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ORIGIN AND HISTORY OF NITRATE IN CONFINED GROUNDWATER IN THE WESTERN KALAHARI

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ABSTRACT

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.

Data are presented for nitrate, dinitrogen and argon concentrations and $^{15}N/^{14}N$ ratios in groundwater, with radiocarbon ages up to 40,000 yr. for three confined sandstone aquifers in the western Kalahari of South West Africa/Namibia. The nitrate is probably generated within the soil of the recharge areas, and its production rate during the period 3000—40,000 B.P. has remained between 0.5 and 1.6 meq NO_3^- l^{-1} of recharge water, with $\delta^{15}N$ between $+4$ and $+8\%_{00}$. Variations in the amount of nitrate and of "excess air" in groundwater recharge are found, and can only reflect changes in the environmental conditions during recharge. They must therefore be caused by the climatic changes that have taken place during the past 25,000 yr.

INTRODUCTION

The semi-arid Kalahari covers large parts of Botswana, South West Africa/ Namibia and northern South Africa. Groundwater represents the major, and sometimes sole water resource. The area is sparsely populated and essentially devoted to livestock-farming. Despite the virtual absence of industry or use of fertilizers — traditionally suspected sources of nitrate pollution — the groundwater in some parts of the area commonly contains higher levels of nitrate than those typical world-wide (Adam, 1980; Levin, 1980).

Chemical surveys of borehole water in the study area, located on the western edge of the Kalahari (Fig. 1), suggest that the median nitrate concentration is ~ 1.3 meq NO_3 l^{-1}, with most of the nitrate being found in the shallow phreatic water (Kirchner and Tredoux, 1975; Tredoux et al., 1979). In contrast, the goundwater in the deeper confined aquifers has generally low amounts of nitrate and this has been interpreted as being the result of denitrification (Tredoux and Kirchner, 1982).

In a previous paper (Vogel et al., 1981), we showed that the decrease in nitrate in a confined aquifer is matched by an equivalent increase in extra nitrogen gas in the water. By analysis of ^{15}N and radiocarbon, furthermore, it was possible to prove that the nitrate is bacterially denitrified to

nitrogen gas over a period of 15,000 yr. while the water moves through the aquifer. In addition to these findings, the analysis of the dissolved gas makes it possible to reconstruct the initial nitrate content of the water (prior to denitrification) as well as the amount of "excess air" originally dissolved during infiltration.

The quantity of "excess air" incorporated into groundwater is related to the environmental conditions prevailing during recharge (Heaton and Vogel, 1981); and this also applies to the initial nitrate content. These two parameters can therefore be expected to reveal variations related to past climatic changes. The present study is devoted to an investigation of this hypothesis, with special attention being paid to the source of the nitrate.

Study area

The study area, shown in Fig. 1, forms part of the Stampriet artesian basin, for which the geology and physiography have been described by Tredoux and Kirchner (1982). Throughout most of the area boreholes tap water from one of three aquifers: the confined Nossob sandstone, the overlying confined Auob sandstone, both of Karoo age; and from the overlying, unconfined Kalahari Beds. Windblown Kalahari sand, with thick calcrete layers, forms the surface cover over much of the area. Most of the high nitrate groundwater is found in the phreatic water of the Kalahari aquifer (Kirchner and Tredoux, 1975; Tredoux and Kirchner, 1982) and will the the subject of a separate paper (Heaton, 1983). At present, only the confined aquifers are considered.

Groundwater from the Karoo-age sandstone was sampled in three areas (Fig. 1). In the vicinity of the town of Stampriet the Auob boreholes are commonly artesian and free-flowing. This, together with the fact that the flow pattern has been precisely established by means of radiocarbon ages (Vogel et al., 1981; J.C. Vogel, unpublished data, 1982), makes the aquifer particularly suitable for geochemical investigations. Boreholes in the area east of the town of Aranos yield sub-artesian groundwater from the Auob sandstone while, thirdly, artesian and sub-artesian water from the Nossob sandstone was sampled from boreholes in the vicinity of Leonardville.

The average annual rainfall in the basin amounts to $\sim 200-300$ mm, most of this falling from January to March. The "soil", which is essentially sand and classified as Cambic Arenosol (F.A.O.–UNESCO, 1977), probably contains very little nitrogen or organic carbon (Van der Merwe, 1962). Nitrogen-fixing grasses occur in the area, however, and the common *Acacia* trees may also be nitrogen-fixers (Vogel et al., 1981).

ANALYTICAL METHODS

Nitrate

Samples for nitrate analysis were collected in polyethylene bottles and preserved with ~ 70 ppm $HgCl_2$. Chemical analysis was performed by the
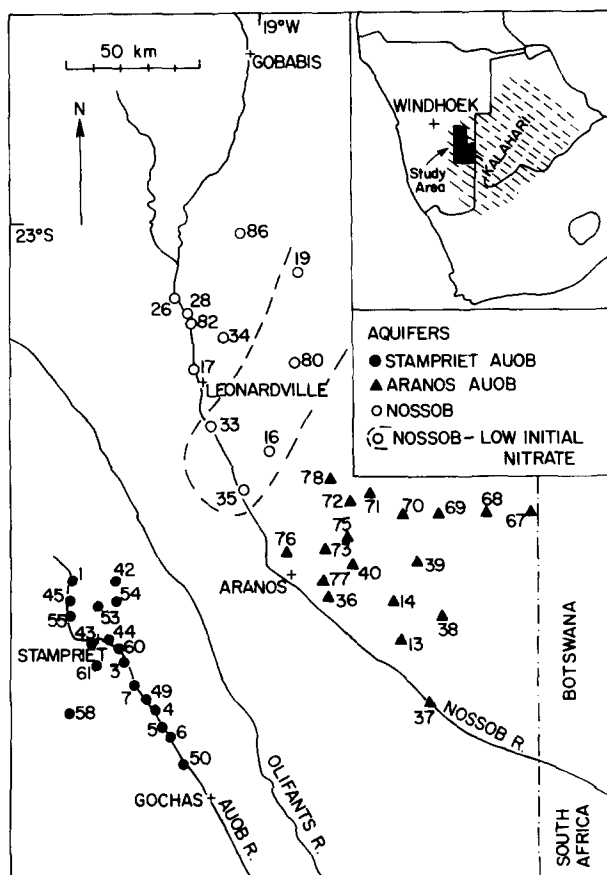
Fig. 1. Locations of boreholes sampled, with sample numbers. Insert shows position of study area in South West Africa/Namibia, on the western edge of the Kalahari.

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The method employed for the conversion of nitrate to dinitrogen for isotopic analysis was based on that of Bremner (1965), as also described by Kreitler (1975). This involves reduction of nitrate to ammonia with Devarda's alloy, oxidation of the ammonia to dinitrogen (N_2 gas) with sodium hypobromite, and purification of the gas in hot copper and copper oxide ovens. Samples of standard $NaNO_3$ and NH_4Cl solutions showed yields of 98—100% and 94—100% for the Devarda's alloy and hyprobromite conversions, respectively.

Dinitrogen, argon and helium

Water is drawn into an evacuated glass flask from which the dissolved dinitrogen, argon and helium are subsequently removed with a Toepler pump, measured manometrically, and analysed by mass spectrometry
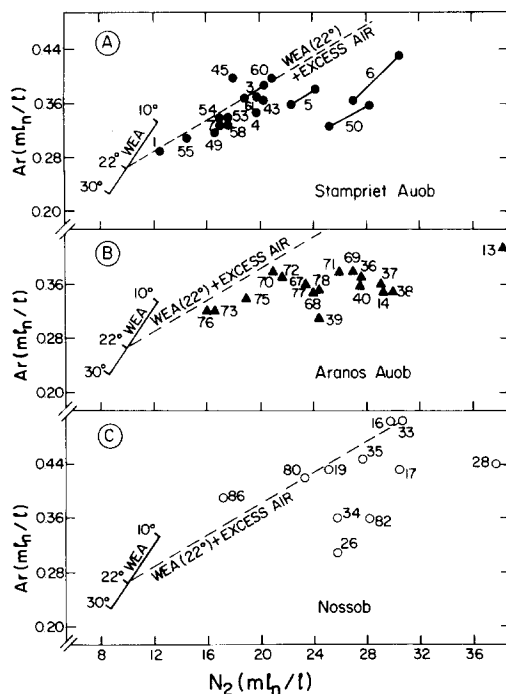
Fig. 2. Concentration of dissolved dinitrogen (N_2) and argon in confined groundwater. *Solid line* marked WEA shows the concentrations expected for water in equilibrium with the atmosphere at 660 Torr at $10°$, $22°$ and $30°C$ (from solubility data in Weiss, 1970). *Broken line* shows trend of concentrations when excess air has been added to WEA at $22°C$. Samples to the right of the *broken line* have had extra N_2 added by denitrification.
A. From the Auob sandstone in the vicinity of Stampriet. *Tie lines* — see footnote[*1] to Table I.
B. From the Auob sandstone in the vicinity of Aranos.
C. From the Nossob sandstone.

(Heaton and Vogel, 1981). Analytical precision (2σ) is $\pm 3.6\%$ for N_2 and $\pm 5.2\%$ for Ar. After analysis the gas is passed through hot copper to ensure removal of oxygen prior to $^{15}N/^{14}N$ ratio analysis of the dinitrogen. Gas concentrations are expressed in millilitres, normalised to S.T.P., per litre of water ($ml_n \ l^{-1}$).

$^{15}N/^{14}N$ ratios

Nitrogen-isotope ratios of the dinitrogen dissolved in groundwater or produced from nitrate were measured in a Varian® GD*150* mass spectrometer with tank nitrogen as a reference. Atmospheric air, cycled through hot copper to remove oxygen, was used as a standard. Measurements of pure tank nitrogen and argon mixtures enabled small corrections to be made to account for the interference effect of argon in the air standards and dissolved gas samples.

TABLE I

Measured concentrations of argon, dinitrogen, nitrate, radiocarbon (^{14}C) and helium, and nitrogen isotope ratios

Aquifer sample[1]	Ar ($ml_n\,l^{-1}$)	N_2 ($ml_n\,l^{-1}$)	$\delta^{15}N$ (‰)[2]	NO_3^- ($meq\,l^{-1}$)	$\delta^{15}N$ (‰)[2]	^{14}C (pmC)	He (rad)[3] ($10^{-3}\,ml_n\,l^{-1}$)
Stampriet Auob:							
St 1	0.289	12.6	+0.1	0.89	+ 5.1	60.6	2.6
3	0.367	19.0	+0.1	1.57	+ 6.2	17.7	11
3(b)	0.389	20.5	+0.1				13
4	0.350	19.6	−2.2	0.54	+17.7	5.7	34
5	0.362	22.4	−3.1	0.35	+34.9	3.3	44
5(b)	0.384	24.1	−2.8				48
6	0.431	30.6	−0.3	0.06		2.6	66
6(b)	0.372	26.9	−0.2				56
7	0.330	17.0	−1.0	1.14	+ 7.7	11.1	14
7(b)	0.333	17.4	−0.9				14
42				1.06	+ 5.1	38.4	
43	0.366	20.3	+0.1	1.06	+ 5.6	37.8	3.9
44				0.99	+ 7.1	41.1	
45	0.399	18.1	+0.7	0.79	+ 5.5	58.0	1.2
49	0.320	16.7	−1.1	0.81	+11.2	7.4	22
50	0.356	28.2	+2.9	<0.01		0.5	93
50(b)	0.333	24.9	+2.9	<0.01			81
53	0.339	17.4	+0.1	1.11	+ 5.6	39.4	3.3
54	0.338	16.9	+0.1	1.11		43.5	1.6
55	0.310	14.4	+0.2	0.86		50.6	3.3
58	0.333	17.7	−0.8	0.77		6.1	18
60	0.397	20.9	+0.2	1.43		30.8	3.7
61	0.374	19.9	+0.4	1.57		21.8	6.5
Aranos Auob:							
St 13	0.416	38.5	+3.2	<0.01		2.8	4.2
14	0.353	29.3	+3.3	<0.01		1.0	2.2
36	0.373	27.5	+3.1	<0.01		0.4	35
37	0.363	29.1	+3.0	<0.01		0	13
38	0.351	29.6	+3.1	<0.01		0	7.6
39	0.306	24.4	+3.6	<0.01		0.7	1.6
40	0.359	27.4		<0.01		2.1	1.8
67	0.356	23.3	+2.0	<0.01		1.3	6.3
68	0.346	24.1	+1.2	0.14		0.3	2.9
69	0.383	26.9	0.0	0.19		0.3	1.5
70	0.377	21.2	−1.0	0.96		1.3	0.4
71	0.378	25.7	+1.3	0.19		0.7	0.26
72	0.373	21.8	+0.5	0.39		5.7	0.4
73	0.316	16.6	−0.1	0.21		5.9	0.62
75	0.341	19.1	+0.2	0.21		6.2	0.7
76	0.326	16.0	+0.4	0.96		5.3	6.2
77	0.356	23.3	+2.1	<0.01		4.0	3.9
78	0.352	24.3	+2.4	<0.01		2.3	0.39
Nossob:							
St 16	0.510	29.8	+1.3	<0.01		1.0	4.2
17	0.427	30.4	+2.0	<0.01		0.5	42
19	0.425	25.0	+0.3	0.16		4.9	0.14
26	0.308	25.7	+2.3	0.35		6.1	12
28	0.436	37.4	+2.6	<0.01		0.7	22
33	0.508	30.6	+1.6	<0.01		0.8	34
34	0.363	25.7	+2.6	<0.01		0.1	6.0
35	0.447	27.7	+1.8	<0.01		0.3	62
80	0.418	23.3	+1.5	<0.01		1.2	0.39
82	0.356	28.2	+3.6	<0.01		1.6	11
86	0.388	170	+0.5	<0.01	+ 8.0	41.6	0.06

[1] Samples marked (b) represent repeat sampling and analysis of borehole after an interval of ~ 1 yr.
[2] Versus atmospheric N_2.
[3] Radiogenic helium (Heaton, 1981).

The $^{15}N/^{14}N$ ratios are expressed in δ values, with reference to atmospheric nitrogen where:

$$\delta^{15}N(\permil) = [(^{15}N/^{14}N_{sample} - {}^{15}N/^{14}N_{atmos})(^{15}N/^{14}N_{atmos})^{-1}] \times 10^3$$

Replicate analyses of dinitrogen indicate a precision (2σ) of $\pm 0.4\permil$ for the mass spectrometry. Analyses of standard showed a long-term precison of $\pm 0.6\permil$ (2σ).

Radiocarbon age determinations

^{14}C determinations were carried out using standard procedures (Vogel, 1967). The ages were calculated using an initial ^{14}C content of 85% and, in some cases, applying small corrections for dilution by "dead" carbonate solution (Vogel et al., 1981).

RESULTS AND DISCUSSION

The concentrations of nitrate, dinitrogen, argon and ^{14}C in groundwater from 47 boreholes in all the aquifers are listed in Table I, together with the $\delta^{15}N$-values of the nitrate and dinitrogen.

Excess air

Dinitrogen and argon concentrations, listed in Table I, are displayed for the different areas in Fig. 2. The interpretation of similar N_2--Ar figures for other areas in South Africa, and previously reported data for a few Stampriet Auob samples, has been discussed elsewhere (Heaton and Vogel, 1981; Vogel et al., 1981). This interpretation is only summarized here with reference to the three stages of development envisaged for groundwater from the study area.

(1) Rain or surface water recharging through the unsaturated zone will have dinitrogen and argon concentrations reflecting solution equilibrium with atmospheric dinitrogen and argon at the prevailing temperature and atmospheric pressure. In the study area the present-day mean annual air temperature is 22°C and the atmospheric pressure, at an altitude of 1200 m, is ~ 660 Torr. Water recharging in this region would lie at the point for water in equilibrium with the atmosphere (WEA) at 22°C in Fig. 2.

(2) Air bubbles trapped at the base of the unsaturated zone, however, may be subsequently carried down to below the water table and dissolve under the increased hydrostatic pressure. Such water has a component of "excess air" (Heaton and Vogel, 1981) and lies on the line "WEA (22°C) + excess air" (Fig. 2).

(3) If dissolved nitrate is denitrified to dinitrogen a component of "extra N_2" is added, and the water sample will plot to the right of the WEA $(22°C)$ + excess air line in Fig. 2.

The method for calculating the amount of "excess air" and "extra N_2" is given in the Appendix.

Initial nitrate

The concentration of the nitrate presently existing in the water, together with the amount of extra N_2, represents the amount of nitrate in the water prior to denitrification which we term the *initial nitrate*, $(NO_3)_0$. Mass balance of the nitrogen-isotope ratios also allows the δ^{15}N-value of the initial nitrate to be calculated — $\delta(NO_3)_0$ (see the Appendix). The calculated values for $(NO_3)_0$, $\delta(NO_3)_0$ and excess air are listed in Table II together with the radiocarbon-derived age of the water.

The calculated concentrations of the initial nitrate, present in the confined groundwater prior to denitrification, are plotted against the radiocarbon age of the water in Fig. 3. Within the three aquifers, located over an area of $\sim$ 25,000 km^2 (Fig.1), the initial nitrate concentrations have generally remained in the range 0.5—1.6 meq l^{-1} for the period 3000 to 40,000 B.P. (years before present). The variations within, and exceptions to this general range, are discussed in later sections.

High nitrate concentrations in this part of the Kalahari are not, therefore, a recent phenomenon solely associated with the phreatic water in the Kalahari Beds. They were also, in the past, characteristic of the confined groundwater. The low nitrate concentrations presently measured in the old confined groundwater are a result of denitrification. The existence of high
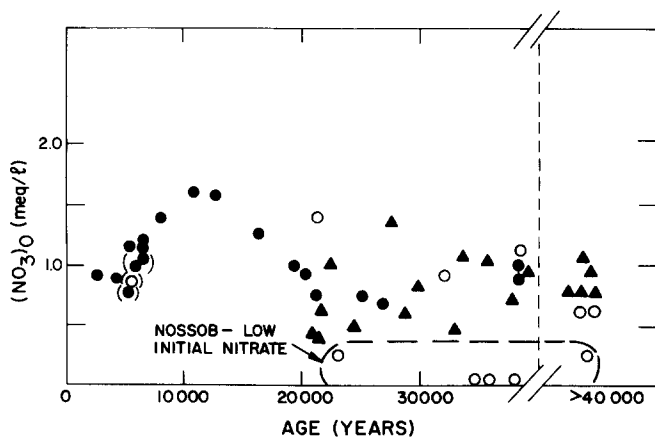

Fig. 3. Concentration of initial nitrate, $(NO_3)_0$, the nitrate present prior to denitrification in groundwater from the different aquifers, as a function of the radiocarbon age of the water. From data in Table II. For aquifer symbols, see Fig.1.

TABLE II

Calculated[*1] concentration and isotopic composition of the initial nitrate, amount of excess air, and radiocarbon age

Aquifer sample	Excess air $(ml_n l^{-1})$	Initial nitrate		Age (yr.)	Foot-note
		$(NO_3)_0$ $(meq l^{-1})$	$\delta (NO_3)_0$ $(\%_{00})$		
Stampriet Auob:					
St 1	3.0	0.91	+4.4	2,700	
3	11.2	1.59	+5.8	12,500	
3(b)	13.5				
4	9.0	0.77	+6.6	21,000	
5	10.2	0.75	+7.2	25,000	
5(b)	12.5				
6	17.2	0.70		26,500	
6(b)	11.0				
7	7.2	1.26	+5.3	16,200	
7(b)	7.5				
42		(1.06	+5.1)	6,400	*2
43	11.2	1.20	+4.6	6,500	
44		(0.99	+7.1)	5,800	*2
45		(0.79	+5.5)	4,200	*2
49	6.0	0.99	+6.9	19,300	
50	8.8	1.01	+6.6	38,300	
50(b)	6.5	0.88	+6.6		
53	8.3	1.19	+4.8	6,200	
54	8.2	1.15		5,400	
55	5.2	0.89		3,400	
58	7.4	0.94		20,200	
60	14.5	1.39		7,900	
61	12.0	1.62		10,700	
Aranos Auob:					
St 13	16.5	1.39	+7.5	27,500	
14	9.8	1.04	+7.7	35,900	
36	11.5	0.76	+9.2	>40,000	
37	10.7	0.96	+7.5	>40,000	
38	9.5	1.08	+7.0	>40,000	
39	4.8	0.95	+7.6	39,000	
40	10.5	0.82		29,900	
67	10.1	0.48	+7.3	33,500	
68	9.1	0.77		>40,000	
69	13.0	0.79		>40,000	
70	12.4	1.09		33,500	
71	12.5	0.72		38,400	
72	12.0	0.61		21,700	
73	5.9	0.39		21,400	
75	8.6	0.42		21,100	
76	6.9	1.02		22,400	
77	10.1	0.48	+7.8	24,600	
78	9.7	0.60	+7.7	28,900	

TABLE II (*continued*)

Aquifer sample	Excess air $(ml_n l^{-1})$	Initial nitrate $(NO_3)_0$ (meq l^{-1})	$\delta(NO_3)_0$ (‰)	Age (yr.)	Foot-note
Nossob:					
St *16*	26.6	0.0	(−32)	35,700	*3
17	17.1	0.62	+7.7	>40,000	
19	17.6	0.27		23,000	
26	4.9	1.41		21,200	
28	18.4	1.16	+6.9	38,500	
33	25.9	0.03	(+127)	38,000	*3
34	10.8	0.64	+8.3	>40,000	
35	19.0	0.26	(+15)	>40,000	*3
80	16.8	0.01	(+173)	34,500	*3
82	10.0	0.93	+9.1	32,100	
86		(0.80	+8.0)	5,700	*2

*1 Calculated using equations in the Appendix, assuming WEA at 22°C.
*2 Values assume samples have not been denitrified.
*3 Very low calculated extra N_2 (see text) makes $\delta(NO_3)_0$ unreliable.

initial nitrate concentrations for at least the past 40,000 yr. indicates that the source of nitrate must be a natural one, and is not the result of pollution.

Some samples (St *16, 19, 33, 35* and *80*) from part of the Nossob aquifer show relatively low initial nitrate concentrations of less than 0.3 meq l^{-1} ("Nossob-low initial nitrate", Fig. 3). This reflects the fact that whilst these samples presently contain very little nitrate, they also contain very little extra N_2 (Fig. 2C). The location of these samples is shown in Fig. 1. Tredoux and Kirchner (1979) found that the Nossob water in this same area had a generally lower salinity than elsewhere. The data suggest that the confined groundwater in this part of the Nossob aquifer is recharged from a different source and that the environment of its recharge area, in terms of nitrate production, is quite different to the environment prevailing over most of the study area.

$\delta^{15}N$ of initial nitrate

In Table II the calculated $\delta^{15}N$-values for the initial nitrate are shown. Values have remained within the range +4 to +8‰ during 3000 to 40,000 B.P. The significance of these values is discussed in terms of the potential sources of nitrate.

SOURCE OF NITRATE

There are three possible sources for nitrate in this groundwater (if the rare occurrence of nitrate minerals in the host-rock is ignored), namely the rain, animal waste and soil bacteria.

Rain water nitrate

Nitrate dissolved in rain water could be concentrated by evaporation in the semi-arid climate prior to being flushed into the soil by occasional heavy rainfall. Published values for $\delta^{15}N$ of nitrate in rain generally lie in the range -8 to $+2\%_{00}$ (Freyer, 1978); twenty-four rain-water samples collected near Pretoria yielded values between -17 and $+4\%_{00}$, with a weighted average close to $-2\%_{00}$. Whilst analyses of rain in the study area have not been made, the isotopic data suggest that direct, isotopically unmodified infiltration of evaporated rain does not respresent the source of the initial nitrate.

Animal-waste nitrate

Nitrate derived from the excrement of wild animals could represent a potential source of "natural" nitrate in localised areas (e.g., waterholes), and the accumulation of domestic livestock around boreholes has been proposed as a possible cause of nitrate pollution in the *phreatic* groundwater of the study area (Adam, 1980). Nitrate derived from animal waste, however, may be considerably enriched in ^{15}N as a result of ammonia volatilization; reported $\delta^{15}N$-values for animal waste nitrate are in the range $+10$ to $+22\%_{00}$, average $+14\%_{00}$ (Kreitler, 1975, 1979; Gormley and Spalding, 1979).

This is supported by our investigation of high-nitrate ($5-15\,\mathrm{meq\,l^{-1}}$) phreatic groundwater in the study area, from boreholes close to livestock enclosures, which has $\delta^{15}N$-values between $+9$ to $+19\%_{00}$ (Heaton, 1983). The isotopic composition of the initial nitrate in the confined groundwater, $+4$ to $+8\%_{00}$, suggests that it was not significantly derived from accumulated animal waste.

Soil nitrate

The most probable source of nitrate is that produced by bacterial processes in the soil, following fixation of atmospheric dinitrogen. Whilst vegetation in the western Kalahari is sparse pod-bearing *Acacia*, of which some species are known to be nitrogen-fixers (Nakos, 1977) are the commonest trees in the area, and nitrogen-fixing grasses also occur (Vogel et al., 1981). In some semi-arid environments algal crusts may be particularly important in fixing nitrogen (Rychert et al., 1978).

Atmospheric dinitrogen has $\delta^{15}N = 0\%_{00}$, and it is probable that fixation occurs with little change in isotopic composition (Delwiche and Steyn, 1970; Delwiche et al., 1979). Within the soil-nitrogen cycle, however, certain processes accompanied by large isotopic fractionations, such as denitrification and ammonia volatilization, may lead to an enrichment in the soil ^{15}N relative to that of atmospheric dinitrogen.

The published values for $\delta^{15}N$ of the total nitrogen in soils world-wide generally lie in the range $+3$ to $+12\%_{00}$ (Shearer et al., 1978; Sweeney

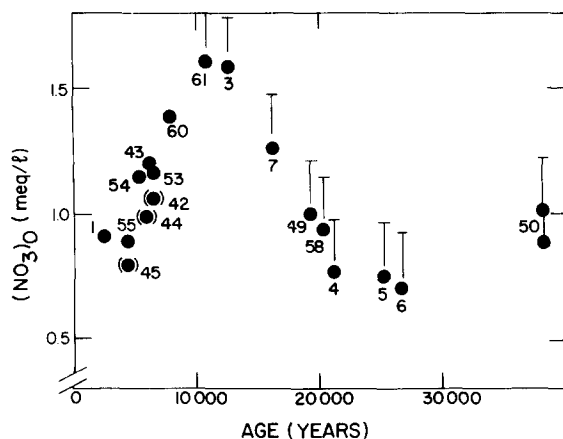Fig. 4. Concentration of initial nitrate, $(NO_3)_0$, in groundwater from the Stampriet Auob aquifer, as a function of the radiocarbon age of the water, from data in Table II. *Bar* above the $> 10,000$ yr. old samples shows concentration if groundwater recharged at $17°C$ (see the Appendix).

et al., 1978); with the average value for soil nitrate at $\sim +5\%_{00}$ (Wada et al., 1981). The isotopic composition of the initial nitrate in the confined aquifers, $+4$ to $+8\%_{00}$, is therefore consistent with the nitrate being derived by leaching of nitrate formed by organic processes in the soil of the recharge areas.

TEMPORAL VARIATIONS

Initial nitrate

Within the general range of initial nitrate concentrations, $0.5-1.6$ meq l^{-1}, shown in Fig. 3, there is evidence of a possible temporal variation. This is particularly apparent for the water from the Stampriet Auob aquifer shown separately in Fig. 4.

Prior to $\sim 20,000$ B.P. the nitrate concentrations in the Stampriet recharge area were in the range $0.7-1.0$ meq l^{-1} — similar to that of the Aranos Auob water of the same age (Fig. 3). After 20,000 B.P. however, the nitrate concentration increased to a maximum of ~ 1.6 meq l^{-1} at $\sim 10,000$ B.P. Nitrate thereafter declined to the pre-20,000 B.P. levels at ~ 3000 B.P. (Fig. 4).

The clarity of the hydrological situation in the Stampriet Auob aquifer and the ideal, artesian conditions under which most of the samples were collected (Vogel et al., 1981) suggest that the pattern exhibited in Fig. 4 is a valid one. There is no evidence for the high-nitrate 10,000-yr. old water being recharged from a different source area, or being contaminated by phreatic water. The general features of the temporal variation in the initial nitrate are not, moreover, greatly affected by our uncertainty in the temperature for WEA (caption to Fig. 4; Appendix).
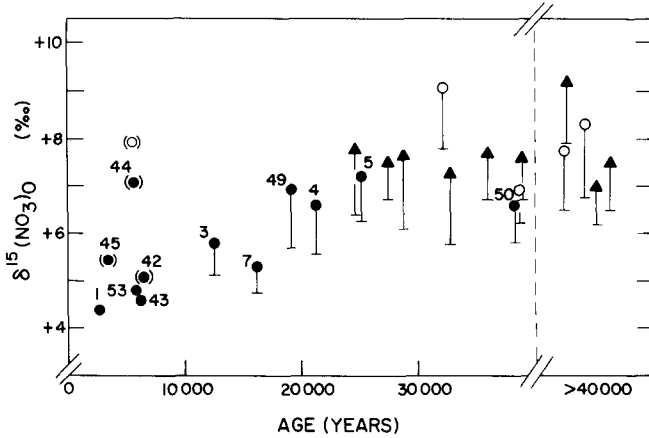
Fig. 5. Isotopic composition, $\delta(NO_3)_0$, of initial nitrate in groundwater from the different aquifers, as a function of the radiocarbon age of the water. From data in Table II. For aquifer symbols, see Fig. 1; sample numbers are shown for the Stampriet Auob samples. *Bar* below the $>10,000$ yr. old samples shows concentration if groundwater recharged at 17°C (see the Appendix).

It would appear that the factors controlling the production of nitrate in the recharge area of the Stampriet Auob aquifer have changed during the past 20,000 yr. The possible climatic significance of this variation is discussed further on.

Isotopic composition of initial nitrate

In Fig. 5 the δ^{15}N-value of the initial nitrate is shown as a function of the groundwater age. Relatively young water ($<10,000$ yr. old) from the Stampriet Auob has δ^{15}N between $+4.4$ and $+5.5\%_0$ (excluding sample St *44*). These are measured values based on the δ^{15}N analysis of nitrate only, requiring no knowledge of the recharge temperature.

Older water ($>20,000$ yr.) from the Stampriet Auob, and from other aquifers have higher calculated δ^{15}N-values for the initial nitrate, generally between $+6.5$ and $+8\%_0$. These calculated values are based, however, on the assumption that the groundwater recharged at 22°C (see WEA in the Appendix). Temperatures may have been lower than this during the ice-age. If temperatures had been 5°C lower during the period 20,000 to 40,000 B.P., then the calculated δ^{15}N-value for the initial nitrate of this older water would be in the range $+5.5$ to $+7.0\%_0$ (Fig. 5).

The interpretation of possible temporal variations in δ^{15}N is therefore hindered by our uncertainty as to the precise temperature during infiltration. It can only be stated that there is no evidence for variations larger than $\pm 2\%_0$ for the δ^{15}N-value of the nitrate produced in this area during the past 40,000 yr. If the surface temperatures 20,000 to 40,000 B.P. were 5—10°C colder than at present, then the data suggest variations were generally as little as $\pm 1\%_0$.
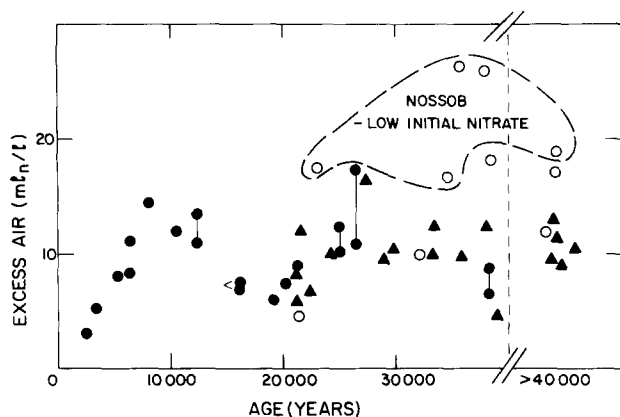
Fig. 6. Amount of excess air in groundwater from the different aquifers, as a function of the radiocarbon age of the water. From data in Table II. For aquifer symbols see Fig. 1. *Tie lines*, see footnote[*1] to Table I.

The lack of large temporal variations in the isotopic composition of the initial nitrate implies constancy in some parts of the nitrogen cycle in the soils of the recharge area. Soil-denitrification and ammonia volatilisation for example, which may be important in semi-arid climates (Klubek et al., 1978; Westerman and Tucker, 1978), are accompanied by large isotopic fractionations. Any significant variation in the magnitude of these two processes should be reflected in variations in the isotopic composition of the initial nitrate.

Excess air

The amount of excess air present in groundwater is believed to be a conservative parameter reflecting conditions in the recharge area — notably the physical structure of the unsaturated zone, and the pattern and intensity of rainfall (Heaton and Vogel, 1979, 1981). Variations in excess air with time are shown in Fig. 6.

Over most of the area the groundwater has incorporated between 4 and 16 ml_n excess air l^{-1} during the past 40,000 yr. These values are generally higher than those found in groundwater in South Africa (typically in the range 0—10 ml_n l^{-1}; Heaton and Vogel, 1981). The "low initial nitrate" water in part of the Nossob aquifer is somewhat distinguishable by generally having very high amounts of excess air (Fig. 6). This lends support to the suggestion, based on the nitrate data, that groundwater in this part of the Nossob aquifer is derived from a different source.

Water from the Stampriet Auob aquifer is again plotted separately, in Fig. 7. As in the case of initial nitrate concentrations, temporal variations are found for the amount of excess air. These variations, moreover, show a similar pattern to that of the initial nitrate (Fig. 4) with changes occurring close to 20,000 and 10,000 B.P.
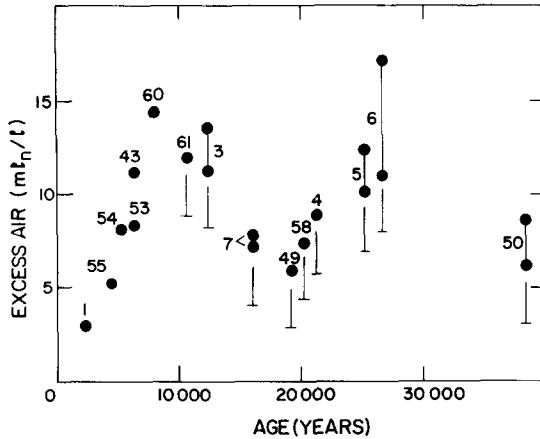
256

Fig. 7. Amount of excess air in groundwater from the Stampriet Auob aquifer, as a function of the radiocarbon age of the water. From data in Table II. For *tie lines*, see footnote[*1] to Table I. *Bar* below the $> 10,000$ yr. old samples shows amount of excess air if groundwater recharged at $17°C$ (see the Appendix).

It should be noted that the equation for the calculation of the initial nitrate concentrations includes a subtracted value for excess air (Appendix). An erroneous measurement, of argon for example, could not cause high calculated values for both initial nitrate and excess air.

Excess air and the initial nitrate are independent conservative parameters. The possible palaeoclimatic significance of the temporal variations in these parameters may now be considered.

Climatic controls on nitrate and excess air

The temporal variations in the production of nitrate and the incorporation of excess air in the recharge area for the Stampriet Auob aquifer might be related to local changes in climate. Isotopic data suggest that the nitrate is derived from organic processes in the soil. The amount of nitrate produced will depend on the population and type of vegetation, humus and bacteria, the degree of nitrification, soil-denitrification and ammonia volatilization, and the ease with which nitrate is flushed through the soil by percolating water. All these factors will be controlled by different elements of the prevailing climate.

If the amount of excess air is related to the intensity and distribution of rainfall, this will obviously be influenced by climate. Certain climatic agencies could also affect the physical structure of the unsaturated zone in the Stampriet recharge area -- such as the thickness of wind-blown sand, the formation of calcretes, the humus content of the soil and the depth of the water table.
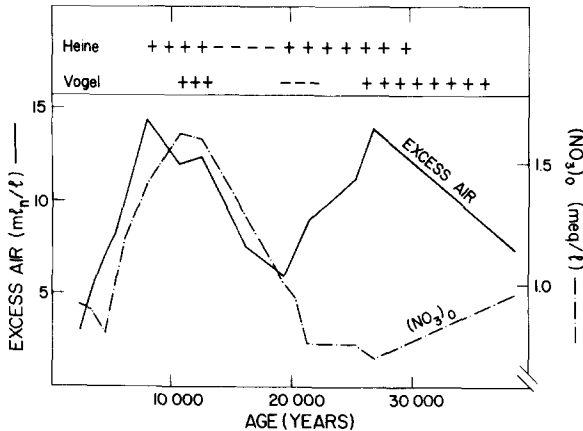
Fig. 8. Comparison of the changes in excess air and initial nitrate in the Stampriet Auob groundwater (from Figs. 4 and 7), with changes in the humidity in the western Kalahari (Heine, 1979, 1982) and flood-flow of the Kuiseb River (Vogel, 1982). + = more humid/flooding; − = humid/flooding.

Palaeoclimate of southern Africa

Studies of the palaeoclimate of southern Africa are being undertaken using a variety of techniques, and there is some agreement as to the timing of the major climatic changes in the sub-continent. Data concerning the precise timing and the nature of these changes in the western Kalahari, however, are scarce and sometimes conflicting (Heine, 1982).

Our own interpretations of the palaeoclimate in the region are based largely on the radiocarbon dating, by Vogel (1982), of fluvial phenomena in the Namib desert southwest of Windhoek (Fig. 1). The rivers in this area are replenished by flood-waters originating from catchment in upland regions near Windhoek. The status of the rivers, in terms of greater or lesser flood-flow that at present, is therefore related to the climate in this upland region, which is $\sim 200\,km$ to the northwest of the study area in Fig. 1. These interpretations (Vogel, 1982) are partly in agreement with the humidity/aridity data of Heine (1979, 1982).

The temporal variations in initial nitrate and excess air are compared in Fig. 8 with a schematic summary of the climatic interpretations of Heine (1979, 1982) and Vogel (1982). The data suggest that, for the recharge area of the Stampriet Auob aquifer:

(1) Greater flooding or rainfall between 35,000 and 26,000 or 20,000 B.P. and between 14,000 and 8000 B.P., may have favoured the incorporation of larger amounts of excess air (Fig. 8). If higher rainfall was associated with heavier, intermittent downpours this would be consistent with our ideas as to the processes by which excess air is incorporated during recharge (Heaton and Vogel, 1981).

(2) The wet period between 14,000 to 8000 B.P. may also have favoured the greater production or increased leaching of nitrate in the soil, although the wet period from 35,000 to 20,000 B.P. (Fig. 8) is not reflected in the nitrate content of the groundwater.

Unlike the production of excess air, which we believe to be an essentially physical phenomenon, the bacterial production of nitrate will be related to the complex, combined effects of both rainfall and temperature. A fuller understanding of the cause of the high initial nitrate concentrations in the Stampriet recharge area between 6000 and 16,000 B.P. must await more detailed information on the past variations of the different climatic parameters.

CONCLUSIONS

The younger groundwater in the Kalahari commonly contains high concentrations of nitrate, and this is especially apparent in the phreatic water of the Kalahari Beds. Prior to denitrification, however, the older groundwater in the confined sandstone aquifers also initially contained between 0.5 and 1.6 meq $NO_3^- l^{-1}$. The formation of this nitrate is not a modern phenomenon, but has occurred in recharge areas located over 25,000 km^2 during the period 3000—40,000 B.P. The nitrate must, therefore, have a natural origin.

Isotopic data suggest that this nitrate is derived from the soil of the recharge areas. The leaching of nitrate may represent an important loss of nitrogen from the soil.

Temporal variations in the production of nitrate and excess air have occurred in the recharge area of the Stampriet Auob aquifer during the past 25,000 yr. The maximum nitrate and excess air production occurred between about 8000 and 12,000 yr. ago, and the timing of the variations suggests that they might be linked to past changes in the climate of this part of the Kalahari. Although the production of nitrate varied (by a factor of 2.5), this is not reflected by significant *measurable* variations in the $^{15}N/^{14}N$ ratio of the nitrate. The constancy of this ratio, between +4 and +8‰, probably reflects constancy in the source of the nitrate and in some of the processes in the soil-nitrogen cycle.

Groundwater from part of the Nossob aquifer is distinguished by having generally high amounts of excess air and, in particular, no evidence for having significant concentrations of initial nitrate. This suggests that the environment of the recharge area for this water was quite different to that prevailing over most of the study area.

APPENDIX — CALCULATION OF EXCESS AIR, INITIAL NITRATE CONTENT AND ITS ISOTOPE RATIO (Table II)

Symbols and values used

$(NO_3)_0$, $\delta(NO_3)_0$	concentration $(meq\,l^{-1})$, and $\delta^{15}N$-value $(^0/_{00})$ of the initial nitrate
NO_3, δNO_3	measured concentration and $\delta^{15}N$-value of the nitrate presently existing in the water (Table I)
N_2, Ar, He	measured total concentrations of dinitrogen, argon and helium in the water $(ml_n\,l^{-1}$, Table I)
δN_2	measured $\delta^{15}N$-value of N_2 (Table I)
$N_{2\,WEA}$, Ar_{WEA}	the concentrations of dinitrogen and argon in water in equilibrium with the atmosphere (WEA) $(ml_n\,l\,;1)$; at 660 Torr, $22^\circ C$ these are 9.97 and 0.261, respectively (Weiss, 1970); whilst $22^\circ C$ is the present-day mean annual air temperature, and samples with young radiocarbon ages lie close to the "WEA $(22^\circ C)$ + excess air line" (Fig. 2), older groundwater recharged during the last ice age may have equilibrated with the atmosphere at low temperatures. At 660 Torr, $17^\circ C$, $N_{2\,WEA} = 10.94$ and $Ar_{WEA} = 0.288$; the effect of this temperature uncertainty is noted in the discussions
EA	amount of excess air $(ml_n\,l^{-1})$
0.781, 0.00934	volumetric fractions of dinitrogen and argon in the atmosphere
0.0893	meq nitrate equivalent to $1\,ml_n\,N_2$
0.14	expected radiogenic argon/radiogenic helium production ratio for typical sandstone; this factor allows correction for the possible radiogenic (i.e. non atmospheric) argon which may be produced by aquifer rocks; uncertainty in the true ratio stems from the fact that: (1) sedimentary rocks typically retain more argon than helium (Podosek et al., 1980) which would result in a ratio < 0.14, but (2) higher ratios have sometimes been found in thermal water in southern Africa (Mazor, 1977); this uncertainty has generally little effect on the calculated results

Calculations

The measured dissolved argon in groundwater originates from argon dissolved in equilibrium with the atmosphere, entrapped excess air and radiogenic argon:

$$Ar = Ar_{WEA} + 0.00934\,EA + 0.14\,He$$

thus

$$EA = (Ar - Ar_{WEA} - 0.14\,He)/0.00934$$

Similarly, the dinitrogen originates from dissolved air, excess air and the extra dinitrogen produced by denitrification:

$$N_2 = N_{2WEA} + 0.781\,EA + [(NO_3)_0 - NO_3]/0.0893 \qquad (A\text{-}1)$$

from which

$$(NO_3)_0 = NO_3 + 0.0893\,(N_2 - N_{2WEA} - 0.781\,EA)$$

Extra nitrogen is believed to be the only product of denitrification. Concentrations of NO_2 and NH_4 in the water samples were below the detection limit ($\sim 0.01\,meq\,l^{-1}$). We have no evidence for N_2O contents higher than $\sim 0.01\,meq\,l^{-1}$; this is based on the recovery of N_2O as gas from the water samples, and its effect on the ^{13}C measurement of dissolved CO_2 (Craig and Keeling, 1963).

The $\delta^{15}N$-value of the extra dinitrogen is calculated from the $\delta^{15}N$-value of the total N_2 together with the fact that:

(1) N_{2WEA} should have a value of $+0.7‰$ (Klots and Benson, 1962); and (2) the atmospheric N_2 totally dissolved as excess air should have a value of $0‰$ (by definition). For $\delta^{15}N$, eq. A-1 then becomes

$$\delta N_2 \cdot N_2 = 0.7\,N_{2WEA} + 0 + [\delta(NO_3)_0 \cdot (NO_3)_0 - \delta NO_3 \cdot NO_3]/0.0893$$

thus:

$$\delta(NO_3)_0 = [0.0893\,(\delta N_2 \cdot N_2 - 0.7\,N_{2WEA}) + \delta NO_3 \cdot NO_3]/(NO_3)_0$$

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