Relationship between nitrogenous pollution of borehole waters and distances separating them from pit latrines and fertilized fields

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Abstract: The occurrence of the following nitrogenous pollutants, namely ammonium, nitrite and nitrate ions, was investigated in groundwater (borehole) sources of two villages in North West Province of South Africa. The study was carried out for two reasons. The Department of Water Affairs and Forestry (DWAF) in Mmabatho had expressed anxiety over anomalous levels of nitrate ion (which can be reduced to the toxic nitrite ion) in some groundwater sources in the province (and this included some groundwater sources in the two villages). The concentrations of the nitrogenous pollutants were monitored by differential pulse polarography (DPP). This electrochemical method was selected because it is fast, has low detection limits and is virtually free of interferences. The study indicated that the main pollutant in the groundwater sources was nitrate ions whose concentrations were higher than 25 ppm in some borehole waters. This is more than two times higher than the 10 ppm N specification recommended by the South African National Standard (SANS) for drinking water. The study also indicated that the concentrations of ammonium and nitrite ions in the borehole waters studied are not a health risk to the communities. Important sources of groundwater pollution are pit latrines and maize fields treated with nitrogen fertilizers. It was found that groundwaters (borehole water) were polluted with nitrate ions when the distances of the pit latrines and fertilized maize fields were respectively less than 18 m and 13 m from the boreholes. The pollution was more pronounced when the water table was shallow.

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1. Introduction

The majority of people in South Africa drink untreated groundwaters and they are mainly from boreholes (Modise and Krieg, 2004). It is important, therefore, to check whether borehole waters are polluted. An important type of pollution is due to NO_3^- , NO_2^- and NH_4^+ ions, which are inorganic ions containing nitrogen. Studies have shown that the concentrations of nitrate ions (NO_3) is high in many groundwaters in South Africa (Modise and Krieg, 2004; Fourie and van Ryneveld, 1995; Sililo and Saayman 2001; Tredoux et al, 2000; Bhagwan et al, 2006; Conrad et al, 1999; Tredoux, 2004; Fourie and van Ryneveld, 1994; Xu and Braune, 1995; Terblanche, 1991; Jackson, 1998). and that it is particularly high in a belt running in a north-easterly direction from the Northern Cape through the North West Province to Limpopo Province (Tredoux, 2000).

Nitrate ion is a health risk because it is reduced to the toxic nitrite ion (NO₂⁻) by microbiological processes in our stomachs. Nitrite ions reduce the oxygen-carrying capacity of blood and may cause methaemoglobinemia in infants (Girard and Hillaire-Marcel, 1997; Jacks et al, 1999; Ramaraju et al, 1999; Wakida and Lerner, 2005; Chiroma et al, 2007; Banks et al, 2007; Ohou et al, 2008; Suthar et al, 2009; Hesseling et al, 1991; Lewis et al, 1980) and they can also react with amino compounds, in many media, to form nitrosoamines which are strongly carcinogenic (Girard and Hillaire-Marcel, Ramaraju et al, 1997; Wakida and Lerner, 2005; Suthar et al, 2009).

Nitrogenous pollutants reach groundwater sources by several pathways, the most important of which are seepage of water containing these pollutants from the following sources (Water Quality Management Policies and Strategies in RSA. April, 1991) : decayed vegetation and animal matter; pit latrines; sewage; domestic and farm effluents; fertilizers applied to farm lands. The main purpose of this study was to investigate pollution due to pit latrines and nitrogenous fertilizers The main purpose of this study was to investigate pollution due to pit latrines and nitrogenous fertilizers and the objectives were to: determine the concentrations of NO_3^- , $NO_2^$ and NH_4^+ ions in some selected borehole waters; find out whether there is a correlation between these concentrations and the distances separating the boreholes and pollution sources (pit latrines and

fertilized maize fields); make suggestions for preventing pollution of borehole waters.

A pit latrine is easy to construct and maintain. A hole having a depth of about 2 metres is generally dug in the ground over which a seat is placed and this is enclosed in some structure that has a roof and a door (Palmer, 1981). Liquid waste will infiltrate into the surrounding soil and the amount that can be absorbed by the soil will depend mainly on its composition and texture. Nitrogenous pollution due to pit latrines has been studied by many workers (Bhagwan et al, 2006; Conrad et al, 1996; Tredoux, 2004; Fourie and Ryneveld, 1994; Xu et al, 1995; Terblanche, 1991; Jackson, 1998; Girard and Hillaire-Marcel, 1997; Jacks, 1999; Banks et al, 2007; Ohou et al, 2008; Palmer, 1981; Reed, 1994). Their studies show that nitrogenous pollution depends on many factors, some of the more important of which are: number and sizes of pit latrines; distance of pit latrine from boreholes; depth of aquifers; soil and rock composition and their textures around the aquifers.

Two villages (Schoongezicht and Welverdiend) situated in the Ditsobotla District of North West Province were selected for the study. This area was chosen because of information supplied by the Department of Affairs (Mmabatho) that waters in these areas are polluted with nitrate ions. Topography of area is illustrated in Figure 1.

The land slopes very gently to the north-east at a gradient of 1 in 50 metres (Brinn, 1991). Welverdiend is at a lower altitude than Schoongezicht and water flows from Schoongezicht to Welverdiend. The water levels at Schoongezicht and Welverdiend were respectively about 9 metres and 6 metres below ground level. Water samples from nine boreholes were studied. Details of the boreholes relevant to this study are shown in Table 1.

Row 7 in this Table shows the distances separating the pit latrines and maize fields from the boreholes. Rows 2, 3, 4, 5 and 6 give, respectively, information about borehole location, borehole number, equipment with borehole, borehole depths and water level depths. Row 8 gives the number of pit latrines close to each borehole.

2. Materials and Methods (a) Apparatus

BAS–100B/W Electrochemical Workstation was used to obtain polarograms for the standard solutions and the water samples. Oyster pH meter was used for measuring the pH and temperatures of the water samples collected.

b) Collection and storage of groundwater samples

Water samples from the nine boreholes were collected once a week for six weeks during the winter season, June/July. Sampling was done in the morning and the water samples were collected in 1 litre polyethylene bottles. The pH and temperature of each water sample was then recorded and 1 millilitre of 10 ppm $HgCl_2$ solution (preservative) was added to each sample. Until analysis, the samples were kept in a refrigerator.

(c) Preparation of standard solutions of NO_3^- , NO_2^- and NH_4^+ ions for obtaining calibration curves

Analar potassium nitrate (KNO₃), sodium nitrite (NaNO₂) and ammonium sulphate, $(NH_4)_2SO_4$, were used respectively to prepare 1 000 ppm N stock solutions of NO₃⁻, NO₂⁻ and NH₄⁺ ions. These solutions were then appropriately diluted to prepare the solutions for obtaining calibration curves (concentration range: 2 ppm – 20 ppm).

(d) Preparation of o-nitrophenol from NO₃⁻ ions (Metrohm Application Bulletin No. 70e,1979; Vinger, 1998)

 2.0 cm^3 of the NO₃ solution was mixed with 2.0 cm^3 of phenol in a beaker. 8.0 cm^3 of concentrated sulphuric acid was then added slowly while swirling the contents of the beaker, to prepare o-nitrophenol.

(e) Preparation of diphenyl nitrosoamine from NO₂⁻ ions (Barsotti et al, 1982; Vinger, 1998)

 3.0 cm^3 of diphenylamine was added to a solution containing 2.0 cm^3 of the NO₂ solution and 10.0 cm^3 of potassium thiocynate (KCNS). Diphenyl nitrosoamine is then formed.

(f) Preparation of methyleneimine from NH₄⁺ ions (McLean, 1978; Vinger, 1998)

To 5.0 cm³ of the buffer solution of pH 4, 5.0 cm³ of formaldehyde and 15.0 cm³ of the NH_4^+ ion solution were added. The mixture was then heated on a water bath for 5 minutes, to form methyleimine.

(g) Procedure for obtaining a Differential Pulse Polarogram (DPP)

 10 cm^3 of the solution (of o-nitrophenol, dipheny

nitrosoamine or methyleimine) was transferred into a polarographic cell. The solution was purged for 5 minutes with high purity nitrogen gas (to remove dissolved oxygen) and its DPP was recorded using appropriate instrument parameters. A typical DPP, for an o-nitrophenol solution (prepared from NO_3), is shown in Figure 2.

(h) Determination of concentrations of NO_3^- , NO_2^- and NH_4^+ ions

Differential pulse polarography (Skoog et al, 1992), (DPP), the most sensitive polarographic method, was used for the determination of the concentrations of NH_4^+ , NO_3^- and NO_2^- ions in the water samples collected from the boreholes. For recording the differential pulse polarograms, a BAS–100B/W electrochemical workstation was used. The working electrode (WE) was a dropping mercury electrode (DME) and the counter (AE) and reference electrodes (RE) were respectively a coiled platinum wire and silver /silver chloride.

Determination of nitrate ions

The concentration of nitrate ion (NO₃⁻) was determined by reacting it with phenol in an acidic medium to form ortho-nitrophenol (Metrohm Application Bulletin No. 70e, 1979) and then obtaining a differential pulse polarogram of the solution obtained.

$$(1)$$
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Determination of nitrite ions

The concentration of nitrite ion (NO_2) was determined by reacting it with diphenylamine at a pH of about 1.5 to form diphenylnitrosoamine (Barsotti et al, 1982) and then obtaining its differential pulse polarogram.



Determination of ammonium ions

The concentration of ammonium ions (NH_4^+) was determined by first converting it into methyleneimine (CH₂=NH) by reacting with excess formaldehyde (HCHO) in an acidic medium (McLean et al, 1978)

$$H_2C=O + NH_4^+ \longrightarrow CH_2 \cdot NH + H_3O^+$$
 (3)
Formaldehyde Methyleneimine

and then obtaining a differential pulse polarogram of the methyleneimine solution obtained.

The concentration of each nitrogen species in a water sample was determined from the peak current (i_p) by making use of a calibration curve of peak current versus concentration.

Determination of concentrations from polarograms

The concentrations of NO_3^- , NO_2^- and NH_4^+ ions in the various water samples were determined from the peak currents (i_p , see Figure 2) in the appropriate polarograms, by making use of calibration curves that were obtained from plots of peak current (i_p) versus concentration of the ion.

The concentrations of NO_3^- , NO_2^- and NH_4^+ ions, obtained from the peak currents of the various borehole water samples over the six weeks sampling period are given in Table 2.

3. **Results and discussion**

The results in Table 2 do not show any trends in the concentrations of the ions from week to week. The average value (for the six weeks) of the concentration of each ion in each borehole was therefore taken to be its best value and this is shown in Table 3.

The ammonium and nitrite ion concentrations (columns 2 and 3 in Table 3) in all the water samples tested are below the South African National Standard (SANS – 241) (South African National Standard, SANS 241, 2005) specification for drinking water, which is less than 2 ppm for $\rm NH_4^+$ and 10 ppm for $\rm NO_2^-$ ion. These ions should not therefore cause any health problems in the borehole waters tested.

Now consider NO₃⁻ ions. Their concentrations in four of the borehole water samples tested are greater than the SANS specification for drinking water , which is less than 10 ppm NO₃⁻. In two of these borehole water samples (77265 and Masibi) nitrate concentrations are greater than 20 ppm which are high-risk concentrations (A Guide for the Health Related Assessment of the Quality of Water Supplies, 1996). In two of the borehole water samples (77272 and 77266) the nitrate concentrations are between 10 and 20 ppm and these are in the lowrisk range (Reed, 1994).

Table 4 shows the relationship between the nitrate ion concentration (c) and the distance (d) separating the boreholes and the pollution sources (pit latrines, P.L., and maize fields, M.F.).



Figure 1: A diagram showing the topography of the Bethel-Itsoseng area and the positions of the two villages (Schoongezicht and Welverdiend).

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	Schoongezicht				Welverdiend						
Place	Bontle	Field	Clinic	Field	Masibi	Field	Field	Motswai	Cafe		
B/No	77085	77272	77271	77893	Private	77266	77265	77355	Private		
Equipment	Hand pump	Windmill	Hand pump	Windmill	Hand pump	Windmill	Hand pump	Hand pump	Hand pump		
Depth (m)	37	76	71	Not known	Not known	Not known	Not known	Not known	Not known		
Water level (m)	3	9	9	Not known	Not known	7	6	Not known	Not known		
Location	13 m from 2 pit latrines	12 m from maize field	In the field	30 m from maize field	11 m from 4 pit latrines	50 m from 2 pit latrines	10 m from maize field	84m from 5 pit latrines	26 m from 1 and 24 m from 2 pit latrines		
No. of pit latrines	2	0	4	0	4	2	0	5	3		
B/No	=	Borehole n	umber		Masibi =	Mr Masib	i's place				
Bontle	= Bontle Primary School						Café =	Regoikant	tse café		
Motswai	=	= Motswaiso Middle School									

TABLE 1:	Selected	villages and	boreholes	sampled
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TABLE 2:	Concentrations	in ppm of NH ₄	⁺ , NO ₂ ⁻ and N	O3 ⁻ ions in borehole	e water samples.
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		Week 1 Week 2		Week 3		Week 4		Week 5		Week 6								
B.N.	^C NH₄ ⁺	CNO2	CNO3	^C NH ₄ ⁺	CNO2	CNO3	^C NH ₄ ⁺	CNO ₂	CNO3	^C NH₄ ⁺	CNO2	CNO3	^C NH₄ ⁺	CNO2	CNO3	^C NH₄ ⁺	^C NO ₂ :	CNO3
77893	ND	1.00	3.19	ND	0.62	3.20	0.003	ND	2.44	1.34	ND	6.58	1.89	ND	3.88	0.23	ND	1.41
77265	ND	ND	31.9	1.80	ND	33.6	1.01	ND	18.6	0.39	ND	43.2	2.89	ND	20.8	0.03	ND	25.4
77266	ND	ND	10.0	ND	ND	11.1	ND	ND	6.89	2.10	0.11	9.89	5.37	ND	13.1	ND	ND	11.8
77085	ND	ND	11.2	2.00	ND	11.3	ND	ND	7.13	0.82	0.09	9.53	2.91	ND	9.59	0.16	ND	10.3
77271	1.44	N.D	9.09	3.10	ND	10.2	0.02	ND	6.74	ND	ND	11.1	ND	ND	9.59	0.20	ND	8.19
77355	ND	3.89	2.25	1.50	ND	3.50	ND	ND	3.71	ND	0.10	4.84	ND	ND	6.31	0.44	ND	4.01
77272	-	-	-	0.50	ND	10.4	0.63	ND	8.54	1.56	ND	14.2	2.82	ND	10.8	0.85	ND	12.2
Café	ND	ND	6.49	1.60	ND	7.20	0.50	ND	5.92	1.04	0.35	5.87	ND	ND	10.7	ND	ND	7.30
Masibi	ND	0.94	14.3	8.30	ND	21.6	ND	ND	21.8	ND	ND	34.9	ND	ND	30.2	ND	0.09	36.2
ND	=	1	not detected															

B.N. = borehole number

TADLE J. AVELAGE CONCENTRATIONS IN JUNI OF WILL , 1907 AND 1903 IN DOLENDIE WALL SAMPLES IN AN OWER	TABLE 3: Average concentrations in pr	om of NH4 ⁺ , NO ²⁻ and NO ⁴	$\frac{1}{3}$ in borehole water samples f	or all 6 weeks.
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Borehole number	$^{C}NH_{4}^{+}$	$^{C}NO_{2}$	* ^C NO ₃ -
77893	0.6	0.3	3.5
77265	1.0	0	28.9
77266	1.2	0.02	10.5
77085	1.0	0.02	9.8
77271	0.8	0	9.2
77355	0.3	0.7	4.1
77272	1.3	0	11.2
Café	0.5	0.06	7.2
Masibi	1.4	0.17	26.5

* The precision of the concentration of the nitrate ion results has been expressed in terms of the standard deviation.

Table 4: Relationship		tween conce	ntration of	nitrate ion	s and dista	nce from	pollution s	ource.	
Danahala	77265	Masihi	77272	7776	77095	77271	Cafe	77355	

Borehole	77265	Masibi	77272	77266	77085	77271	Cafe	77355	77893
с/ррт	29.0	26.5	11.2	10.5	9.8	9.2	7.3	4.1	3.5
d/m	10	11	12	50	13	-	26	84	30
Pollution	M.F.	P.L.	M.F.	P.L.	P.L.	P.L.	P.L.	P.L.	M.F.
source		(4)		(2)	(2)	(4)	(3)	(4)	



Figure 2: A typical differential pulse polarogram (DPP) to determine nitrate ions

The data in Table 4, except for borehole 77266, suggest a correlation between nitrate ion concentration and the distance separating the boreholes from the pollution source. They show that water samples in boreholes that have the highest concentrations of nitrate ions (77265 and Masibi) are at the closest distances to a pollution source, and those that have the lowest concentrations (boreholes 77385 and 77893) are far away from pollution sources.

From this study it appears that effluents from pit latrines and fertilizers applied to maize fields cause nitrate pollution of borehole waters. The nitrate pollution occurs if the pollution source is less than about 12 metres from boreholes.

This results obtained from this study is essentially in agreement with earlier reports by Xu and Braune, (1995); Ohou et al, (2008); Conrad et al, (1999); and Tredoux, (2004).

5. Conclusions and recommendations

This study suggests that pollution of borehole waters is likely if the distance separating the boreholes from a pollution source (pit latrines, fertilized maize fields) is less than about 12 metres.

The following could be done to prevent or reduce pollution of borehole waters:

(a)Proper construction, operation and maintenance of sanitation systems. There is a need for appropriate legislation, and its enforcement, concerning the specifications, siting, design, construction and maintenance of pit latrines and septic tanks.

(b)Planting of trees and reeds around boreholes. Nitrogenous pollutants will then be absorbed by the

roots of these trees and reeds.

(c)Controlled application of fertilizers to maize fields.

(d)Education of the people in rural communities as to how pollution of borehole waters can be prevented.

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