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## A Study of the Relative Levels and Factors in the Analysis of Total Ammonia Nitrogen in Some Surface and Groundwater Bodies of Swaziland

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**Abstract:** Water samples from selected surface water systems, namely three major rivers, three industrial discharges, one reservoir, one pond and tap water and groundwater systems made up of fifteen boreholes and shallow wells, were analyzed for ammonia ( $\text{NH}_3\text{-N}$ ), using the UV spectroscopic (Salicylate) method. Pooled mean values ( $\text{mg NH}_3\text{-NL}^{-1}$ ) are 0.14-0.29 for rivers, ponds, reservoirs and tap water; 14.80-16.70 for industrial effluents and 0.11-0.43 for the boreholes and shallow wells. These values are below the recommended maximum contaminant level (MCL) of  $<0.6 \text{ mg L}^{-1}$ , by USEPA and SWSC (Swaziland Water Services Corporation), for drinking water  $1.0 \text{ mg L}^{-1}$  for rivers and the  $22.8 \text{ mg L}^{-1}$  by USEPA for industrial effluent. However, they all exceed the  $0.02 \text{ mg L}^{-1}$  MCL recommended by USEPA for fish health and aquatic life in general, as well as the  $0.1 \text{ mg L}^{-1}$  for uncontaminated natural water. The most dominant factors considered in this study to have greatly influenced the levels of ammonia in both surface and groundwater samples analyzed include the degree of agricultural and industrial activities, population density, climate, rainfall pattern and soil/rock type in the area. More specifically the location (rural, sub-urban or urban) and depth are other factors that influence the ammonia levels in groundwater bodies.

**Key words:** Total ammonia nitrogen, natural sources, anthropogenic sources, algal bloom, toxicity to aquatic life

## INTRODUCTION

The natural occurrence of ammonia in water bodies is traceable to the breakdown of nitrogenous organic and inorganic wastes in soil and water and its presence is usually considered as indicative of such wastes and sanitary pollution in general (Bolalek and Graca, 1996; Gangbazo *et al.*, 1995; Murray, 2008). Other natural sources of ammonia in water bodies include excretion by biota, atmospheric gas exchange and reduction of the  $\text{N}_2$  gas in water by micro-organisms (Bolalek and Graca, 1996; Gangbazo *et al.*, 1995; Manahan, 1994; Chapman, 1992). Anthropogenic sources of ammonia in water bodies include industrial discharges (e.g., from ammonia based pulp and paper industry), agricultural practices, (through fertilizers, animal feed and waste), municipal sewerage or domestic waste in general, improper disposal of ammonia products, internal combustion engines, atmospheric deposition of burnt municipal waste and from cement mortar pipe linings (Bolalek and Graca, 1996; Gangbazo *et al.*, 1995; Chapman, 1992; Wikipedia, 2006; Issely, 2004; WHO, 1993; Brian, 2005; Environment Agency, 2008). It is well known that nitrogen and phosphorus are usually the major elements that limit algal growth in water bodies. Ammonia and nitrate are the most important forms of nitrogen responsible for controlling algal growth, being available for uptake by plants. Hence, just like phosphorus, when ammonia (or nitrate) is present in excess amounts in water bodies, it can accelerate plant growth which can eventually result in algal blooms, fishkill and toxicity to rooted aquatic plants.

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In a parallel manner, the quality of the affected water body becomes drastically impaired in the process (Wikipedia, 2006; Issely, 2004; Brian, 2005; Spruill *et al.*, 1998). The dissolved Total Nitrogen Ammonia (TAN) in water comprises the unionized form,  $\text{NH}_3$  and ionized form,  $\text{NH}_4^+$ , both of which are in equilibrium (Chapman, 1992; Brian, 2005; Sawyer, 2008; Bradshaws, 2005). However, it has been established that  $\text{NH}_3$  is the principal form of toxic ammonia (Brian, 2005; Sawyer, 2008; Bradshaws, 2005; Murray, 2008). Even at very low concentrations ammonia can be highly toxic to aquatic animals, which generally are less tolerant of ammonia than plants hence it is classified as dangerous for the aquatic environment (Wikipedia, 2006; Brian, 2005; Environment Agency, 2008). According to reports, it is toxic to some fresh water organisms at concentrations ranging from 0.53 to 22.8  $\text{mg L}^{-1}$  (Brian, 2005). Ammonia poisoning in fish can result in diverse adverse health effects including loss of equilibrium, hyper excitability, increased respiratory activity and  $\text{O}_2$  uptake, loss of appetite, lethargy, increased heart rate, coma and death (Issely, 2004; Brian, 2005). It has been shown experimentally that the lethal concentrations for a variety of fish species range from 0.2 to 2.0  $\text{mg L}^{-1}$  (Brian, 2005; Fish Doc, 2004). However in some cases, concentrations as low as 0.02  $\text{mg L}^{-1}$  may be lethal (Johnson and Wiedorholt, 2004). Toxic concentrations of ammonia in humans may result in loss of equilibrium, convulsions, coma and death. However, toxicological effects are observed only at levels  $\geq 200 \text{ mg kg}^{-1}$  of body weight (WHO, 1993; Brian, 2005). In general, excess ammonia may accumulate in an organism and cause alterations of metabolic process or increase the pH of the body (Issely, 2004).

The concentration of the unionized ammonia, which determines the toxicity of the water body with respect ammonia, depends on the pH, temperature and total ammonia concentration (Manahan, 1994; Chapman, 1992; Brian, 2005; Murray, 2008; Ornamental Fish, 2008). Hence, toxicity increases as both pH and temperature increase (Chapman, 1992; Fish Doc, 2004; Bradshaws, 2005; Sawyer, 2008).

Other factors that influence the levels of ammonia in surface waters or groundwater systems include the location (i.e., the degree of urbanization and population density) intensity and nature of agricultural practices around the site (especially those involving application of ammonium fertilizers and intensive animal rearing) (Wikipedia, 2006; Brian, 2005; Bolalek and Graca, 1996; Gangbazo *et al.*, 1995). The total levels of ammonia and ammonia compounds in unpolluted waters are usually  $<0.1 \text{ mg NH}_3\text{-N L}^{-1}$ . Similarly in both surface and ground waters levels of total ammonia nitrogen are usually  $<0.20 \text{ mg L}^{-1}$ . In the presence of  $\text{O}_2$  ammonia in natural water systems is rapidly oxidized by some bacteria to nitrite and nitrate (Chapman, 1992; WHO, 1993; Murray, 2008; Environment Agency, 2008; Harrison, 2008). Ammonia is often added to drinking water during treatment, where it reacts with chlorine to produce the disinfectant-chloramines (Gray, 1994). These natural and anthropogenic activities would inadvertently influence the levels of  $\text{NH}_3\text{-N}$  in surface, drinking and ground water bodies. The  $\text{pK}_a$  of the ammonium ion is 9.26 hence  $\text{NH}_3\text{-N}$  in water is predominantly present as  $\text{NH}_4^+$  rather than the toxic component,  $\text{NH}_3$  (Manahan, 1994; Sawyer, 2008).

The MCL for ammonia in surface water recommended by USEPA is based primarily on chronic and acute exposure of aquatic organisms to unionized ammonia. And, since the toxicity of  $\text{NH}_3$  and the equilibrium between the TAN components ( $\text{NH}_3$  and  $\text{NH}_4^+$ ) are influenced by pH and temperature, the USEPA criteria in parallel, vary with pH and temperature (Gangbazo *et al.*, 1995; Murray, 2008; Sawyer, 2008). For most natural surface waters, a chronic criteria of  $\leq 2.1 \text{ mg L}^{-1}$  -TAN has been set by USEPA for pH ranges of 6.5-9.0 and temperature range of 0-30°C. This criterion can thus be exceeded at TAN levels as low as 0.07  $\text{mg L}^{-1}$  at a high pH of  $\sim 9.0$  and high temperatures of  $\sim 30^\circ\text{C}$  (Sawyer, 2008; Bradshaws, 2005). Indeed the exact value at pH 9 and 30°C is 0.04  $\text{mg L}^{-1}$  -TAN and 0.1  $\text{mg L}^{-1}$  -TAN at pH 8.5 and 25°C etc. (Fish Doc, 2004). USEPA also fixed a general criterion of 0.02  $\text{mg L}^{-1}$  - $\text{NH}_3\text{-N}$  for fresh water or marine environment and fish health, while it fixes a limit (MCL) of 1.00  $\text{mg L}^{-1}$  for rivers (WHO, 1993; Murray, 2008; USEPA, 2005, 2006). The Swaziland

Water Services Corporation (SWSC) and USEPA recommend a limiting value of  $<0.6 \text{ mg L}^{-1}$  TAN for drinking water and water for domestic use in general (Murray, 2008; USEPA, 2005, 2006).

The aim of this study is first and foremost to compare observed levels of Total Ammonia Nitrogen (TAN) between selected surface and ground water bodies in Swaziland and on the basis of recommended criteria (by USEPA and other organizations), determine the extent of pollution of the water bodies by TAN and hence how safe they are for human use and aquatic life. We shall, as much as possible endeavour to rationalize the obtained levels on the basis of observable sources of nitrogen ammonia and factors influencing its concentrations in these aquatic bodies.

## **MATERIALS AND METHODS**

### **Instrumentation**

The HACH-DR 2010 data logging, microprocessor controlled spectrophotometer-an advanced water quality laboratory series, was used for the measurement of total  $\text{NH}_3\text{-N}$  ( $\text{mg L}^{-1}$ ), the reaction time and wavelength.

### **Reagents**

Ammonia salicylate reagents powder pillows, ammonia cyanurate reagents powder pillows, concentrated sulphuric acid, 5 M NaOH solution, distilled-deionized water.

### **Sample Collection, Pretreatment and Storage**

Samples were collected from twelve different surface water sampling points, comprising rivers (upstream and downstream), a pond, a reservoir, a tap water and industrial effluents and from fifteen groundwater bodies, located in Manzini and Lubombo regions of Swaziland between October, 2005 and March, 2006. The samples were collected in thoroughly cleaned 500 mL brown borosilicate glass bottles. For each sampling trip, four samples were collected from each site. Samples were preserved by adding 1.0 mL of concentrated  $\text{H}_2\text{SO}_4$  to each 500 mL of sample and subsequent storage in the refrigerator at  $4^\circ\text{C}$  on reaching the laboratory. This allows for samples to be preserved for up to 28 days. However, analysis were usually carried out within 48 h after sampling (Chapman, 1992; Stewart, 1989; APHA, 1992; Cunniff, 1998). For all the sites, sampling was carried out monthly over a period of five months. Sampling sites were chosen so as to ensure adequate reflection and representation of the major sources of  $\text{NH}_3\text{-N}$  pollution of aquatic bodies as well as the factors likely to affect its levels in them.

### **Analysis (Salicylate Method)**

Prior to analysis, samples were warmed to the room temperature and then neutralized with 5.0 M NaOH solution. The wavelength was set at 655 nm. A 10 mL cell riser was inserted into the cell compartment. Two clean 10 mL sample cells were each filled with 10 mL of sample, one being taken as sample and the other as a blank. To the one taken as sample, the contents of one ammonia salicylate reagent powder pillow were emptied into it, stoppered and shaken to dissolve. A 3 min reaction time was allowed. Afterward, the contents of one ammonia cyanurate reagent powder were added to the same sample cell, stoppered, shaken to dissolve and another 15 min reaction time allowed to occur. The instrument was then zeroed with blank after which the prepared sample was measured and the result given in  $\text{mg NH}_3\text{-N L}^{-1}$ .

### **Method/Data Validation**

To validate the method employed for analysis, ammonia reference standards from HACH Company, USA, were serially diluted with distilled-deionized water and subsequently analyzed in exactly the same way as the samples. The average recovery and the student t-test at the 95% confidence level were calculated.

## RESULTS AND DISCUSSION

The method validation analysis gave a mean recovery of 108.4%. Additionally, the student t-test employed indicated that there was no significant difference between the true  $\text{NH}_3\text{-N}$  ( $\text{mg L}^{-1}$ ) concentration of the HACH reference standard and the mean  $\text{NH}_3\text{-N}$  ( $\text{mg L}^{-1}$ ) value obtained using the spectrophotometric (salicylate) method which was employed for this study.

Table 1 and 2 depict the range and the pooled means for the  $\text{mg L}^{-1}$ .

$\text{NH}_3\text{-N(TAN)}$  for each site of the surface water and groundwater over a period of five months, plus the particularly influential feature/factor for each respective site. The overall range for all the surface water sites is thus 0.14 (SWSC)-18.00 (PMI)  $\text{mg L}^{-1}$   $\text{NH}_3\text{-N}$  with a mean value of 3.66 and an upper value of 4.46  $\text{mg NH}_3\text{-N L}^{-1}$ . The overall (pooled mean) range for the surface water sites is also 0.14-16.70  $\text{mg NH}_3\text{-N L}^{-1}$ . On the other hand, for the groundwater sites the overall (lowest-highest) range in  $\text{mg NH}_3\text{-N L}^{-1}$  is 0.08 (KK) -0.45 (SP), with a mean minimum value of 0.15 and a mean maximum value of 0.19  $\text{mg NH}_3\text{-N L}^{-1}$ . The pooled mean range for all the groundwater sites being 0.11-0.43  $\text{mg NH}_3\text{-N L}^{-1}$  (TAN). A close look at these ranges, the mean values of their lower and upper limits and the ranges of their respective pooled means, clearly indicate higher levels of the  $\text{mg NH}_3\text{-N L}^{-1}$  (TAN) in the surface water sites than in the groundwater sites. The observed, generally higher values of  $\text{NH}_3\text{-N}$  in the surface waters may be traceable partly to the various natural sources of  $\text{NH}_3\text{-N}$  such as breakdown of nitrogenous organic materials, excretion by biota, atmospheric gaseous exchange and reduction of N as well as anthropogenic sources such as industrial waste waters, agricultural practices and domestic wastes in general. These sources have much greater tendencies to cumulate the ammonia nitrogen in the surface waters than in the groundwater systems. The rates at

Table 1: Pooled mean value of  $\text{mg L}^{-1}$   $\text{NH}_3\text{-N(TAN)}$  and dominant feature/factor for each surface water sampling site

Sampling site	$\text{NH}_3\text{-N}$ $\text{mg L}^{-1}$ , Range (pooled mean)	$\bar{X}_p \pm s_p$ ( $\text{NH}_3\text{-N}$ $\text{mg L}^{-1}$ )	Dominant features/Factors				Nature of vicinity and activity going on
			Nature of site	Population density/Location	Soil/Rock (type of area)		
UUC	0.15±0.02-0.19±0.00	0.19±0.00	River	Sub-urban medium	Lochiel granite		Agriculture and industrial
UDC	0.21±0.00-0.34±0.01	0.29±0.00	River	Sub-urban, low	Lochiel granite		Agriculture and industrial
LUC	0.20±0.08-0.39±0.00	0.28±0.00	River	Sub-urban, high	Lochiel granite		Agricultural and industrial
LDC	0.19±0.04-0.40±0.00	0.27±0.00	River	Sub-urban, high	Gabro and dolerite		Urban, domestic
MUC	0.16±0.00-0.32±0.03	0.21±0.00	River	Sub-urban, medium	Ngwane gneiss		Urban, domestic
MDC	0.14±0.01-0.22±0.00	0.18±0.00	River	Urban, high	Sabie river basalt		Agricultural, domestic
SWSC	0.10±0.02-0.17±0.04	0.14±0.00	River	Urban, high	Lebombo rhyolite		Agricultural, domestic
TPW	0.14±0.00-0.24±0.01	0.18±0.00	Reservoir	Urban, high	Ngwane gneiss		Industrial, domestic
PMI	15.0±0.00-0.18±0.78	16.70±0.00	Tap water	Urban, low	Ngwane gneiss		Urban
FMI 1	14.5±0.89-16.5±0.80	15.30±0.00	Factory effluent	Sub-urban, medium	Ngwane gneiss		Industrial, agricultural
FMI 2	13.0±1.78-16.5±0.89	14.80±0.00	Factory effluent	Sub-urban, medium	Ngwane gneiss		Industrial
SPM	0.14±0.02-0.20±0.00	0.17±0.00	Pond	Sub-urban, high	Sand stone and Nkondolo group		Sub-urban, agricultural

UUC: Usuthu River up Control, PMI: Paper Manufacturing Industry, UDC: Usuthu River down Control, FMI 1: Food Manufacturing Industry 1, LUC: Lusushwana River up Control, FMI 2: Food Manufacturing Industry 2, LDC: Lusushwana River down Control, SMP: Simunye Pond, MUC: Mbuluzi River up Control, TPW: Tap Water, MDC: Mbuluzi River down Control and SWSC: Swaziland Water Services Corporation

Table 2: Pooled mean, concentration range of the  $\text{mg L}^{-1}$   $\text{NH}_3\text{-N}$  (TAN) and dominant feature/factor for each groundwater site

Sampling site	$(\text{NH}_3\text{-N})$ $\text{mg L}^{-1}$ range	$\bar{X}_p \pm S_p$ $(\text{NH}_3\text{-N})$ $\text{mg L}^{-1}$	Dominant feature/Factor			
			Location/ population density	Rock type	Top soil type	Vicinity type and activity
ML	0.10-0.13	0.11	Sub-urban, low	Usuthu intrusive	Loam	Sub-agric. grazing
MA	0.12-0.14	0.13	Sub-urban, low	Usuthu intrusive	Loam	Domestic sub-agric.
LU	0.10-0.12	0.11	Sub-urban, high	Usuthu intrusive	Loam	Domestic sub-agric.
TS	0.15-0.17	0.16	Sub-urban, mod.	Usuthu intrusive	Loam	Sub-agric domestic
KM	0.11-0.13	0.12	Rural, high	Sabie basalt	Silt	Sub-agric.
SL	0.09-0.14	0.12	Rural, low	Sabie basalt	Silt	Grazing field
NK	0.10-0.17	0.13	Rural, low	Rhyolite acitic ignimbrates	Loam	Grazing field
TK	0.13-0.21	0.19	Rural, low	Sabie basalt	Loam	Agricultural
MF	0.10-0.13	0.12	Rural, low	Rhyolite acitic ignimbrates	Silt	Sub-agric
KK	0.08-0.13	0.12	Rural, low	Lebombo rhyolites	Silt	Sub-agric
LM	0.15-0.17	0.16	Rural, low	Lebombo rhyolites	Loam	Agric. Domestic, laundry
TW	0.33-0.45	0.39	Rural, low	Sabie basalt	Loam	Grazing and laundry
TP	0.14-0.20	0.17	Rural, low	Sabie basalt	Silt	Grazing
HL	0.11-0.12	0.12	Rural, low	Rhyolite acitic ignimbrates	Loam	Grazing
SP	0.40-0.45	0.43	Industrial	Usuthu intrusive	Loam	Industrial

ML: Malkerns, MA: Mahlanya, TP: Tsambokhulu Primary, LU: Ludzeludze, TS: Tsekwane Butchery, HL: Hhalane, KM: Ka-Mswati, SL: Sihlongwaneni, SP: Swazi Paper Mills, NK: Nkalashane, TK: Tsambokhulu, MF: Mafucula, KK: Kuhlmukeni, LM: Lomahasha and TW: Timbutini Well, (Sub-Agric = Subsistence farming)

Table 3:  $\text{NH}_3\text{-N}$  (TAN)  $\text{mg L}^{-1}$  values in surface water and groundwater bodies relative to that of an uncontaminated, natural water and some selected criteria

Surface water					Ground water				
Sampling site	$\bar{X}_p$ ( $\text{mg L}^{-1}$ ):				Sampling site	$\bar{X}_p$ ( $\text{mg L}^{-1}$ ):			
	$\text{NH}_3\text{-N}$	$\bar{X}_p / X_{fh}$	$X_p / X_o$	$X_p / X_{dwc}$		$\text{NH}_3\text{-N}$	$\bar{X}_p / X_{fh}$	$X_p / X_o$	$X_p / X_{dwc}$
UUC	0.19	9.5	1.9	0.32	ML	0.11	5.5	1.1	0.18
UDC	0.29	14.5	2.9	0.48	MA	0.13	6.5	1.3	0.22
LUC	0.28	14.0	2.8	0.47	LU	0.11	5.5	1.1	0.18
LDC	0.27	13.5	2.7	0.45	TS	0.16	8.0	1.6	0.27
MUC	0.21	10.5	2.1	0.35	KM	0.12	6.0	1.2	0.20
MDC	0.18	9.0	1.80	0.30	SL	0.12	6.0	1.2	0.20
SWSC	0.14	7.0	1.4	0.23	NK	0.13	6.5	1.3	0.22
TPW	0.18	9.0	1.8	0.30	TK	0.19	9.5	1.9	0.32
PMI	16.70	835.0	167.0	27.80	MF	0.12	6.0	1.2	0.20
FMI-1	15.30	765.0	153.0	25.50	KK	0.12	6.0	1.2	0.20
FMI-2	14.80	740.0	148.0	24.67	LM	0.16	8.0	1.6	0.27
SMP	0.17	16.5	1.7	0.28	TW	0.38	19.0	13.8	0.63
					TP	0.17	8.5	1.7	0.28
					HL	0.12	6.0	1.2	0.20
					SP	0.43	21.5	4.3	0.72

$X_{fh} = 0.02 \text{ mg L}^{-1}$ :  $\text{NH}_3\text{-N}$  (fish health),  $X_o = 0.10 \text{ mg L}^{-1}$ :  $\text{NH}_3\text{-N}$  (uncontaminated natural water),  $X_{dwc} = 0.6 \text{ mg L}^{-1}$  =  $\text{NH}_3\text{-N}$  (SWSC and USEPA criterion for drinking water)

which they accumulate ammonia nitrogen into the surface waters, for instance through run off of agricultural fertilizers, animal wastes and municipal waste are much faster than the rate at which these runoffs can leach into the groundwater bodies.

Moreover, it has been claimed that groundwater bodies (deep well and boreholes) yield water of the highest degree of organic bacterial purity (Holden, 1970). This situation results in a reduction of the pollution effects due to these sources, hence the observed lower  $\text{mg L}^{-1}$   $\text{NH}_3\text{-N}$  levels in the groundwater bodies relative to their surface water counterparts.  $\text{NH}_3\text{-N}$  (TAN)  $\text{mg L}^{-1}$  values in surface water and groundwater bodies relative to that of an uncontaminated, natural water and some selected criteria are shown in Table 3.

Table 3 depicts the pooled mean of each of all the sites relative to the set criteria for fish health (and aquatic life generally,  $X_{fh}$ ,  $0.02 \text{ mg L}^{-1}$   $\text{NH}_3\text{-N}$ ), for uncontaminated natural water

$X_0$  (0.10 mg L<sup>-1</sup> NH<sub>3</sub>-N) and for drinking water  $X_{dwc}$  (0.6 mg L<sup>-1</sup> NH<sub>3</sub>-N). The observed ranges can be summarized as follows:

In each of the three cases, surface water samples manifest higher levels of NH<sub>3</sub>-N than the groundwater series. This observation becomes more obvious in the upper limit values where the surface water values of these parameters are some multiples of their groundwater counterpart values.

Table 4 further enables us to see at a glance the percentages of the surface water sites and groundwater sites that contain higher NH<sub>3</sub>-N (mg L<sup>-1</sup>) values than the criteria,  $X_{fh}$ ,  $X_0$  and  $X_{dwc}$  stated and defined in Table 3 and 5. Table 3 reveals that all the sites (both surface water and groundwater), contain mg L<sup>-1</sup> NH<sub>3</sub>-N levels higher than both  $X_{fh}$  and  $X_0$ . On the other hand 25% of the surface water (which, are factory effluents) contain higher mg L<sup>-1</sup> NH<sub>3</sub>-N values than  $X_{dwc}$ . All the sampled groundwater bodies have their mg L<sup>-1</sup> NH<sub>3</sub>-N levels lower than  $X_{dwc}$ -the drinking water criterion. The other parameters included in the table namely  $X_{6.5,25}$ ;  $X_{7.5,25}$ ;  $X_{8.5,25}$  and  $X_{9,30}$  are the expected values of mg L<sup>-1</sup> NH<sub>3</sub>-N at the specified pH and temperature (the subscript). They all confirm the earlier observation that more of the surface water sites contain higher NH<sub>3</sub>-N mg L<sup>-1</sup> levels than the groundwater series. The condition  $X_{6.5,25}$  i.e, at a pH 6.5 and temperature of 25°C has been chosen because these are the average values recorded for most of the sampling sites. Most of them also are in conformity with the observations above. Comparison of highest (maximum) and lowest (minimum) NH<sub>3</sub>-N values in surface water with those in the groundwater bodies on geographic basis is shown in Table 6.

The highest and the lowest values of mg L<sup>-1</sup> NH<sub>3</sub>-N for both surface water and groundwater samples analyzed also go to confirm the same assertion that the surface waters have higher values of this nutrient within them.

Table 4: Percentage of sampling site type with NH<sub>3</sub>-N, mg L<sup>-1</sup> values above selected, important criteria/parameters

Parameters/ Criteria	Interpretation	Value- mg L <sup>-1</sup> NH <sub>3</sub> -N (TAN)	% of sampling point with levels above in	
			Surface water	Groundwater
$X_0$	For natural uncontaminated fresh/marine water	0.10	100.00	100.00
$X_{fh}$	For fish health	0.02	100.00	100.00
$X_{dwc}$	USEPA/SWSC drinking water criterion	0.60	25.00	0.00
$X_{6.5,25}$	Chronic value at a pH 6.5 and temp. of 25°C	11.00	25.00	0.00
$X_{7.5,25}$	Chronic value at a pH 7.5 and temp. of 25°C	1.00	25.00	0.00
$X_{8.5,25}$	Chronic value at a pH 8.5 and temp. of 25°C	0.10	100.00	100.00
$X_{9,30}$	Chronic value at a pH 9 and temp. of 30°C	0.04	100.00	100.00

Table 5: Summary of the ranges of  $\bar{X}_s/X_{fh}$ ,  $X_p/X_0$  and  $X_p/X_{dwc}$  for surface water and groundwater samples

Parameters	Range	
	Surface water	Groundwater
$X_p/X_{fh}$	7.0-835.0	5.5-21.5
$X_p/X_0$	1.4-167.0	1.1-4.3
$X_p/X_{dwc}$	0.23-27.83	0.18-0.72

Table 6: Comparison of highest (maximum) and lowest (minimum) NH<sub>3</sub>-N values in surface water with those in the groundwater bodies on geographic basis

Feature	Highest value: mg L <sup>-1</sup> NH <sub>3</sub> -N (TAN)		Lowest value: mg L <sup>-1</sup> NH <sub>3</sub> -N (TAN)	
	Surface water	Ground- water	Surface water	Ground-water
Concentration	16.70	0.43	0.14	0.11
Sampling point	P.M.I	SPM	SWSC	ML,LU
Specific type of site	Factory effluent	Ground water	Reservoir	Ground water
Region of location	Manzini	Manzini	Manzini	Manzini
Dominant feature/factor/activity	Industrial, agricultural	Industrial	Domestic	Domestic, medium agric. practice

Table 7: Overall range and mean values of  $\text{mg L}^{-1} \text{NH}_3\text{-N}$  (TAN) levels for specific categories of surface water and groundwater bodies studied

Water body	Overall range: $\text{mg L}^{-1} \text{NH}_3\text{-N(TAN)}$	$W = x_h - x_l$	Pooled mean $x_p$ ( $\text{mg L}^{-1} \text{NH}_3\text{-N}$ )
Factory effluents	14.80-16.70	2.10	15.60
Rivers: Up control	0.19-0.28	0.09	0.23
Rivers: Down control	0.18-0.29	0.09	0.25
Pond	0.17	-	0.17
Reservoir	0.14	-	0.14
Drinking (tap) water	0.18	-	0.18
Groundwater	0.11-0.43	0.32	0.17

$\bar{x}_h$  : Highest pooled mean,  $\bar{x}_l$  : Lowest pooled mean and w: Range

Table 7 depicts the overall ranges and the mean values of  $\text{mg L}^{-1} \text{NH}_3\text{-N}$  (TAN) for the specific categories of all the sampled surface water and groundwater bodies. The values are in the following increasing order for the itemized categories:

Reservoir < Pond = Ground water < Drinking water < River (Up control) < River (Down control) < Industrial-effluents

The industrial effluents are the highest contributors of  $\text{NH}_3\text{-N}$  to aquatic environments, especially the rivers into which they discharge. The pulp and paper mills are the most notorious with regards to environmental pollution with ammonia nitrogen. Indeed, among the industrial effluent samples, the one having the lowest pooled mean value (FMI-2) of  $14.8 \text{ mg L}^{-1} \text{NH}_3\text{-N}$ , is 51.03 times higher than another surface water site (UDC =  $0.29 \text{ mg L}^{-1} \text{NH}_3\text{-N}$ ) with the highest  $\text{NH}_3\text{-N}$  ( $\text{mg L}^{-1}$ ) value apart from the industrial effluents. A similar analogy with the groundwater shows that the same point (FMI -2) has 34.42 as much  $\text{mg L}^{-1} \text{NH}_3\text{-N}$  as that found in the groundwater site with the highest  $\text{mg L}^{-1} \text{NH}_3\text{-N}$  value (i.e, SP =  $0.43 \text{ mg L}^{-1} \text{NH}_3\text{-N}$ ).

According to Holden (1970), contaminant/pollutant levels in ponds and reservoirs including  $\text{NH}_3\text{-N}$  can vary from almost pure water to grossly polluted waters depending on the nature of the gathering grounds, the sampling and storage methods. This may partly account for the low average value, indeed the lowest average of all the surface waters, of  $0.14 \text{ mg L}^{-1} \text{NH}_3\text{-N}$  obtained for the reservoir (SWSC), while an average value of  $0.17 \text{ mg L}^{-1} \text{NH}_3\text{-N}$  was obtained for the Simunye pond-a value that is very close to that of MDC ( $0.18 \text{ mg L}^{-1} \text{NH}_3\text{-N}$ )-which is a river sampling point. The  $\text{mg L}^{-1} \text{NH}_3\text{-N}$  in the drinking water is relatively high when compared with those of reservoir, pond and groundwater bodies. As part of drinking water treatment, ammonia is usually added to water being processed for public consumption in order to combine with residual chlorine in water to form the chloramines ( $\text{NH}_2\text{Cl}$  and  $\text{NHCl}_2$ ), both of which are good disinfectants (Gray, 1994; Baird and Cann, 2005; Pepper *et al.*, 1996). It is however, possible that not all the added ammonia is used up in converting the residual chlorine in the water to chloramines, thereby enhancing the original level of the ammonia in the drinking water to some extent. This might probably account for the observed high levels of the  $\text{NH}_3\text{-N(TAN)}$  in drinking water relative to those of the reservoir, pond and groundwater sources.

Table 1-4 and 7 show that all the sampling points, both the surface water and groundwater series contain multiples of the  $\text{mg L}^{-1} \text{NH}_3\text{-N}$  USEPA criterion for fish health ( $X_h = 0.02 \text{ mg L}^{-1} \text{NH}_3\text{-N}$ ) and much higher values than the guideline for natural, uncontaminated water ( $X_o = 0.1 \text{ mg L}^{-1} \text{NH}_3\text{-N}$ ). First these values are indicative of strong anthropogenic contributions to the ammonia levels in the aquatic environment of these regions (Lubombo and Manzini) in Swaziland. Secondly, with the obtained  $X_p/X_h$  values in Table 3 and their ranges in Table 5, one would expect a lot of fish-kill in most of the surface waters in these regions. One of the reasons this is not occurring against expectations would be the prevalent pH (usually in the range 6.5-7.5) and temperature (usually average of  $25^\circ\text{C}$ ), which inadvertently elevates the chronic levels for fish and other aquatic life-in general.



## CONCLUSION AND RECOMMENDATIONS

The fact that all the samples analyzed in this study possess levels of  $\text{NH}_3\text{-N}$  ( $\text{mg L}^{-1}$ ) that are much higher than the USEPA criteria for fish health, ( $X_h$ ) and for uncontaminated natural waters ( $X_o$ ), shows strong anthropogenic contributions toward elevated levels of ammonia (TAN) in aquatic environment and those related to the paper and pulp industries are the most notorious in this respect. The  $\text{mg L}^{-1}$   $\text{NH}_3\text{-N}$  levels in surface waters were found to be generally higher than those found in groundwater systems of these two regions of the country. The dependence of the  $\text{mg L}^{-1}$   $\text{NH}_3\text{-N}$  level on pH and temperature may be the reason why massive fish-kills and other toxic effects of high levels of this species have not been observed in these regions. However, an uncontrolled discharge of industrial effluents with high concentrations of this nutrient can trigger its levels to beyond the chronic values for aquatic life and eventually result in massive fish-kills as well as unsafe waters for human uses. Also, treatment of drinking water through addition of ammonia to form the chloramine disinfectants should be properly carried out to avoid unintended elevation of  $\text{NH}_3\text{-N}$  levels in the public water supplies. Finally, regular monitoring of this nutrient should be entrenched into the water-quality programme at a nation-wide level.

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