [33], obtained relatively higher values of $4.0 \pm 0.2 - 15 \pm 1$ mg/L NO_3–N for drinking (tap) water samples in major cities in Eastern Cape of neighboring South Africa.

Table 4. Ranged averages of mg/L NO_3–N and mg/L NO_2–N in drinking water samples from selected cities.

Sampling point	mg/L NO_3–N	mg/L NO_2–N x 10^{-3}
UNISWA (Science Lab)	0.70 ± 0.10	7.93 ± 0.81
UNISWA (Science Car Park)	1.09 ± 0.25	6.07 ± 0.16
Manzini (Market)	1.58 ± 0.07	1.07 ± 0.12
Manzini (Trade Fair)	1.52 ± 0.02	1.40 ± 0.10
Mbabane (Market)	1.35 ± 0.02	1.90 ± 0.10
Mbabane (Water Corp Lab)	1.25 ± 0.04	1.73 ± 0.06
Pooled Mean ($X_p + s_p$) mg/L	1.25 ± 0.163	$(3.35 \pm 0.30) \times 10^{-3}$
Point with highest value	Manzini Market	UNISWA (Science Lab)
Point with lowest value	UNISWA (Science Lab)	Manzini Market

Table 5. Recommended maximum contaminant levels (MCL) or maximum allowable concentrations (MAC) for nitrates and nitrites in drinking water* [1, 2, 5, 11, 19, 20].

	Nitrate (mg/L)		Nitrite (mg/L)	
Organization	NO_3–N	NO_3^-	NO_2–N	NO_2^-
USEPA	10	45	1	3
WHO	10	50	-	3
EEC	11	50	-	0.1
Canada	10	-	1	-
USSR	-	10	-	1
Swaziland	WHO standard	WHO standard	WHO standard	WHO standard

*To convert from mg/L NO_3–N to mg/L NO_3^- multiply by 4.427 [31].
*To convert from mg/L NO_2–N to mg/L NO_2^- multiply by 3.284 [31].

Industrial effluents

The pooled means of 74 ± 5.3 mg/L NO_3–N and 0.182 ± 0.047 mg/L NO_2–N (Table 6) obtained for the industrial effluents are much higher than the respective values obtained for the species in the river water samples (Tables 1-4). These sort of large differences in nitrate/nitrite levels between such divergent sources are not unexpected [34].

Generally raw wastes and effluents from factories and sewage treatment usually have high levels of ammonia and other nitrogenous wastes [5, 34]. Additionally prevailing temperatures within factories and their effluents encourage rapid multiplication of the bacteria population. These two factors can greatly elevate the levels of nitrate and nitrite in the effluents through aerobic and anaerobic bacteria activities. [2, 7, 8, 33]. The SWAZICAN is a pine-apple fruit-

juice canning industry. The fruits are very low to soil and can therefore have some of the applied nitrate fertilizer transferred onto their outer parts during rainfall or harvesting. External washings of the fruits plus reminants of nitrite employed as preservative are likely sources of the observed high levels of nitrates/nitrites in this factory effluent. In practice effluents from pulp/paper mills are treated locally and then recycled for further processing. Such treatment involves mainly removal of suspended solids in a clarifier [34] – a step probably taken more for economic than for environmental reasons. This would consequentially result in a rapid accumulation of ammonia and other nitrogenous wastes in the effluents, as well as aerobic/anaerobic bacteria producing additional nitrate and nitrite in the effluent, and hence accounting for high levels of the species in the samples we analyzed.

Table 6. Pooled averages* of the mg/L NO_3–N and mg/L NO_2–N in industrial effluents from two manufacturing industries.

Industrial source of effluent	mg/L NO_3–N	mg/L NO_2–N
Swazican (Malkerns)	72.3 ± 6.81	0.205 ± 0.065
Swazi Paper Mills (Matsapha)	75.67 ± 3.21	0.158 ± 0.016
Pooled mean (X_p + s_p) mg/L	74.0 ± 5.32	0.182 ± 0.047

*Mean of three replicates.

Method validation test

Accuracy tests carried out on spiked water samples gave mean recoveries of 99.2% for NO_3–N and 96.1% for NO_2–N. These values can be considered as quite adequate given that the predicted/acceptable percent recovery for NO_3–N in water samples is 83-113% and 93-114% for NO_2–N [34].

CONCLUSIONS AND RECOMMENDATIONS

All the rivers sampled for analysis in this study have mg/L NO_3–N contents both in excess of the expected natural levels as well as the USSR MCL of 9 mg/L NO_3–N (i.e. 40 mg/L NO_3^-) for fisheries and aquatic life. Additionally, the NO_3–N level in one of the rivers (Lusushwana) has increased by between seven to sixteen times within a 10 year period [32]. These observations are of great concern and call for the establishment of comprehensive water quality assessments and monitoring programs at a national level. This is much more so, considering the fact that these rivers serve as sources of drinking water for the free-grazing animals and water being processed for public consumption nationwide. The fact that the levels of both nitrate and nitrite in the drinking water samples were below the MCL/MAC of most international standard organizations should not stop extending such water quality assessment and monitoring programs to drinking water in the country. This is so because water treatment plants obtain their raw water from these nitrate/nitrite polluted rivers and the pollution by these species may eventually reach levels that can render any water treatment for nitrate/nitrite inadequate for drinking purposes. In view of these observations, vis-à-vis the current status of nitrate and nitrite in the main rivers of the country, the need to embark on a more comprehensive monitoring study of these species in the aquatic environment nation-wide cannot be overemphasized.

REFERENCES

1. Gray, N.F. *Drinking Water Quality Problems and Solutions*, John Wiley: New York; **1994**; pp118-132; 180-181; 266.
2. Hill, M.J. *Nitrates and Nitrites in Food and Water*, Ellis Horwood: New York; **1991**; pp. 14-92; 131-187.
3. Puckett, L.J. *U.S. Geol. Surv. Water - Resour. Invest. Rep. 94 - 4001*, USGS, Reston, Virginia, **1994**.
4. De, A.K. *Environmental Chemistry*, 3rd ed., Willey Eastern: New Delhi; **1994**.
5. Chapman, D. (Ed.) *Water Quality Assessment. A guide to the use of biota, sediments and water*, Chapman and Hall: London; **1992**; pp 71-76; 281-282; 412-416.
6. Puckett, L.J. *Environ. Sci. Technol.* **1995**, 29, 408A.
7. Nolan, B.T. *J. Environ. Qual.* **1999**, 28, 1518.
8. Speiran, G.K. *U.S. Geol. Surv. Water - Supply Pap. 2479*, USGS, Richmond, Virginia, **1996**.
9. Puckett, L.J.; Cowdery, T.K. *J. Environ. Qual.* **2002**, 31, 782.
10. Nolan, B.T.; Barbara, C.R.; Kerie, J.H.; Dennis R.H. *Wat. Conditioning Purification* **1999**, 39, 76.
11. De Zuane, J. *Drinking Water Quality, Standards and Controls*, Van Nostrand Reinhold: New York; **1990**; pp 87-90.
12. Holden, W.S. (Ed.) *Water Treatment and Examination* (Edited for 'The Society for Water Treatment and Examination'), J. and A. Churchill: London; **1970**; pp 83-84.
13. Nolan, B.T.; Hilt, K.J.; Ruddy, B.C. *Environ. Sci. Technol.* **2002**; 36, 2138.
14. Mueller, D.K.; Hamilton, P.A.; Helsel, D.R.; Hilt, K.J.; Ruddy, B.C. *U.S.. Geol. Surv. Water - Resour. Invest. Rep. 95-4031,* USGS, Denver, Colorado, **1995**.
15. Jennings, G.D.; Sneed, R.E. *Water Quality and Waste Management*, North Carolina Cooperative Extension Service; **1996**; Publication No AG 473-4.
16. Committee on Nitrate Accumulation, National Research Council *Accumulation of Nitrate*, National Academy of Sciences: Washington, DC; **1972**; pp 46-75.
17. Horita, K.; Wang, G.; Satake, M. Anal. Chim. Acta **1997**, 350, 295.
18. Roeve, R.N. *Environmental Analysis (Analytical Chemistry by Open learning)*, John Wiley: New York; **1994**.
19. U.S. Environmental Protection Agency *Water: Consumer Facts Sheet on Nitrates and Nitrites*, **2002**; URL: http://www.epa.gov
20. World Health Organization (WHO) *Guidelines for Drinking-Water Quality*, Vol. 1, 2nd ed., WHO: Geneva; **1993**; pp 52-53.
21. U.S. Environmental Protection Agency *Is Your Drinking Water Safe?* EPA: Washington, DC; **1991**, 5709-91-005.
22. Goulder, P.D. *Environmental Pollution Analysis*, Heyden: London; **1978**; pp 87-90.
23. Adams, V.D. *Water and Wastewater Examination Manual*, Lewis Publishers: Michigan; **1991**; pp 124-131.
24. American Public Health Association (APHA) *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association: Washington, DC; **1992**.
25. Takeda, K.; Fujiwura, K. *Anal. Chim. Acta* **1993**, 276, 25.
26. Karlson, M.; Karlberg, B.; Olsson, J.O.R. *Anal. Chim. Acta* **1995**, 312, 107.
27. Mikuska, P.; Vecera, Z.; Zdrahal, Z. *Anal. Chim. Acta* **1995**, 316, 261.
28. Piteau Associates Engineering Ltd (PAEC) *Groundwater Resources of Swaziland*, North Vancouver: Canada; **1992**.
29. Benoliel, M.J. *Int. J. Environ. Anal. Chem.* **1994**, 57, 197.

30. Cunniff, P. (Ed.) *Official Methods of Analysis of AOAC International*, Vol. 1, 16th ed., AOAC International: Gaithersburg, Maryland; **1998**; pp 28-30.
31. HACH Company *DR-2010 Series Datalogging Spectrophotometric: Operations and Procedures Manual*, Hach Company: Colorado; **1999**.
32. Mtetwa, V.S.B. *Uniswa Res. J. Agric. Sci. Tech.* **1996**, 1, 103.
33. Fatoki, O.S. *S. Afr. J. Sci.* **1999**, 95, 237.
34. Calley, A.G.; Foster, C.F.; Stafford, D.A. *Treatment of Industrial Effluences*, Hodder and Stroughton: London; **1977**.