

# Isotopic and chemical aspects of nitrate in the groundwater of the Springbok Flats

THE Heaton

Natural Isotopes Division, National Physical Research Laboratory, CSIR, P.O. Box 395, Pretoria 0001, South Africa

## Abstract

Increases in the concentration of nitrate in groundwater are becoming a world-wide problem and are commonly ascribed to one or more of three factors associated with modern farming methods: increased fertilization, increased animal waste and increased cultivation. A combined isotopic ( $^{15}\text{N}/^{14}\text{N}$ ) and chemical study of the high nitrate groundwater in the basalts of the Springbok Flats (Transvaal, South Africa) indicates that the third factor is the only important source of nitrate. Nitrification of the 'black turf' soils, accelerated by the expansion of cultivation, has resulted in most of the shallow groundwater having nitrate concentrations higher than the 'maximum allowable' limit for domestic water supply and the concentrations are still increasing. Modification of farming practices has been suggested in some countries, as a means for controlling both the increase in groundwater nitrate and the attendant decrease in soil fertility.

## Introduction

### Groundwater nitrate: a world-wide problem

High levels of nitrate in water are considered undesirable, both from the point of view of human health and the detrimental effects on the surface water environment (eutrophication). Many countries, including South Africa, have adopted a 'maximum allowable' limit of  $0,71 \text{ mmol} \cdot \ell^{-1}$  ( $10 \text{ mgN} \cdot \ell^{-1}$ ) of  $\text{NO}_3^- + \text{NO}_2^-$  for domestic water supply, with a lower 'recommended' limit (SABS, 1984).

When groundwater contained high levels of nitrate in the past, it was often possible to relate the nitrate to localized sources of pollution caused by improper disposal of animal (or human) waste. Despite improvements in sanitation, however, rising concentrations of groundwater nitrate are being reported on a regional scale from many countries (Young, 1983).

This world-wide problem is generally ascribed to one or more aspects of the changes which occurred in agriculture since the middle of this century, notably:

- the increased application of artificial nitrogenous fertilizers,
- the increase in cultivation following the conversion of pasture into arable land, with cultivation accelerating the nitrification of soils; and
- the resulting introduction of intensive animal husbandry ('factory farming').

It should be appreciated, however, that in some environments elevated levels of nitrate in groundwater are a 'natural' phenomenon (Heaton *et al.*, 1983).

### Isotopic studies

In many areas all three of the above agricultural practices are occurring together, and it is often difficult to identify which one is primarily responsible for an increase in groundwater nitrate. A number of studies have demonstrated, however, that nitrate derived from different sources can

often be distinguished on the basis of different  $^{15}\text{N}/^{14}\text{N}$  ratios. Fertilizers, soils and animal waste have each been identified in different areas as the primary cause of nitrate in groundwater, with the aid of nitrogen isotope investigations (Kreitler and Jones, 1975; Mariotti and Létolle, 1977; Gormly and Spalding, 1979; Kreitler, 1979; Heaton, 1984).

### The Springbok Flats

An area well-known for the high levels of nitrate in its groundwater in South Africa is the Springbok Flats, ~ 100 km north of Pretoria (Fig. 1). An analysis of water from over 600 boreholes (mainly in the basalt areas of Fig. 1) by Verhoef (1973) indicated a median concentration of  $1,4 \text{ mmol} \text{ NO}_3^- \cdot \ell^{-1}$  ( $20 \text{ mgN} \cdot \ell^{-1}$ ), with about 65% of the boreholes yielding water with a nitrate content higher than the 'maximum allowable' limit for domestic water (Fig. 2). The high nitrate water is almost entirely confined to the basalt areas. Grobler (1976) performed a detailed chemical analysis of soils on one farm and both authors regarded the 'black turf' soils, which form on the basalts, as the major source of nitrate for the groundwater.

In this study the isotopic composition of the nitrate in the groundwater of the Springbok Flats is compared with that of the potential sources of nitrate. Recent chemical changes and other features relating to the chemistry and distribution of nitrate are also examined. All aspects of the investigation verify Grobler's (1976) conclusion that the nitrate is derived by nitrification of the soil following cultivation. The data suggest that the process is still active.

### Study area

The Springbok Flats represent a roughly oval-shaped area, of approximately  $10\,000 \text{ km}^2$ , in the north-eastern part of a relatively low-lying Bushveld region north of Pretoria (Fig. 1). They coincide with an outlier of Karoo (Jurassic-Triassic) basalts and sandstones which have been folded into two shallow, elongated, synclinal basins (Fig. 1). The area is extremely flat, almost featureless, with a topographic gradient rarely exceeding 1 in 100 and no marked drainage system. Rainfall ranges between  $570$  to  $630 \text{ mm} \cdot \text{a}^{-1}$ . Mean annual air temperatures are close to  $19^\circ\text{C}$ , with a mean daily maximum of about  $29^\circ\text{C}$  during the six hottest months, October-March, the period during which 80 to 90% of the rainfall occurs.

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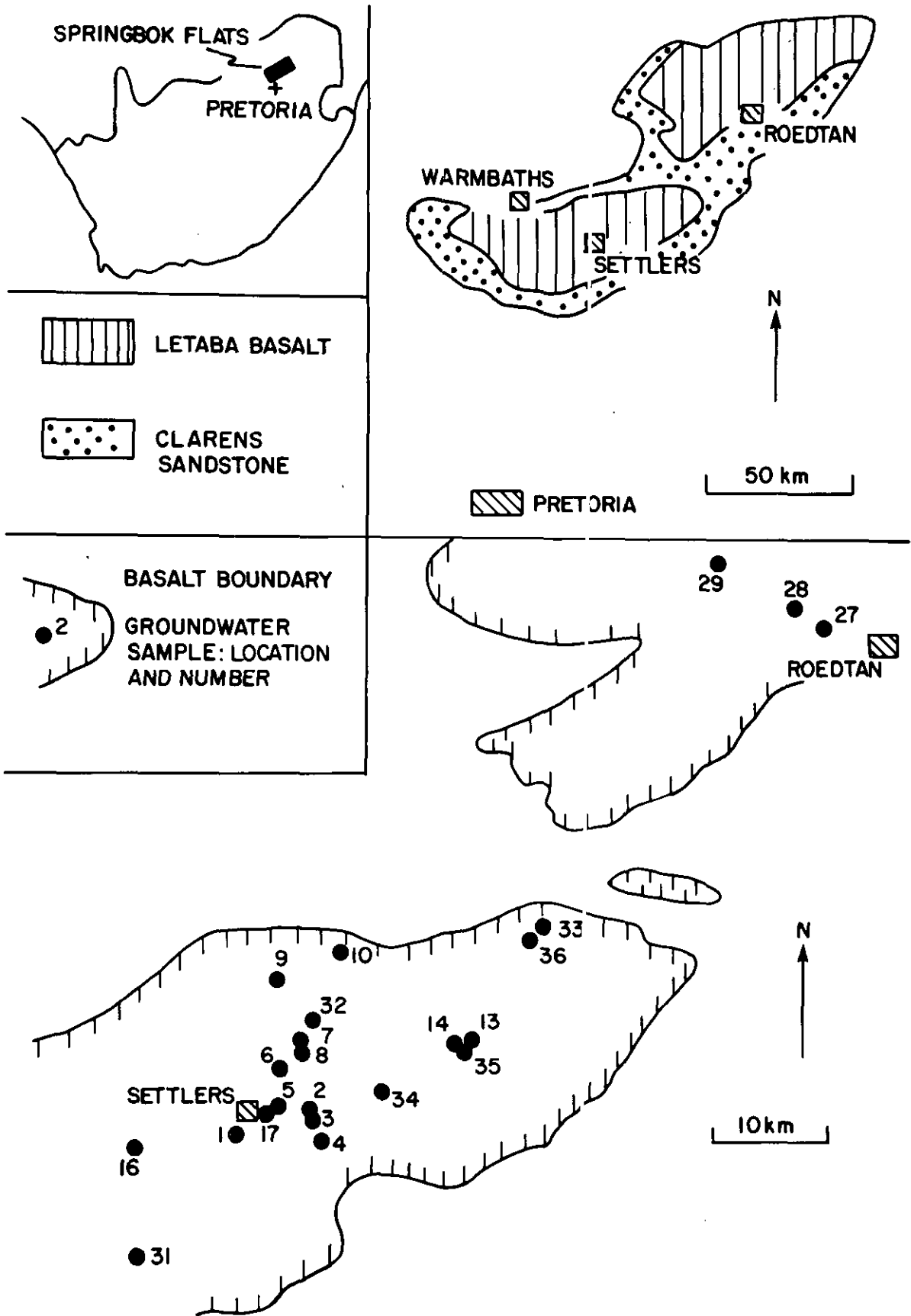


Figure 1  
 Geologic setting of the Springbok Flats, with location of sampled boreholes.

## Soils

Soils developed on the basalts are broadly classified into two types: a predominant, fertile, clay-rich 'black turf' (Arcadia form), and more isolated pockets of less clay-rich 'red soil' (Shortlands form). Sandy soils develop on the sandstones.

The 'black turf' soils were extensively described by Van der Merwe (1962) as part of the 'Subtropical Black Clay Soils' and their main characteristics may be summarized as follows (Van der Merwe, 1962; Fischer, 1968; Grobler, 1976; this study): very black, having a characteristic columnar structure with dense blocks separated by deep vertical cracks, surface layers becoming sticky and impermeable when saturated, but forming a self-mulching flaky crust on drying; high clay content (45 to 75%, predominantly montmorillonite); high moisture content (field moisture 20 to 30% during dry months, field capacity ~ 45% after 5 days drainage from saturation); pH 7 to 8,5; typically 1,5% C and 0,1% N (C/N ratio ~ 13 to 15 for virgin soils); low organics, Na and K; high Ca and Mg (carbonate nodules common in B horizon).

Natural vegetation is a grassy savanna, but about two thirds of the area is now cultivated, largely for maize, autumn wheat, sorghum, sunflowers and cotton.

## Groundwater

The rural community is entirely dependent on groundwater. Boreholes in the basalt areas are generally in the range 20 m to 60 m deep with the water table typically 8 m to 20 m below the surface (Verhoef, 1973; Orpen, 1984). Permeable (i.e. higher-yielding) zones in the basalt are associated with fracturing and discontinuous weathered horizons. Porszasz

(1976) was of the opinion that in the central part of the basalt areas these zones were essentially confined to the top-most 40 m; at the edge of the basalt areas high-yield zones are also found at the basalt-sandstone contact.

Within the two basalt areas Verhoef (1973) identified certain regions with particularly high groundwater nitrate: to the north of Roedtan, and an east-west belt extending through Settlers. On a smaller scale, however, wide variations in nitrate are common; boreholes of the same depth and only 1 to 2 km apart may yield water with concentrations differing by more than 5 mmol NO<sub>3</sub><sup>-</sup> · l<sup>-1</sup>.

## Methods

Twenty-four samples of groundwater, located in Fig. 1, were collected from the southern and northern basalt areas in August and November of 1982 and May 1984, and analysed for their major ions at the National Institute for Water Research. Samples of the 'black turf' soil were collected from the Towoomba Research Station near Warmbaths and different locations in the southern basalt area; the latter set were frozen within 48 h. Nitrate was leached from soils immediately after thawing, using a soil: distilled water ratio of 1:2, and after incubation periods of three to four months (dry soil + 2 parts clean sand + 20% water at 35°C). Organic nitrogen was analysed using standard Kjeldahl techniques (Bremner, 1965). The <sup>15</sup>N/<sup>14</sup>N ratios of groundwater nitrate and the different soil nitrogen compounds were determined using methods outlined elsewhere (Heaton *et al.*, 1983). The ratios are referred to in the usual δ<sup>15</sup>N notation, where:

$$\delta^{15}\text{N}(\text{in } \text{‰}) = \left( \frac{{}^{15}\text{N}/{}^{14}\text{N sample}}{{}^{15}\text{N}/{}^{14}\text{N air}} - 1 \right) \times 10^3$$

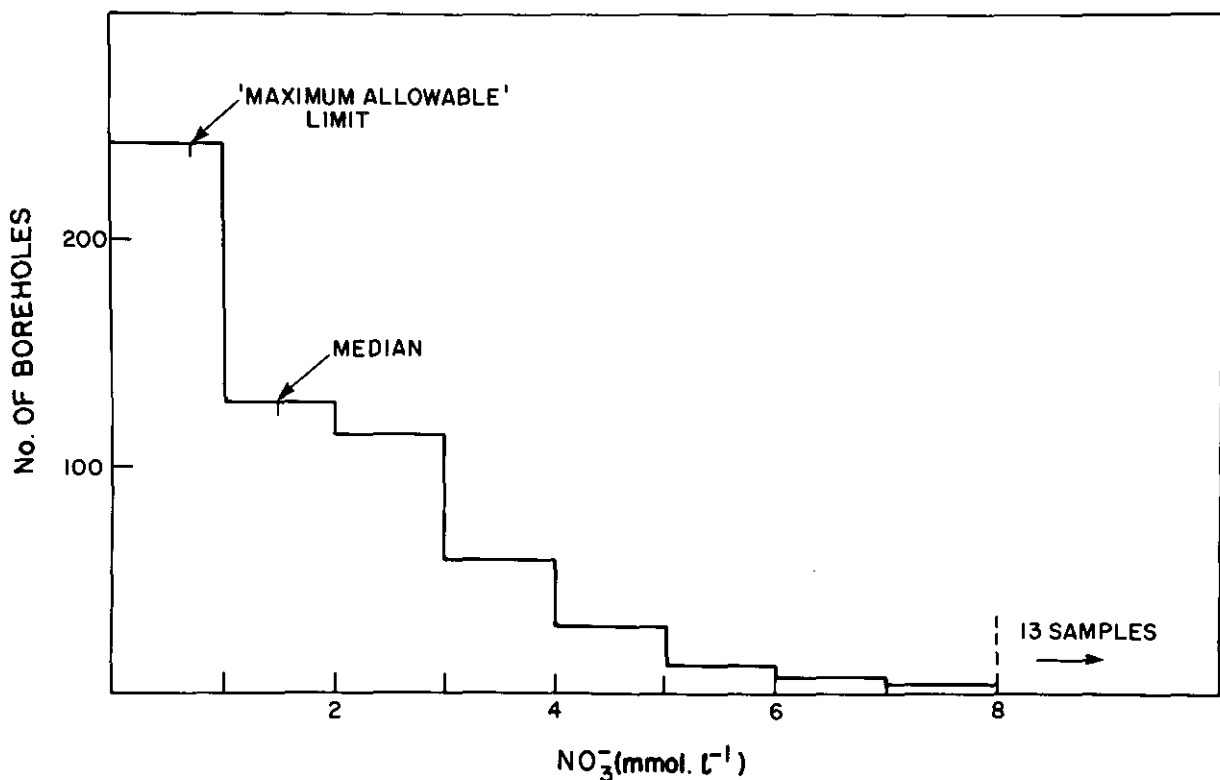


Figure 2  
Nitrate concentrations in 615 boreholes (mainly in the basalt, a few from the sandstone) in the Springbok Flats (from data in Verhoef, 1973).

**TABLE 1**  
**SAMPLE LOCATIONS, NITRATE, <sup>15</sup>N AND OXYGEN CONCENTRATIONS FOR GROUNDWATER IN THE BASALT OF THE SPRINGBOK FLATS**

Sample*	Location		NO <sub>3</sub> <sup>-</sup> * mmol.l <sup>-1</sup>	δ <sup>15</sup> N ‰	O <sub>2</sub> mg.l <sup>-1</sup>
	Lat.S.	Long.E.			
SF 1	24°58,2'	28°31,9'	3,1	+5,6	3,1
2 [? CHES-2]	24°57,3'	28°35,1'	1,3 [?4,0]	+7,1	6,6
3 [? CHES-1]	24°57,3'	28°35,1'	2,1 [?5,8]	+6,3	
4	24°58,7'	28°35,6'	3,7	+6,2	4,6
5 [DSE-1]	24°56,8'	28°33,7'	3,1 [8,8]	+8,1	5,1
6 [? TRN-2]	24°52,3'	28°34,0'	2,7 [?7,1]	+5,8	
7 [BRN-6]	24°54,4'	28°35,2'	2,6 [1,0]	+6,3	5,0
8 [BRN-5]	24°54,4'	28°35,2'	3,0 [0,8]	+6,8	
9 [? LSB-1]	24°51,0'	28°33,9'	2,7 [? 1,0]	+5,2	2,6
10 [? MLN-1]	24°50,0'	28°37,3'	2,5 [? 1,0]	+5,6	3,9
13	24°54,4'	28°44,0'	6,8	+6,7	4,3
14	24°54,5'	28°43,4'	4,6	+6,0	
16 [LKU-1]	24°58,5'	28°26,9'	3,8 [11,9]	+7,0	4,9
17	24°57,2'	28°33,6'	2,3	+6,8	1,1
27 [? SLT-1]	24°35,1'	29°01,8'	5,0 [?9,7]	+5,0	
28	24°33,9'	29°00,2'	4,7	+4,8	
29	24°31,9'	28°56,4'	4,5	+5,9	
31	25°03,5'	28°26,9'	6,2	+7,7	3,9
32[BRN-2]	24°53,3'	28°36,1'	3,1 [2,2]	+7,5	
33	24°48,8'	28°47,3'	2,3	+5,0	
34	24°56,3'	28°38,6'	1,6	+8,4	
35	24°54,4'	28°43,9'	6,1	+7,6	
36	24°49,4'	28°46,9'	2,8	+5,0	
G 2433	near Tuinplaas		6,9	+6,7	

\*Data in brackets are the borehole number and nitrate content reported by Verhoef (1973) for the same borehole.  
 ? = probably the same borehole.

**TABLE 2**  
**<sup>15</sup>N/<sup>14</sup>N RATIO OF NITRATE AND ORGANIC NITROGEN IN 'BLACK TURF' SOILS**

Sample	Location*1	Field	NO <sub>3</sub> <sup>-</sup> *2		NO <sub>3</sub> <sup>-</sup> - incubation		Total organic N	
			δ <sup>15</sup> N(‰)	mmol.kg <sup>-1</sup>	δ <sup>15</sup> N(‰)	mmol.kg <sup>-1</sup>	δ <sup>15</sup> N(‰)	N(%)
Soil 5	Near SF5	Natural veld			+3,8	4,2		
6	Towoomba	Ploughed	+1,9	0,2				
8b	Towoomba	Natural grass					+5,8	0,09
9a	Towoomba	Buffalo grass, ploughed					+5,8	0,10
9b	Towoomba	Buffalo grass, ploughed	+5,7	0,4			+6,2	0,09
10b	Towoomba	Maize					+6,0	0,07
11	Towoomba	Grazed veld	+2,6	0,4			+5,0	0,15
A	Near SF7	Sunflower, ploughed			+7,9	3,8		
B	Near SF5	Grass, mown	-3,6	0,02	+10,0	4,0		
C	Near SF2	Maize, ploughed	+5,3	0,1	+5,7	3,0		
D	Near SF34	Maize, ploughed	+3,3	0,06	+5,4	2,5		
E	Near SF13	Veld	+6,2	0,10				
G	Near SF36	Ploughed	+8,3	2,0	+9,7	8,9		

\*1 Samples were collected from depths of 0,1 to 0,6m.

\*2 Nitrate removed by 'washing' of soils: Towoomba samples after 3 to 16 weeks of storage at room temperature, other samples after storage at -5°C. This may explain the difference in nitrate yields, which are lower than those generally reported by Grobler (1976). Lindau and Spalding (1984) discussed some of the problems attending this type of analysis.

Eleven of the boreholes from which groundwater samples were collected could be positively identified on the basis of lettering on the casing collar of the borehole, or probably identified on the basis of location, with specific boreholes sampled in 1972 by Verhoef (1973). In addition, computer plotting of the locations of about 300 of Verhoef's (1973) boreholes from the northern part of the Flats enabled 29 basalt boreholes to be identified with boreholes sampled in 1981 to 1983 by Orpen (1984). Changes in nitrate concentration in individual boreholes over a 10 year period could thus be assessed. General changes over this period were

assessed by comparison of 237 analyses by Verhoef (1973) and 89 analyses by Orpen (1984) for boreholes distributed over the same ~ 1900 km<sup>2</sup> area of the northern basalts.

## Results and discussion

### Isotopic data

The δ<sup>15</sup>N values of groundwater nitrate from the basalt are listed in Table 1 together with the nitrate and dissolved ox-

xygen concentrations and the locations of the boreholes. Dissolved oxygen concentrations are high, indicating that the isotopic values are unlikely to have been modified by denitrification (Heaton, 1984). Chemical and isotopic data for the soil samples are listed in Table 2.

In Fig. 3 the  $\delta^{15}\text{N}$  values of the groundwater nitrate are plotted as a function of nitrate concentration, and compared with the  $\delta^{15}\text{N}$  values of potential sources of nitrate — rainwater, fertilizer, animal waste and the 'black turf' soils. The data display two distinct features:

- the isotopic composition of the groundwater nitrate is identical to that of the soil nitrate and soil organic nitrogen, and distinctly different from the isotopic compositions of rainwater, fertilizer and animal waste; and
- the isotopic composition of the groundwater nitrate over a wide sampling area shows a narrow range of values ( $\sim 3\text{‰}$ ), and no correlation with nitrate concentrations.

These two features indicate that the nitrate in the groundwater was derived solely from nitrification of the soil and not, for example, by mixing of nitrate from fertilizer with

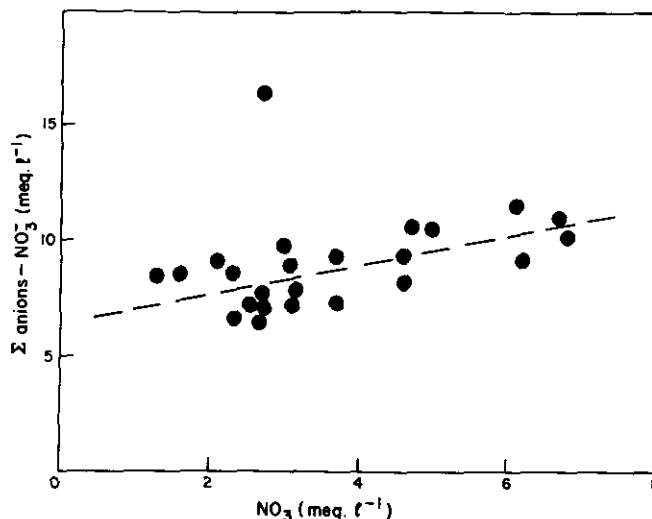


Figure 4  
Concentration of nitrate versus the concentration of the other anions (i.e. total anions minus nitrate) for the groundwater samples listed in Table 1, in milliequivalents per litre (1 meq  $\text{NO}_3^-$  = 1 mmol  $\text{NO}_3^-$ ). Broken line is for linear regression ( $r^2 = 0,45$ ) through 23 of the 24 samples.

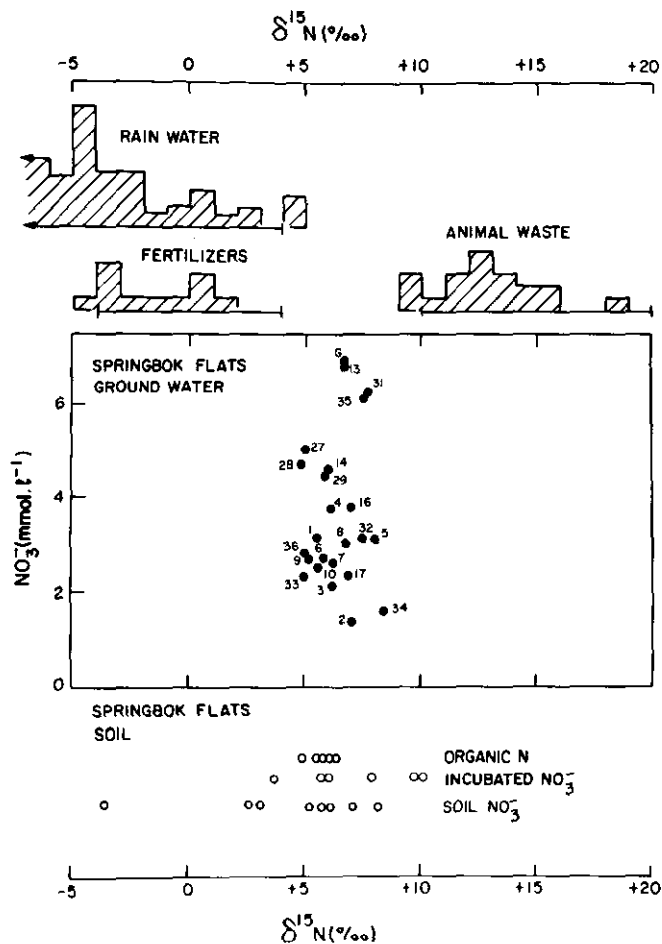


Figure 3

Nitrate concentrations and  $\delta^{15}\text{N}$  values of groundwater in the Springbok Flats (data in Table 1). The typical ranges of  $\delta^{15}\text{N}$  for rainwater ( $\text{NO}_3^- + \text{NH}_4^+$ ), fertilizer ( $\text{NO}_3^- + \text{NH}_4^+$ ) and animal waste-polluted water ( $\text{NO}_3^-$ ) are shown as bars for data for other countries (Kreitler and Jones, 1975; Freyer, 1978; Kreitler, 1979; Spalding et al., 1982) and as histograms for data for Southern Africa (Heaton, 1984, and unpublished data).  $\delta^{15}\text{N}$  values for nitrogen and nitrate from the 'black turf' soils of the Springbok Flats are from Table 2.

nitrate from animal waste. The process by which nitrate was produced from the soil was isotopically uniform over the sampled area. The variations in nitrate concentration in the groundwater must result from areal or temporal variations in the degree of nitrification, or in the amount of dilution during leaching of nitrate from the soil.

Grobler (1976) reported particularly high concentrations of nitrate in soils from cattle kraals but, in view of the small area of kraals as a percentage of the total land area, considered animal waste as a minor source of nitrate. It should be emphasised, however, that boreholes are nevertheless often sited close to animal enclosures or houses (with septic tanks) and regional surveys of groundwater nitrate can tend to be biased by such an association. About half of the samples in Table 1 were from boreholes close to animal enclosures, but none of them showed any isotopic evidence for nitrate derived from animal waste.

#### Nitrate vs. other ions in the groundwater

An unlikely possibility, not addressed by the isotopic data, is that the nitrate is in some way derived from the basaltic formations themselves. A basaltic origin for the nitrate was discounted by Verhoef (1973) on the basis that basalts usually contain very little nitrogen, but a 'geologic' origin of any type can in fact be excluded by consideration of the actual chemistry of the groundwater.

Under special environments nitrate-rich horizons may occur in rock formations, but in all cases the nitrate is accompanied by higher concentrations of other soluble anions (e.g.  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ). The chemistry of samples collected in this study, plotted in Fig. 4, demonstrates that an increase in nitrate is accompanied by very little increase in the other anions. Instead the data in Fig. 4 indicate that the nitrate in the groundwater is derived from a source (soil nitrification) which is separate from that which supplies most of the other anions.

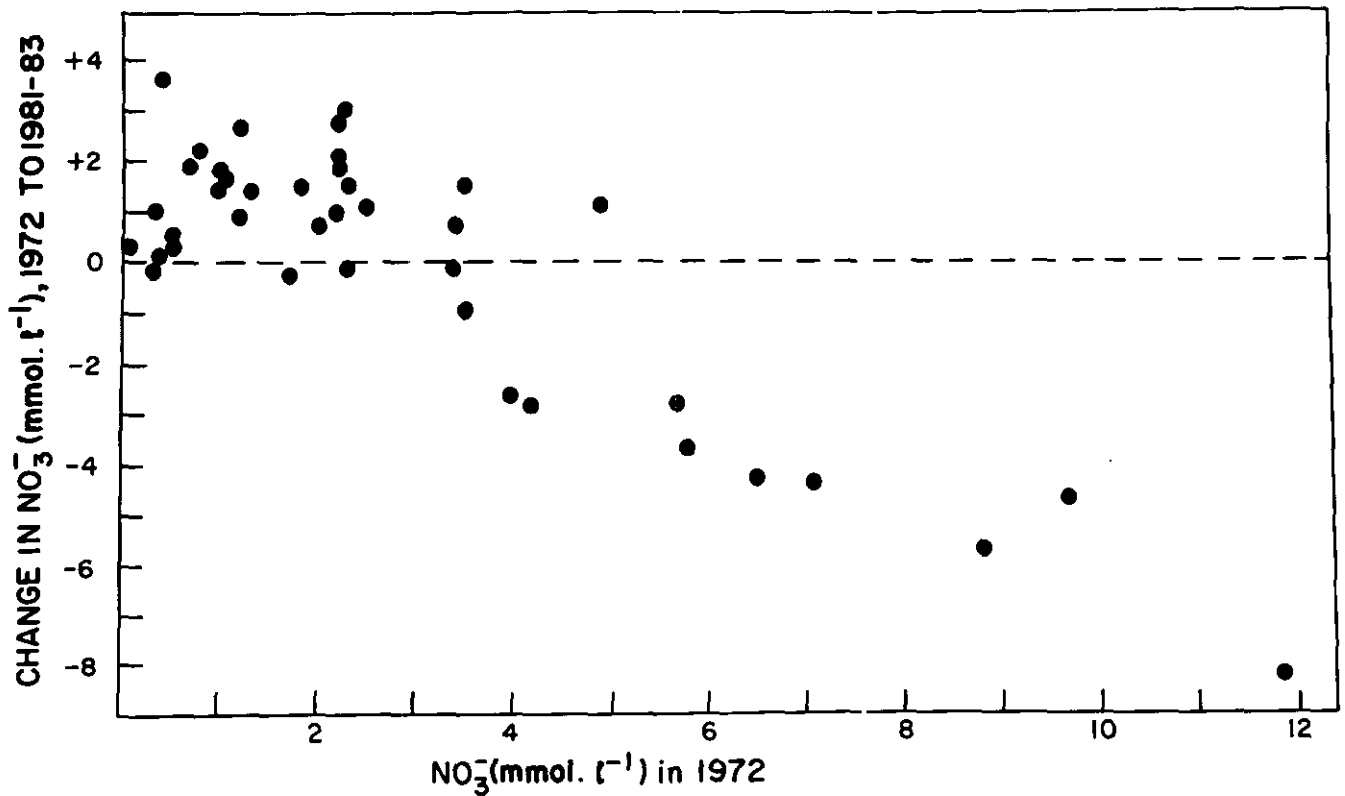


Figure 5  
 The change in nitrate concentrations in 40 boreholes over a 10 year sampling interval (data for the same, or probably the same basalt borehole analysed by Verhoef (1973) in 1972, and by Orpen (1984) or this study during 1981 to 1983) compared with the concentration in 1972.

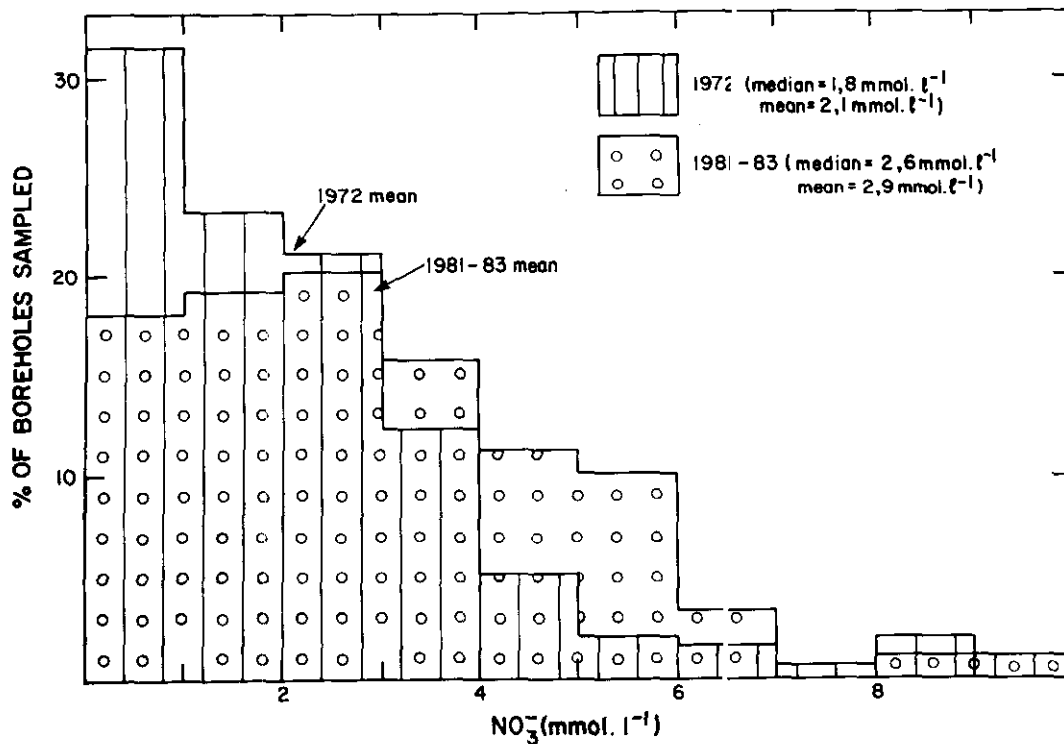


Figure 6  
 Distribution of nitrate concentrations in basalt groundwater in the northern Springbok Flats in 1972 (237 analyses by Verhoef, 1973), median = 1,8 and mean = 2,1  $\text{mmol.l}^{-1}$ , and for the same area in 1981-83 (89 analyses by Orpen, 1984), median = 2,6 and mean = 2,9  $\text{mmol.l}^{-1}$ .

In Fig. 5 the difference in the nitrate concentration of groundwater sampled from boreholes in 1972 and the same boreholes sampled in 1981-83 is plotted against the 1972 concentration. A very definite trend is apparent. Boreholes yielding water with relatively low nitrate concentrations in 1972 have higher levels 10 years later; conversely boreholes with high nitrate concentrations in 1972 show a decrease in nitrate over the same period. The wide range of nitrate concentrations measured by Verhoef (1973) in 1972 appear to be 'contracting' towards intermediate values.

The frequency distribution of nitrate concentrations in groundwater from the northern basalts in 1972 is compared in Fig. 6 with the distribution for the same area in 1981-83. In the ten year interval the distribution pattern has changed and the median and mean nitrate concentrations have both increased by  $\sim 0,8 \text{ mmol.l}^{-1}$  (Fig. 6).

Taken together the data in Figs. 5 and 6 indicate that the nitrate concentrations in the basalt groundwater are presently evolving in two ways:

- nitrate is still being added from the soil; and
- it is being distributed by gradual physical mixing of low and high nitrate groundwater.

Data for the vertical distribution of nitrate in the basalts, from a variety of sources, are summarized in Fig. 7. Whilst there are, unfortunately very few samples from depths of more than 100 m, the available data do tend to support Porszasz's (1976) belief that nitrate concentrations may diminish with depth.

Although the age of the nitrate cannot be determined directly,  $^{14}\text{C}$  analyses on groundwater from nine boreholes in the vicinity of Settlers suggest that much of the groundwater in the shallow portions of the basalt originates from direct recharge from the surface during the past 30 years (Vogel, 1982). The leaching of soil nitrate into the shallow portions of the basalt must therefore also have occurred during the past 30 years.

Groundwater in the deeper sections of the basalt is presumably older than this. If the nitrate concentrations do diminish with depth, then the leaching of nitrate from the soil has only occurred in recent times.

**General discussion**

The isotopic data provide firm support for Verhoef's (1973) and Grobler's (1976) suggestion that the nitrate in the

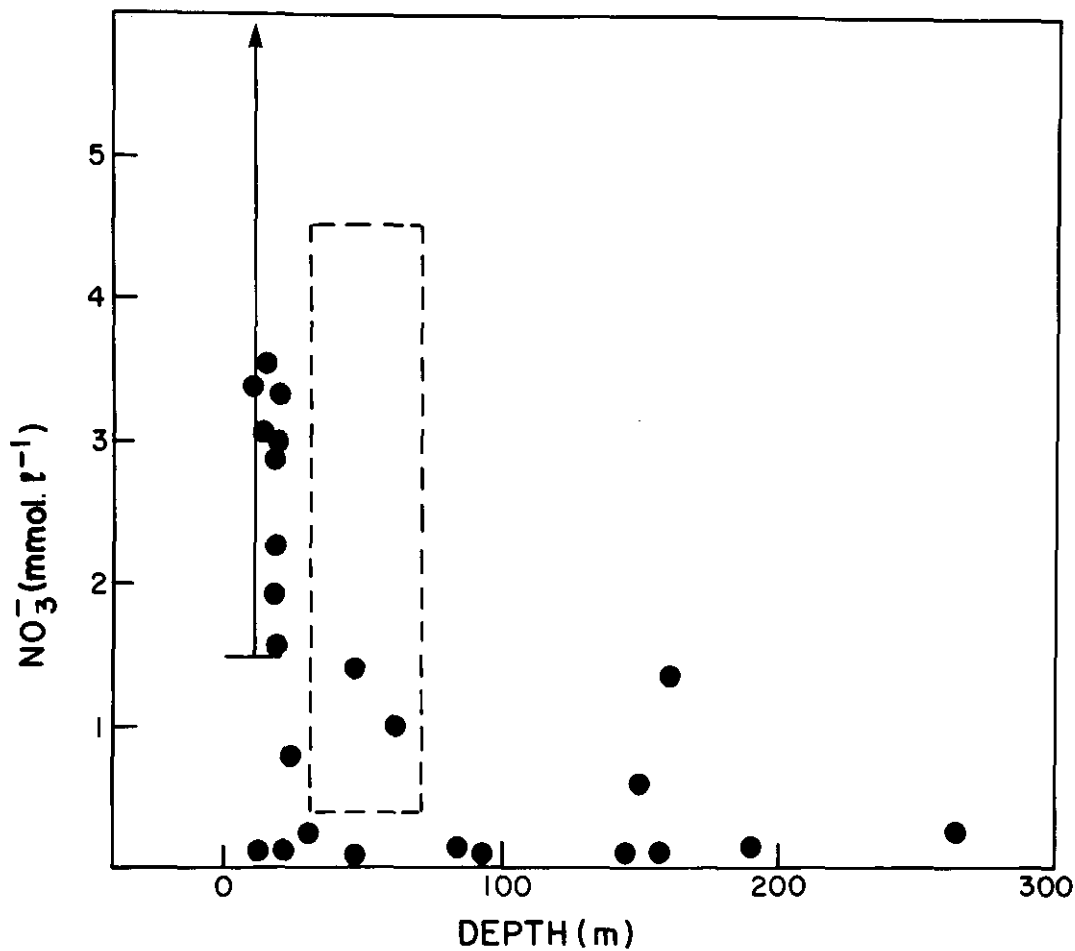


Figure 7  
 Concentration of nitrate in basalt groundwater as a function of depth. Solid line = typical range for water table samples collected at one farm by Grobler (1976); broken box = typical range for basalt groundwater collected by Verhoef (1973); solid symbols = samples from exploration boreholes reported by Hewitt (1980).

groundwater is derived from nitrification of the soil. In addition, consideration of the 'age'-depth relationship and changes in nitrate concentration imply that this input of nitrate is a recently initiated and currently active process.

The amount of cultivated land as a percentage of farming land in the Springbok Flats was estimated by Van der Riet (1974) to have increased from 20% in 1920 to 64% in 1970. The most likely process accounting for the high levels of nitrate in the groundwater is the increased soil nitrification resulting from this increase in cultivation.

Nitrate is the end product of the process of soil mineralization in which organic matter, through a series of steps, is oxidized to nitrate. Under established vegetation soils tend to approach a state of quasi-equilibrium in which their nitrate content is relatively low, both because plants use available nitrate for growth and because some plant-root systems may actively inhibit excess production of nitrate. This equilibrium is severely disturbed, however, when natural vegetation is destroyed during conversion of virgin land into arable land, and when crop land is ploughed after harvesting. The cultivation adds dead organic matter to the soil which is ultimately available for mineralization, oxidative processes such as nitrification are encouraged by increased aeration of the soil, and plants are no longer available to control the build-up of nitrate. As a result, arable land recently derived from virgin land, and soils left fallow between crops, show an increase in nitrate content. If infiltration of rainfall is sufficient to leach the highly soluble nitrate down to depths below the rooting zone, the nitrate is not available for succeeding crops and will eventually percolate down to the groundwater table.

This process is well documented from many parts of the world and, with continued cultivation, gradually results in the loss of organic matter and nitrogen from the soil until some new form of equilibrium is established (Keeney and Bremner, 1964; Stanford and Smith, 1972; Reinhorn and Avnimelech, 1974; Young, 1983). It is almost certain that the same mechanism has been operating, and continues to operate in the soil-groundwater system of the Springbok Flats.

### Mass balance

As a final aspect of this investigation the feasibility of the groundwater nitrate being solely derived from soil nitrogen is assessed by crude estimates of mass balance. For comparative purposes other potential sources are also examined. The estimates are obviously limited by the uncertainty in the values to be assigned to some of the parameters, and significance should only be attached to the general magnitude of the numbers presented.

Using a mean groundwater nitrate concentration of 2,9 mmol.l<sup>-1</sup> from Fig. 6, and assuming the nitrate to be distributed in the top 100 m of basalt having a porosity of 5%, then the total NO<sub>3</sub><sup>-</sup> - N in the groundwater would amount to 2 t N.ha<sup>-1</sup>. If this was added during a period of 50 years the average rate of addition would be 40 kg N.ha<sup>-1</sup>.a<sup>-1</sup>.

Nitrate could have been derived from mineralization of the natural vegetation destroyed when virgin land was originally converted to arable land. The maximum amount of nitrogen in this form would be ~ 0,5 t N.ha<sup>-1</sup> (from maximum total tree and grass biomass data in Huntley and Morris, 1982, for the Nylsvley Nature Reserve, ~ 40 km west of Roedtan, assuming the plant material contains 1% N).

Bate and Gurton (1982) calculated the input of inorganic nitrogen (NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>) by rainfall at Nylsvley to be 1,1 kg N.ha<sup>-1</sup> for 480 mm rain; a slightly higher value would presumably have been recorded for a full year's rain (e.g. 1,4 kg N.ha<sup>-1</sup>.a<sup>-1</sup> for 600 mm rain). Inorganic nitrogen from rain plus dry deposition at Pretoria has been calculated as ~ 5 kg N.ha<sup>-1</sup>.a<sup>-1</sup> (own unpublished data).

From Van der Riet's (1974) estimates of the cost of fertilizer used by farmers in the Springbok Flats and data of the MVSA (1974), the average fertilization rate on arable land in 1971 was not more than 3 kg N.ha<sup>-1</sup>.a<sup>-1</sup>. Although fertilization has increased since the early 70's, present rates are rarely more than 50-60 kg N.ha<sup>-1</sup>.a<sup>-1</sup> for maize with a much lower amount for other crops; and the fertilizer is not applied on a regular basis.

Animal waste, chiefly urine, supplies nitrogen to the soil in a concentrated and easily mineralized form. From Van der Riet's (1974) estimate of a cattle stocking rate of 0,4 head ha<sup>-1</sup> on 'veld' of the Springbok Flats, and assuming an excretion rate of 40 kg N.head<sup>-1</sup>.a<sup>-1</sup>, animal waste would supply 16 kg N.ha<sup>-1</sup>.a<sup>-1</sup>.

For a density of 1 kg.l<sup>-1</sup> and total N content of 0,1% (Grobler, 1976; Table 2), 1 m depth of 'black turf' soil contains 10 t N.ha<sup>-1</sup>. The nitrate in the groundwater would therefore require nitrification and leaching of 20% of this amount.

The effects of cultivation on increased soil nitrification are known to extend to a depth of at least 1 metre, and a value of 20% removal of soil nitrogen through cultivation is comparable to estimates from other parts of the world (Reinhorn and Avnimelech, 1974; Paul, 1976; Verstraete, 1981). Thus, on a mass balance basis, soil nitrogen as a sole source for the groundwater nitrate is quite realistic. Other source rates, such as precipitation, fertilizer and animal waste are too low.

### Summary

- <sup>15</sup>N/<sup>14</sup>N ratios of nitrate in 24 groundwater samples from basalt of the Springbok Flats fall in a narrow range of +4,8 to +8,4‰, showing no variation with concentrations in the range 1,3 to 6,9 mmol NO<sub>3</sub><sup>-</sup>.l<sup>-1</sup>. The isotopic values are similar to those for nitrate and organic nitrogen in the 'black turf' soils, but quite distinct from the values to be expected for nitrate derived from other potential sources such as rainwater, fertilizer and animal waste. An unlikely 'geologic' origin for the nitrate is ruled out by the chemical composition of the groundwater.

- Considerations of the changes in nitrate concentrations over the past 10 years indicate a contraction of low and high concentration values towards an intermediate value, and suggest that the mean concentration of nitrate in the groundwater, from the northern basalt area, has increased by ~ 0,8 mmol.l<sup>-1</sup>.

- Limited data for the probable depth of penetration of nitrate into the basalts, and the age of the shallower groundwater, suggest that the nitrate has only been added in recent times.

### Conclusions

- Collectively, the results indicate that the nitrate in the



basalt groundwater is derived from increased nitrification of the soils resulting from increased cultivation, there being no evidence for a significant contribution of nitrate from any other source. Crude estimates of mass balance support this conclusion.

- Areal variations in the degree of nitrification (and/or leaching of nitrate from the soil) initially led to an uneven distribution of nitrate concentrations, but these are now being evened out by mixing within the aquifer. At the same time, nitrate is still being added to the groundwater.

### Future issues

This investigation has not attempted to discuss the important question as to why high nitrate groundwater should be a particular problem for the 'black turf' soils on the basalts of the Springbok Flats, as opposed to other soils. The climate and characteristic pedologic features referred to above must be important factors. It would be interesting to know, however, whether cultivation of similar soils derived from basic igneous rocks in other parts of the country is also leading to increased levels of groundwater nitrate.

There is a finite limit to the amount of nitrate which can be removed from soils during cultivation, so the concentration of soil-derived nitrate in the groundwater should not rise indefinitely. The final level of nitrate in the groundwater of the Springbok Flats will presumably also depend on:

- the degree of mixing of the shallow, 'polluted' water with deeper water, or flow into the surrounding sandstone aquifer;
- the amount of fertilizer which may be applied in the future to combat the probable decline in soil fertility; and
- the effectiveness of any future management strategies which might be implemented for reduction of the loss of nitrogen during cultivation.

The loss of fertility and the nitrate-'pollution' of groundwater associated with cultivation are a world-wide problem, and controls on cultivation induced nitrification have been called for (Verstraete, 1981). In terms of field management certain practices, such as minimal tillage and the retention of crop residues on the surface of the soil have been recommended (Power, 1981). Fischer (1968) concluded that on the 'black turf' soils of the Springbok Flats minimal tillage and surface application of crop residue may improve moisture retention and maize yields. These practices might therefore serve both the long- and short-term interests of the farming community.

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### References

- BATE, G.C. and GUNTON, C. (1982) Nitrogen in the Burkea Savanna. In: B.J. Huntley and B.H. Walker (eds). *Ecology of Tropical Savannas* (Springer-Verlag, Berlin), 498-513.
- BREMNER, J.M. (1965) Isotope ratio analysis of nitrogen in nitrogen-15 tracer investigations. In: *Methods of soil analysis, part 2, chemical and microbiological properties* (Madison, Wisconsin, Am.Soc.Agronomy) 1256-1285.
- FISCHER, H.H. (1968) Grondbewerkingspraktyke op die Springbokvlakte. Thesis (Univ. Pretoria), unpublished.
- FREYER, H.D. (1978) Seasonal trends of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  nitrogen isotope composition in rain collected at Jülich, Germany. *Tellus* **30** 83-92.
- GORMLEY, J.R. and SPALDING, R.F. (1979) Sources and concentrations of nitrate-nitrogen in ground water of the Central Platte Region, Nebraska. *Ground Water* **17** 219-301.
- GROBLER, D.C. (1976) Verslag oor die ondersoek na die oorsake van die hoë nitraat inhoud van die ondergrondse water in sekere dele van die Springbokvlakte. Dept. Water Affairs, South Africa, Technical note 74.
- HEATON, T.H.E. (1984) Sources of the nitrate in phreatic groundwater in the Western Kalahari. *J.Hydrol.* **67** 249-259.
- HEATON, T.H.E., TALMA, A.S. and VOGEL, J.C. (1983) Origin and history of nitrate in confined groundwater in the Western Kalahari. *J.Hydrol.* **62** 243-262.
- HEWITT, R.F. (1980) An investigation of the groundwater in the vicinity of Settlers, N. Transvaal with particular reference to nitrate and fluoride levels. Unpubl. Rep. Dept. Water Affairs, S.Afr., no GH3140.
- HUNTLEY, B.J. and MORRIS, J.W. (1982) Structure of the Nylsvley savanna. In: B.J. Huntley and B.H Walker (eds.). *Ecology of Tropical Savannas* (Springer-Verlag, Berlin) 433-455.
- KEENEY, D.R. and BREMNER, J.M. (1964) Effect of cultivation on the nitrogen distributions in soils. *Soil Sci. Soc. Am. Proc.* **28** 653-656.
- KREITLER, C.W. (1979) Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas. *J. Hydrol.* **42** 147-170.
- KREITLER, C.W. and JONES, D.C. (1975) Natural soil nitrate: the cause of the nitrate contamination of ground water in Runnels County, Texas. *Ground Water* **13** 53-61.
- LINDAU, C.W. and SPALDING, R.F. (1984) Major procedural discrepancies in soil extracted nitrate levels and nitrogen isotopic values. *Ground Water* **22** 273-278.
- MARIOTTI, A. and LETOLLE, R. (1977) Application de l'étude isotopique de l'azote en hydrologie et en hydrogéologie — Analyse des résultats obtenus sur un exemple précis: le Bassin de Mélarchez (Seine-et-Marne, France). *J.Hydrol.* **33** 157-172.
- MVSA (1974) *Bemestingshandleiding*. Die Misstofvereniging van Suid-Afrika (Pretoria, South Africa). Publ. no. 38.
- ORPEN, W.R.G. (1984) Department of Environment Affairs, Pretoria, South Africa. Personal communication.
- PAUL, E.A. (1976) Nitrogen cycling in terrestrial ecosystems. In: J.O. Nriagu (ed.) *Environmental biogeochemistry* **1** 225-243. Ann. Arbor. Sci., Ann Arbor, Mich.
- PORSZASZ, K. (1976) Fluoride in groundwater in the southern Springbok Flats. Unpubl. Rep. Dept. Water Affairs, South Africa, GH2978.
- POWER, J.F. (1981) Nitrogen in the cultivated ecosystem. In: F.E. Clark and T. Rosswall (eds.). *Terrestrial nitrogen cycle., processes, ecosystem strategies and management impacts*. *Ecol. Bull* (Stockholm) **33** 529-546.
- REINHORN T. and AVNIMELECH, Y. (1974) Nitrogen release associated with the decrease in soil organic matter in newly cultivated soils. *J. Environ. Qual.* **3** 118-121.
- SABS, (1984) Specification for water for domestic supplies. South African Bureau of Standards (Pretoria), SABS 241-1984.
- SPALDING, R.F., EXNER, M.E., LINDAU, C.W. and EATON, D.W. (1982) Investigation of sources of groundwater nitrate contamination in the Burbank-Wallula area of Washington, USA. *J. Hydrol.* **58** 307-324.
- STANFORD, G. and SMITH, S.J. (1972) Nitrogen mineralisation potentials of soils. *Soil Sci. Soc. Am. Proc.* **36** 465-472.
- VAN DER MERWE, C.R. (1962) Soil Groups and Subgroups of South Africa. Department of Agricultural Technical Services (Pretoria, South Africa) *Science Bulletin* No. 356.

- VAN DER RIET, H.M. (1974) Aangepaste boerderystelsels vir die Springbokvlakte. Thesis (Univ. Pretoria), unpublished.
- VERHOEF, L.H.W. (1973) Die chemiese waterkwaliteit van grondwater in die Springbokvlakte. Unpubl. Rep. Dept. Water Affairs, South Africa.
- VERSTRAETE (1981) Nitrification in agricultural systems: Call for control. In: F.E. Clark and T. Rosswall (eds.) *Terrestrial Nitrogen cycle, processes, ecosystem strategies and management impacts*. *Ecol. Bull* (Stockholm) 33 565-572.
- VOGEL, J.C. (1982) National Physical Research Laboratory, CSIR, South Africa. Personal communication.
- YOUNG, C.P. (1982) Data acquisition and evaluation of groundwater pollution by nitrates, pesticides and disease-producing bacteria. *Environ. Geol.* 5 11-18.
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