Isotopic and chemical signatures of water in the Transvaal dolomite springs

by

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EXECUTIVE SUMMARY

Spring water represents a spatial and temporary mixture of groundwater from an entire catchment and contains the fingerprinting of the dynamical mixing of the different recharge sources within the catchment. The chemical composition of spring water, its temperature and the isotopic variations in association with the variability of flow, can potentially be used to infer the relative contribution of shallow and deeper circulating waters.

Since the establishment of the Quadru isotope laboratory at the CSIR in 1968 isotopic (radiocarbon (^{14}C), ^{13}C, tritium (^{3}H), ^{18}O, deuterium (^{2}H)) and chemical data from the Transvaal Dolomite springs have been collected by the CSIR and the Department of Water Affairs and Forestry on an irregular basis. The motivation for repetitive sampling of spring water for isotopes and chemistry is to discover any possible long term trends, seasonal effects or effects related to sporadic occurrences on a time scale in between these two (e.g. wet/dry sequences, bomb ^{14}C occurrences, etc). Base line levels of chemistry are necessary in order to evaluate possible later changes.

Aims of the project

The primary impetus for the present project was the observation that since 1968 very little change has occurred in the ^{14}C content of dolomite spring water even though the ^{14}C content of the atmosphere (and vegetation in the area) had undergone a major increase due to the atmospheric nuclear weapon tests between 1956 and 1962. This bomb-^{14}C (and that of tritium) is a very unique tracer that finds its way through different parts of the hydrological cycle. Measurements to date indicate that (depending on the models used) groundwater ages (or mean residence times in the aquifer) of up to 3000 years could be inferred by standard modeling approaches.

A desire was expressed by the WRC to collate the existing information and evaluate its usefulness for future work. A consultancy project was therefore undertaken with the following aims:

- to obtain additional isotope and chemistry measurements representing both high and low spring flow conditions,
- to collate and summarise the available chemical and isotopic data
- to evaluate these data in terms of
    - the potential to determine recharge and storage of dolomitic compartments
    - the chemical characterisation of water
    - establishing baseline values to assess potential pollution.

This report presents the data obtained from samples collected during field sampling in 1992 and 1994 and also presents data summaries of all isotope data obtained from the dolomite springs by both DWAF and CSIR from 1967 to 1994. The emphasis in this report is on the isotope data. Regular sampling of dolomite spring water by DWAF and chemical analysis of its major elements commenced around 1960. The data that were downloaded from the DWAF database have been assembled in the course of the present project. The flow and chemical time series of spring data have been summarised by Bredenkamp (2000) in a related project.

Methodology

The present study was limited to spring water. A spring (also called fountain, eye or 'oog') is a natural outflow of groundwater at the surface. In the Transvaal Dolomites, this is usually caused by confinement of the water by dykes that delineate individual compartments in the aquifer.

The study area for the field work of the present project was limited to the Bo-Molopo catchment (between Lichtenburg, Mafikeng and Zeerust in North-West Province), the West Rand and the dolomitic aquifers south of Pretoria. Samples are periodically collected by DWAF from the two springs in Kuruman. These and other available data from the Northern Cape area have been included in the database and are available for regional and temporal comparisons.

Samples for analysis of ^{14}C, ^{18}O, deuterium, ^{13}C, ^{87}Sr, major ion chemistry and trace element chemistry (by ICPMS) were collected between 1992 and 1994. pH was measured on fresh water at the spring outlets. These pH data were used to calculate the extent of carbonate saturation in the spring water. Details of the springs that have been samples have been recorded.

The second aim of this project comprised the collation and summarising of recent and historic chemical and isotopic data from the dolomitic springs in the study areas. The results of chemical analyses of major ions in various spring waters, isotope data of same and the associated flow discharge rates of springs were joined in common data base files. Some chemical analyses that were obviously wrong, were removed from the data set.

Characteristics of dolomite spring water

The major ions in the dolomite water are Ca, Mg, and HCO_3 (bicarbonate). This is consistent with the concept that dissolution of dolomite (calcium-magnesium-carbonate) by soil carbon dioxide is the main source of ions dissolved in dolomite water. Higher levels (up to a few hundred mg/L) of Na, SO_4 and Cl are present in some spring water. These appear to be caused by pollution from mining activity, industrial or domestic waste. The main regional feature of the chemical composition of the water is a gradual increase of alkalinity (HCO_3) and its associated Ca and Mg from Pretoria in a westerly direction towards Mafikeng.

The saturation data show that the Ca, Mg, pH and HCO_3 content of the spring water is generally at saturation with carbonate. Only those samples that were collected from open water surfaces are likely to be over-saturated with respect to calcite. This is due to the loss of dissolved CO_2 from the water once it is exposed to the atmosphere or subject to CO_2 removal by plants. CO_2 causes the pH to rise. The low alkalinity spring water of the Pretoria area, on the other hand, are unsaturated (and also have low ^{14}C content). The relation between ^{14}C and tritium suggests that these waters have not been in contact with sufficient carbonate to reach saturation. These under-saturated spring waters are located on the edge of the Pretoria aquifer and it seems likely that the water was recharged through the adjacent quartzites and was limited in its contact with dolomite.

Within broad ranges, there appear to be characteristic ^{14}C values for each of the four distinct study areas. ^{14}C and tritium data indicate residence times of ground water in the aquifers from decades to centuries. This is not reconcilable with the present concepts of storativity and recharge in these aquifers.

Within each of the four areas there is a tendency of increasing ^{18}O content being associated with higher ^{14}C contents and likely surface evaporation. ^{18}O can therefore be a useful tracer to indicate anthropogenic effects.

Trace metal analyses (at the parts per billion level) were inconclusive: the results from two different laboratories disagreed and were non-reproducible. Preliminary statistical analysis did not show clear trends or patterns.

The major ion concentrations (alkalinity, Ca and Mg) generally remained constant with time. One notices occasional lower values of all parameters, which looks suspiciously like a dilution effect. Levels of the minor ions Cl and SO_4 are more variable. These are likely caused by pollution events in the catchment area of which traces may in fact be reaching the springs. Turffontein and Gerhard Minnebron (on the West Rand) were identified as obviously pollution sources since Cl and SO_4 has been steadily increasing in these spring waters over the years. At Rhenosterfontein (near Zeerust) Cl and SO_4 rose significantly in 1980 and then decreased during the next 10 years: clearly a single localized pollution event, In spite of this change in chemical composition the changes of ^{14}C, Ca and Mg in this spring water have been minimal. A feature deserving further investigation in some springs is the apparent gradual increase of some of the chemical parameters with time. This can be due to long-term recharge changes or the result of land-use change.

For the Kuruman springs in the Northern Cape, it has been shown that a relation between flow and ^{14}C exists following the high recharge event of 1976. These variations were interpreted as mixing from a two-box model: a quick response of flow from recharge of the Asbestos Mountains followed by delayed response of the actual (high ^{14}C) water reaching the spring.

The rapid ^{14}C variations in some of the smaller springs in Bo-Molopo (e.g. Rietgat oog, Olievendraai oog, Welgedacht oog) can be described by short turnover rates of bomb-^{14}C through the aquifers. It is possible to match a model curve to these variations and derive an estimate of water turnover time for the aquifer feeding that spring. The larger springs either exhibit little ^{14}C change over time or show patterns inconsistent with simple single box flow models.

Conclusions

The data obtained and collated during this project provide a good baseline for later investigation of isotope and chemical changes due to anthropogenic activities.

The present data set now available indicates that no single generic model can be applied to explain the time dependent behaviour of the various tracers in every one of the springs. Each spring system should be evaluated individually. The data available do not at present allow unequivocal interpretation of the processes of recharge, storativity, turnover time and flow patterns of the groundwater in the Dolomite compartments. In most cases, the situations are more complex than a simple box model can explain. The main shortcoming lies in the development of concepts of flow (what sort of model to use), the uncertainty of the existence of deep water (how old?) and the confirmation of age/mean residence time of the water in each compartment.

To this end it is recommended that:

- studies of compartments be undertaken individually and be targeted on those catchments that are of importance for water supply,
- these surveys include chemistry, isotopes, water levels and flow patterns from both boreholes and springs to clarify the processes within each compartment,
- a wider spectrum of the age related parameters are applied to confirm age patterns in the water, e.g. tritium, CFC, T/He, ^{36}Cl.
- detailed modeling of water and pressure flow in each compartment be undertaken,
- the application of trace metals and radiogenic isotopes (e.g. strontium) be investigated as these have real potential to characterise the kinetics of the interaction between water and aquifer rock.

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1. INTRODUCTION

1.1 Aim of the Project

Naturally flowing springs, of which there are many in the dolomite aquifers of the northern provinces of the country, constitute points of groundwater outflow from the aquifer as a result of faults or due to dykes that retain local groundwater flow and affect its normal drainage into streams and rivers. Spring water represents a spatial and temporary mixture of water from the entire catchment and contains the fingerprinting of the dynamical mixing of the different recharge sources within the catchment. The groundwater quality, the temperature and the isotopic variations in association with the variability of flow, can potentially be used to infer the relative contribution of shallow and deeper circulating waters.

The use of dolomitic groundwater has increased considerably in recent times. This was driven by the increased population pressure resulting in higher water consumption for domestic, industrial and agricultural use. Recent droughts have increased additional demand from these groundwater resources. At the same time the pollution of dolomitic water has become more prevalent and the need to manage it is escalating. Dewatering of dolomitic areas to reduce water inflow into underground mining operations become commonplace and necessitates good knowledge of the aquifer systems involved.

All of these factors have made the study of the dolomitic aquifers and their water resources much more relevant. Such studies should now focus on:

- reviewing the state of knowledge regarding the potential and limitations of these aquifers,
- quantification of key parameters for the different dolomitic aquifers,
- attaining a better understanding of groundwater problems,
- improving the management and utilisation of these water resources,
- setting guidelines for decision-making, revision of groundwater policies and legislation,
- incorporation of the principles of uncertainty and risk of failure, using probability analysis in assured yield analyses,
- continuous monitoring of aquifer performance and periodic reassessment of exploitation potential.

Isotopic (^{14}C, tritium, ^{18}O, deuterium) and chemical data from Transvaal Dolomite springs have been collected by the CSIR and the Department of Water Affairs on an irregular basis since 1968. The measurements to date indicate that (depending on the models used) groundwater ages (or residence times) of up to 3000 years could be inferred by standard modelling approaches. A desire was expressed by the WRC to collate the existing information and evaluate its usefulness for future work.

A consultancy project therefore commenced in November 1992 with the following aims:

- to obtain additional measurements representing both high and low spring flow conditions,
- to collate and summarise available (chemical and isotopic) data
- to evaluate these data in terms of
    - the potential to determine recharge and storage of dolomitic compartments
    - chemical characterisation of water
    - baseline values to assess potential pollution.

This report presents the data obtained from samples collected in during field sampling from 1992 to 1994 and also presents data summaries of all isotope data obtained from the dolomite springs during the period from 1967 up to the end of 1994. The emphasis in this report is on the isotope data. The flow and chemical time series of spring data have in the mean time been summarised by Bredenkamp (2000) in a separate project and are only addressed in the present report as they relate to the isotope data and its interpretation.

1.2 Earlier Work

The earliest isotope studies in the Transvaal Dolomitic aquifers were those of Bredenkamp and Vogel (1970) who published the first measurements from these aquifers and pointed out the possibilities which isotope methods might have to determine recharge into dolomite aquifers by studying the flow pattern and flow rates. This was followed by assessments of recharge through the soils using tritium (Bredenkamp *et al. (*1974), Bredenkamp (1978)). A study by Verhagen *et al.* (1979) in the Gamagara fault zone of the northern Cape also added data of some springs on the Ghaap Plateau. Kronfeld *et al.* (1994) published a study on the use of uranium isotopes and its daughters in the Bo-Molopo area and Talma and Bredenkamp (1985) attempted the modelling of ^{14}C data from the springs as phreatic flow models. Bredenkamp *et al.* (1992) described the ^{14}C, tritium and flow of the Kuruman springs in terms of recharge from two separate environments contributing to the spring flow. Partridge (1985) related rainfall to runoff of the Thaba Sikwe spring to estimate the growth rates of the tufa deposits at Taung. The recharge manual by Bredenkamp *et al.* (1995) elaborated on these concepts that were further developed in a report on the interpretation of monitoring data, which included springs (Bredenkamp 2000). This last report includes detailed data analysis of time series of some of the springs that were also studied during the present project. In the meanwhile there were a number of investigations by DWAF on aspects of the water resources of the dolomites (e.g. Fleisher 1981, van Rensburg *et al.* 1992, Kotze *et al.* 1994) all of which involved some estimates of recharge and flow patterns of the dolomite aquifers.

1.3 Scope of this Project

Dolomite outcrops are common features in the northern part of the country and are all part of the Transvaal Supergroup. The Ghaap group is a more or less contiguous plateau south of Kuruman. of which the occurrence of dolomite is in the Campbell Rand subgroup. Outcrops of the Chuniepoort group are located all over North-West Province, Northern Province, Mpumalanga and Gauteng and dolomite occurrences are found in different formations (Table 1).

Table 1. Lithostratigraphic divisions of the dolomite occurrences (from SACS, 1980 and the SA Geological Map of 1997). The subdivision and nomenclature of the Transvaal supergroup is under review at present.

	Formation	Description: NW province	Description: Gauteng
Transvaal Supergroup Ghaap Group Campbell Rand subgroup			
Transvaal Supergroup Chuniespoort Group Malmani subgroup	Frisco	Chert-free dolomite	not present
	Eccles	Chert-rich dolomite	Chert-rich dolomite with stromatolites
	Lyttelton	Chert-free dolomite	dark chert free dolomite with stromatolitic mounds.
	Monte Christo	Chert-rich dolomite	Light coloured chert rich stromatolitic dolomite
	Oaktree	Dark-coloured dolomite	Dolomite becoming darker upwards; Chocolate coloured weathering.

The regional distribution of springs in the dolomites indicates the following potential study areas (see Fig. 1):

1. the Ghaap Plateau (**GH**) comprising essentially the dolomite outcrops south of Kuruman in the Northern Cape province;
2. the Bo-Molopo (**BM**) area located between Mmabatho, Lichtenburg and Zeerust. This is probably the best studied area (Bredenkamp and Vogel 1970; Kronfeld *et al.* 1994; Bredenkamp *et al.* 1992);
3. the West Rand (**WR**), the dolomite outcrops in the area between Potchefstroom, Ventersdorp and Krugersdorp. A number of the springs overlying gold mining areas (Oberholzer, Wonderfontein) are no longer flowing. This area includes springs draining into the Mooi River (Turfontein, Gerhard Minnebron, Boonste Oog van die Mooirivier) and the Schoonspruit springs near Ventersdorp;
4. the Pretoria area (**PT**), consisting of two aquifers in the Fountains and Rietvlei areas including Sterkfontein and Elandsfontein to the south (Temperley 1980);
5. the northern and eastern rim of the dolomite outcrops in a half circle from Potgietersrust towards Sabie. In this area only a few springs are presently known. This area has recently been receiving more attention from the Department of Water Affairs. No data have been published at this stage.

6. the dolomite exposures around Delmas and Bapsfontein. These were not visited during the present investigation and no isotope data have been published.

In view of the limited resources available to this project and the existence of historical data, the study area for the field work of the present project was limited to the Bo-Molopo and Pretoria regions: mainly because there is a fair amount of data available on a small area in each case, which can allow for better comparison and characterisation. The sampling did, however, also include the West Rand area and these data have been included in the data base. Isotope data have been, and are still being, collected by DWAF from the two springs in Kuruman (Kuruman 1 and 2). Other available spring data from the Northern Cape area have been included in the database and are available for regional and temporal comparisons.

The present study is limited to spring water. A spring (also called fountain, eye or ‘oog’) is a natural outflow of groundwater at the surface. In most cases flow is caused by confinement of the water by dykes delineating the dolomite compartments. Some springs (Kaaloog, Mooirivier Boonste oog) are the sources of permanent rivers. In a number of cases (Grootfontein, Rietgat) the groundwater table has dropped significantly with time to reduce water flow and boreholes have then been drilled and pumped in order to maintain supply. Samples from such boreholes are still considered to be from the same spring and have been included in the data set.

2. SAMPLING AND ANALYSIS

The first aim of the present project was to re-sample the springs during the period 1992 to 1994 to supplement the existing database. Sampling was done by CSIR staff. Assistance was provided by DWAF staff based at the Bo-Molopo State Water Scheme to locate the various sample sites. The sample locations are shown in Appendix A. More detailed descriptions and sampling conditions of the springs are given in Appendix B.

While it has been attempted to obtain water samples at the point where the water emerges from underground, this is not always possible. In some cases samples could only be obtained representing the drainage from a larger area (usually reed covered). In other cases the inflow of spring water into a large pool (and outflow from the rock) is ill-defined and samples are necessarily collected at a weir. It will be evident from the detailed sample description (Appendix B) what the situation is in each case. In a few cases (e.g. Kaaloog, Malmani Oog and Molopo Oog) it has been possible to collect samples representatative of inflow as well as outflow of the pool (Kaaloog, Malmani Oog) with various results. No isotope samples were collected if only standing water was found at the spring site since these samples would have been contaminated anyway.

Suitable samples were collected for ^{14}C, ^{18}O, deuterium, ^{13}C, ^{87}Sr, major ion chemistry and trace element chemistry (ICPMS). Not all parameters were always analysed due to cost limitations and lack of interest in specific parameters. Radiocarbon samples were collected in plastic drums, transported to the laboratory, CO_2 was extracted in NaOH and analysed. Water samples for ^{18}O and ^{13}C analyses were collected in plastic bottles and analysed by mass spectrometry at the laboratory of Quadru at CSIR in Pretoria. Major ions were analysed by the Water Quality laboratory of DWAF at Roodeplaat, Pretoria. Samples for strontium isotope analyses were collected, filtered through 0.45µ Millipore filters into acid rinsed plastic bottles, acidified, extracted and were analysed by solid source mass spectrometry at (formerly) Ematek, CSIR (Dr B Eglington). This was an associated investigation to determine whether strontium isotopes can be used to characterise water from different dolomite compartments. Aquifer rocks were also sampled for correlation purposes. Water for trace metal analysis was sampled, filtered through 0.45µ Millipore filters into acid rinsed plastic bottles, acidified and analysed by ICPMS at the Institute for Climate, Soil and Water of the Agricultural Research Council (A Loock). This was also another attempt to characterise water from different dolomite areas and compartments. Some ICPMS samples were duplicated and analysed in other laboratories for comparison.

Field pH measurements (Appendix C) were taken during the 1992-1994 sampling runs. A Radiometer pH meter with combination electrode was used to measure pH of water at the sampling points. The reproducibility of the pH meter under laboratory conditions is in the order of 0.1. The reproducibility of repeat measurements on the same springs appears to be in the order of 0.3 units. This can probably be ascribed to temperature and buffer effects that need to be controlled more carefully.

Field pH data can be used to calculate the carbonate saturation indices of calcite and dolomite and gypsum in the water using a spreadsheet formula derived from the routines of PHREEQE (Simonic 2001). The saturation index of a mineral (=log(IAP/K, where IAP is the Ion activity product of the individual ions making up the mineral and K the solubility product) is a measure of saturation of that mineral in water. Negative values indicate that the water is unsaturated with respect to that compound and positive that it is over-saturated and that carbonate is likely to precipitate. The data show that not all spring waters are actually saturated with either calcite or dolomite (Appendix C). This has some bearing on the interpretation of the radiocarbon content and the alkalinity of the water. The use of field measurement for saturation calculations should result in a more accurate assessment than saturation calculated from pH measurements done on stored samples in laboratories days (or weeks) later. Fleisher (1981) reported that waters from the dolomites were generally over-saturated with respect to calcite. It is likely that he used laboratory pH measurements, which are known to be higher than field pH measurements.

Appendix D lists the isotope data acquired during the project period 1992 to 1994. The chemistry data from that period are included in the data summaries discussed later.

3. DATA COLLATION

The second aim of this project comprises the collation and summarising of available (recent and historic) chemical and isotopic data from dolomitic springs. Results of chemical analyses of major ions in various spring waters, isotope data of same and the associated flow discharge rates of springs were put together in common data base files. The data sources are:

- data from newly acquired samples collected in the course of the present project by CSIR during 1992 to 1994 of which the chemical analyses were done by DWAF at Roodeplaat.
- isotope and chemistry samples collected by DWAF (M Simonic) during a detailed survey in 1992 and 1993 of the Ghaap Plateau and Bo-Molopo areas, of which the data for spring water have been included in this data compilation,
- historic CSIR data based on samples collected by CSIR or DWAF in the past consisting of isotope analyses by CSIR and chemical analyses done by both CSIR or DWAF.
- data from the routine spring sampling programme by DWAF (Bredenkamp 2000). This forms the bulk of the chemical data set.

The names of the springs with some details of DWAF station numbers, CSIR borehole numbers, locations, etc. are shown in Appendix A. A three-letter abbreviation (ASL, BUF, etc) was used to identify each spring. This abbreviation was also used throughout this report in other tables and figures. Results of isotopic analyses obtained since 1992 are presented in Appendix D with various other sample details. These data and the historic DWAF and CSIR data are available in electronic format.

The data coverage is quite variable. A few springs have been repeatedly sampled for isotope analyses since 1968, but most only since 1976. There were hiatuses in 1978-1980, 1984-1990 which inhibit the drawing of proper time series lines. Chemical sampling and flow data from DWAF records, where it was taken, is more regular. A number of springs have dried up during the last 15 years. In some cases, this is due to localised pumping; otherwise it is probably the result of general drought conditions as described in Appendices B and E.

The quality of the data extracted from various sources dating back a few decades is difficult to assess. Isotopic data were all included in the database. In most cases, the isotope variations with time are quite small indicating reasonable reliability. Although the reverse need not be true in the case of the major ion chemistry analysis, a calculation of the ion balance (=(cation-anions)/(cations + anions)*2) provides some check on the precision of the major element analyses. Of the 2 510 major element analyses considered, 2 % were more than 15 % out of balance and 11 % more than 10 % (Fig. 2). There was no indication that the sampling or analytical quality had changed between 1975 and 1995, since the ion balance deviations varied within the same limits during that time (Fig. 3). Samples with ion balances greater than 15 % were removed from the database.

In the course of evaluating the sulphate data of two adjacent springs Turffontein lower eye (TFL) and Gerrit Minnebron (GMB) it was found that a number of spikes and dips in both data sets coincided (Fig. 4a). When sample names were exchanged between these two sources for those days, a much smoother and acceptable time series emerged (Fig. 4b). The implication is that sample bottles could have been exchanged due to mislabelling between these two sources. Nevertheless the time series still showed a low and high sulphate component, which could be due to other mislabelling events. This example indicates a source of error that is difficult to trace and requires details of the actual sampling routine each time.

The ratio of conductivity to total ion content was used as a further check on analysis quality. This indicated that, in doubtful cases, conductivity was wrong. These conductivities were corrected by factors of 2 to 3 (to account for dilutions done in the lab) in order to be able to use conductivity as measure of total salt content (in preference to TDS). No other checks or changes were made to the database. In some cases, outliers along a time series are evident but it was not possible to assess the likely reasons and their presence was tolerated.

The data were assembled in dBase III+ files. Links between these files can be established using the three character field 'EYE' and used to set up a relational database. The main disadvantage of dBase files is that the software forces ‘0’ in a field that has no entry. This implies that ‘0’ in a field can mean either ‘analysis not done’ or ‘zero result’. It is usually evident from the context what the case is. Where available, a zero result in the form of ‘less than’ has been converted into a negative number; e.g. ‘–2’ should be interpreted as ‘<2’.

The following data files were set up:

1. **Spr_loc.dbf:** Names, geographical positions, applicable 1:50 000 maps and DWAF station numbers (where available) (Appendix A)
2. **Spr_dta.dbf:** Listing of analytical data (field, isotope and chemistry) for those springs for which isotope data are available and to which chemistry has been added where available.
3. **Spr_chem.dbf:** 'Cleaned up' chemical data (as described above) for those springs in Spr_loc.dbf for which chemical data are available.
4. **Spr_flow.dbf:** Annual flow data for springs (identified in Spr_loc.dbf) drawn from the DWAF data bank.
5. **Tr_met.xls**: ICPMS results of the water samples analysed by ARC (Pretoria) and the University of Lausanne, Switserland.

4. CHARACTERISATION OF DOLOMITE WATER

The general features of the chemical and isotopic results and their variations are described in this section. For some purposes, separate geographical presentations of the four regions, Ghaap Plateau (GH), Bo-Molopo (BM), West-Rand (WR) and Pretoria (PT) as defined earlier, are used (Fig. 1). This is used in preference to the drainage regions used by DWAF since a major division line (between drainage region A10 and A30) bisects the Bo-Molopo aquifer area.

The discussion (4.1 to 4.7) will first deal with the various parameters and their general distribution. Thereafter (4.8) various inter-relations and their likely significance will be dealt with. Time series will be discussed in the chapter 5.

4.1 Major ion chemistry

The major ions in the dolomite water are Ca, Mg, and bicarbonate (Fig. 5 and 6). This is consistent with the concept that dissolution of dolomite (calcium-magnesium-carbonate) by soil carbon dioxide is the main source of dissolved salts. For this reason the sum of Ca and Mg very nearly equals (on a mole per mole basis) the alkalinity of the water, with exceptions only occurring where there is excess sulphate in the water as is the case in Turffontein and Gerhard Minnebron (Fig. 5). Ca and Mg quantities are fairly equal (Fig. 6). Excess Mg over Ca is very likely due to the removal of Ca from water due to deposition of $CaCO_3$ in the actively growing springs of Boetsap and Thaba Sikwe eyes, or possibly loss of calcium due to calcium carbonate deposition during transport of samples to the laboratory. Excess Ca over Mg only occurs in the spring water with excessively high sulphate levels and can be due to the source of the pollution, or preferential solution by sulphuric acid from mine related activities (Fig. 6).

In some sources higher levels (up to a few hundred mg/L) of Na, SO_4 and Cl are visible. These are likely to be caused by some form of pollution (mine activity related or industrial/domestic waste) e.g. for Turffontein, Gerhard Minnebron, etc. Hobbs (1988) has shown that recharge from an urban polluted river into the dolomitic aquifer around Centurion (south of Pretoria) can be traced this way. Sodium and chloride are linearly related (Fig. 9) and indicate that addition of NaCl is the only source here. There is not much evidence of Na increase due to ion exchange: understandable since ion-exchangeable material is absent in the carbonate aquifer. Nitrate and sulphate levels (Fig. 7) are quite low and indicate the present day absence of significant domestic and agricultural pollution. While it is known that these constituents are found in localised boreholes, they have obviously not reached such proportions as to be noticeable in most spring water. Nevertheless, the nitrate content of a number of spring waters is significantly above (Fig. 7c) that of the recommended limit for drinking water (10mgN/L) and needs to be monitored.

The main regional feature of the chemical composition of the water is the gradual increase of alkalinity (and associated Ca + Mg) in a westward direction (Fig. 7a). This is certainly the case between Pretoria (28° E) and the BoMolopo area (26° E). (There are not sufficient data points available from the Ghaap Plateau to confirm or deny the general trend from the east). The likely reasons for this feature will be discussed later. Apart from the obviously polluted springs, the Cl content of the water is quite low and can readily be used for calculation of recharge, by comparison with the chloride content of rainfall (Bredenkamp 2000).

The saturation index data show that those water samples that had been exposed to the atmosphere for some time (and classified as 'open' in Appendix C) are more likely to be over-saturated with calcite. This is due to the loss of dissolved CO_2 from the water once it has been exposed to the atmosphere or to plants, thereby causing the pH to rise. Chemical equilibrium theory indicates that carbonate over-saturation of water should cause carbonate to deposit. It has long been speculated why carbonate deposition in streams arising from the dolomites does not occur. The present data show that such waters become over-saturated when water has been exposed to the atmosphere for some time and excess carbon dioxide has been lost (Fig. 8). Apart from over-saturation, the process of carbonate deposition also requires some nucleation mechanism such as turbulence or existing deposits (Barnes 1965). Boetsap eye, the only water sample from source that is actively forming a tufa deposit, has the highest saturation index for calcite of the samples analysed during this project. This has implications for the evaluation of the dolomite solution process as it affects the interpretation of the ^{14}C content of the water. This aspect will be followed up in a more recent sampling run which includes samples from the Ghaap Escarpment (Talma, in preparation).

4.2 Radiocarbon

The study of ^{14}C variations in the dolomite spring water with time and locality is the main thrust of this project. The transport of bomb-produced radiocarbon should give clear indications of the flow rate through and recharge of the dolomite aquifers. Within broad ranges there appear to be characteristic ^{14}C values for each of the four study areas (Fig.10 and Table 2).

Table 2. Summary of regional variations of ^{14}C in spring water.

AREA	Longitude range (East)	^{14}C range (pmc)
Pretoria (PT)	28° 11' – 28° 21'	50 – 85
West Rand (WR)	26° 11' – 27° 33'	70 – 95
Bo-Molopo (BM)	25° 45' – 26° 22'	70 – 110
Ghaap Plateau (GH)	23° 04' – 24° 36'	65 – 110

Each spring exhibits a ^{14}C content within a narrow range (Appendix E). At least in the Bo-Molopo area there appears to be a relation between ^{14}C content and the catchment area of the spring (Fig. 11). The catchment areas were estimated on the basis of the dykes that are known to exist in this area (Fig. 12) This suggests that large catchments produce spring water with lower ^{14}C component and hence suggest longer residence times for the water within that catchment. Regionally there is a clear relation between ^{14}C content and alkalinity (Fig. 13) in the sense that higher ^{14}C contents are associated with higher alkalinity.

There are a few situations where an 'upper' and a 'lower' spring exist in close proximity (usually within 1 km). A comparison of the ^{14}C contents of such pairs could reveal something about the structure of water masses within the aquifer. In a few cases, it is known that the upper spring is more susceptible to drought, which might indicate that the upper water body should be 'younger'. Table 3 summarises the radiocarbon contents of the known pairs of springs.

Table 3. ^{14}C Comparison of spring pairs.

Area	Spring pair	^{14}C content (pmc)	
		Upper eye	Lower eye
BM	Dinokane spring	86	95
BM	Kaaloog	88*	78
BM	Malmani Oog	70	101*
BM	Paardevlei Oog	94	99
BM	Stinkhoutboom Oog	89	90
BM	Tweefontein	86	92*
NC	Kuruman Oog 2/1	83	73
WR	Turfontein Oog	90*	89
PT	Erasmus/Grootfontein (Rietvlei/ Pretoria)	54	59

* In these cases the eyes drain into large, reed-covered areas from which the drainage was sampled for ^{14}C. The contribution which growing reeds make to the ^{14}C content of the water, in which it is growing, is not known.

Excluding those cases where swampy conditions might have introduced ^{14}C into the water (which is not established at all), it is remarkable that many of the lower eyes seem to produce water with higher ^{14}C content and thus younger age. It is therefore not a general rule that the upper eye would intercept the younger water from a catchment.

4.3 Tritium

Bomb tritium, which has reached high values (over 50 TU in the 1970's, Fig. 24), could, at that time, be used fruitfully to identify water that had recharged since 1960 (Vogel *et al.*, 1974). Tritium analyses have been done at CSIR on spring water between 1969 and 1980 (Table 4). The comparison with ^{14}C (Fig. 14) shows that elevated tritium values (above the 2TU background prevailing at that time) start to appear in the Pretoria aquifer at ^{14}C contents of just greater than 70 pmc while in the Bo-Molopo region a better initial value would be 85-95 pmc. The concept that the initial ^{14}C content of groundwater for the purpose of dating can be set at 85 pmc is therefore supported in this area as well. The range of tritium values therefore indicates residence times from decades to centuries and essentially confirms the ^{14}C data. In particular, Grootfontein (Bo-Molopo) has generally shown an absence of bomb tritium (Table 4). More recent tritium data on these spring waters are required.

Table 4. Tritium data of spring water analysed between 1969 and 1980.

EYE	AREA	Name	Date	Tritium TU	^{14}C pmc
DFN	BM	Doornfontein	Jul.77	12.6±0.9	98.6
ERR	PT	Erasmus Spring	Jul.79	0.0±0.9	51.0
GFO	BM	Grootfontein Oog	Sep.69	1.0±0.6	83.2
GFO	BM	Grootfontein Oog	Oct.71	0.8±0.5	86.4
GFO	BM	Grootfontein Oog	May.72	2.4±0.5	85.6
GFO	BM	Grootfontein Oog	Feb.73	0.0±0.5	85.1
GFO	BM	Grootfontein Oog	Aug.74	0.6±0.6	85.5
GFO	BM	Grootfontein Oog	Jul.75	0.6±0.6	86.2
GFO	BM	Grootfontein Oog	Aug.79	3.9±1.0	86.4
GFR	PT	Grootfontein (Rietvlei)	Jul.79	0.0±1.0	58.5
GMB	WR	Gerrit Minnebron	Jul.79	1.0±1.0	73.0
KFN	BM	Kleinfontein Oog	Jul.75	0.9±0.6	88.4
KFN	BM	Kleinfontein Oog	Jul.77	3.2±0.7	86.6
KKO	GH	Klein Kono Oog	Jul.77	6.8±0.6	103.9
KU1	GH	Kuruman Oog 1	Jul.77	0.8±0.7	76.1
LBO	BM	Lichtenburg Oog	Jul.75	1.7±0.6	(100)
LBO	BM	Lichtenburg Oog	Aug.76	2.9±0.8	102.5
LBO	BM	Lichtenburg Oog	Jul.77	2.0±0.7	97.9
MMO	BM	Mooimeisiesfontein	Jul.75	1.8±0.7	85.2
MOL	BM	Molopo Oog (Bosman)	Jul.77	0.7±0.7	82.6
PFL	PT	Pretoria Fountains Lower eye	Jul.79	2.8±1.1	77.6
RGO	BM	Rietgat Oog	Aug.69	9.2±0.9	98.4
RGO	BM	Rietgat Oog	Aug.76	18.9±1.0	128.6
TFU	GH	Turffontein Upper Eye	Jul.79	4.1±0.8	(88)
VRR	PT	V Reenen (Rietvlei)	Jul.79	1.9±0.7	74.3
WGT	BM	Wondergat	Jul.80	11.2±1.2	112.7
WIL	PT	Willows (Rietvlei)	Jul.79	0.5±0.7	60.6

Notes:

- The tritium content in rainfall between 1969 and 1980 ranged from 35 to 14 TU.
- The pre-bomb (pre-1955) background tritium value was about 4 TU.
- The maximum bomb-tritium of 60 TU (during1963-5) would have decayed to 25 TU in 1980.
- (^{14}C) indicates ^{14}C content interpolated from measurements at other times.

Wondergat (a sinkhole with standing water) and Rietgat Oog (fed by nearby dam water) have the highest tritium content suggesting that at least 20% of the water originates from post-bomb (10-20 years old) vintage. For the other samples the modern contributions appear small and support the low ^{14}C content.

At the present time (2001AD), the atmospheric tritium levels are much lower and decay of tritium in the water has reduced the levels to the pre-bomb levels of 3-5 TU (Verhagen, pers. comm.). Detailed evaluation of the tritium content of the spring waters will have to take account of this variation over the past few decades.

4.4 Carbon-13

The procedure for field collection of radiocarbon samples for the CSIR radiocarbon laboratory, involves transfer of CO_2 liberated from groundwater into a NaOH solution. In the laboratory, CO_2 is extracted from this concentrate for ^{14}C analysis. ^{13}C is then also analysed on this CO_2 and reported routinely (Appendix D). Because of variations in extraction efficiency during both steps, the ^{13}C results of these extractions are known to be less accurate (Weaver et al 1999). More accurate ^{13}C values can be obtained by vacuum extraction of water from pre-evacuated glass flasks filled in the field, from which CO_2 is extracted in the laboratory. A limited number of such vacuum extractions were made in the course of time and the ^{13}C results can be compared with those of the ^{14}C extracts (Fig. 15). While, in general, the correspondence is within 1 ‰, there are a number of cases where greater differences are found. These data confirm that reasonable care must be taken when evaluating ^{13}C data. The following discussion will, therefore, be restricted to those samples for which flask ^{13}C data are available (33 samples in all).

The total inorganic carbon (TIC) of which the ^{13}C (and ^{14}C) content is analysed, consists of CO_3, HCO_3 and dissolved (free) CO_2. The latter, which can be up to 20 % of the total, can readily escape from an open water surface, thus altering the ^{13}C content of the remaining sample. This process is probably partly responsible for the erratic ^{13}C yield of CO_2 extracted for ^{14}C analysis. It also implies that water samples collected from open water surfaces may not represent the ^{13}C content of the groundwater as it emerged at the actual spring. There is no correlation between ^{13}C and TIC content in spring waters (Fig. 16).

4.5 Oxygen-18

^{18}O variations, (expressed as ‰ deviations from SMOW) range over a wide range covering the values generally found in rainwater (IAEA 1992). With a few exceptions there is a general pattern of low ^{18}O values in the range -5.9 to -1.5 ‰ with the mode located near -4‰. Apart from the low values on the Ghaap Plateau, there is no distinctive geographical spread from Pretoria to the Bo-Molopo area (Fig. 17).

Within each of the four areas there is a tendency of increasing ^{18}O content being associated with increasing ^{14}C contents (Fig. 18). Some specific characteristics can be identified:

- Rietgat is a spring/borehole complex at the Rooigrond jail fed by a nearby dam which explains the high ^{18}O content of the water.

- Both Turfontein (TFU and TFL) and Gerhard Minnebron (GMB) on the West Rand that show significant sulphate pollution (Fig. 4) also have higher (evaporated) ^{18}O content.
- The anomalous ^{14}C value of the lower Schoonspruit Oog (SSL) is caused by its contamination with bomb ^{14}C and evaporated ^{18}O at a time just before that specific source dried up.
- Within the Bo-Molopo area, the same trend could suggest that recent water derived from agricultural impacts shows more evaporation than the pre-agricultural recharge.

^{18}O can therefore be a useful tracer to indicate anthropogenic effects in a qualitative sense.

4.6 Trace metals

A number of samples were collected in 1993 for trace metal analysis by ICPMS. Samples were collected in acid rinsed plastic bottles after filtered through 0.45µ Millipore filters, acidified with ultra pure HNO_3 and submitted to two different laboratories. The results from the two laboratories were different and non-reproducible. Preliminary statistical analysis did not show clear trends or patterns. It is known that filtering procedures can influence the eventual results. and this may be part of the reason for the inconsistency. This approach was not followed up since it would seem that better control over sampling and analytical conditions are required. The data that have been obtained are available in electronic format (section 3: file Tr_met.xls).

4.7 Strontium isotopes

The ^{87}Sr/^{86}Sr ratio was analysed on a number of samples collected from all four study areas during the field work of 1992 and 1993. This was a venture initiated by Dr B Eglington, then of Ematek, CSIR, in which he wished to collect data from various water sources to explore the use of Sr isotopes as tool to trace water types and identifying pollution sources (Eglington *et al.* 1993). The sampling procedures used were the same as described above for ICPMS analysis. Repeat analyses were quite acceptable (Appendix F) and indicate that the technique is sufficiently robust.

The spread of Sr isotope ratios over the entire area is quite wide (Fig. 19) and covers most of the range found in South African geology. In the Bo-Molopo area where the sample density is higher, it is possible to find a regional pattern with a certain characteristic value covering a number of compartments (Fig. 20). The characteristic ratios transcend the subdivisions of the dolomite formation in the area. Strontium analysis of dolomite rock samples collected near each spring site, show no close correspondence between water and rock (outcrop near the spring) (Table 5). Nevertheless, the high ratio of RNF can partly be explained by higher ^{87}Sr in the rock, therefore some relation seems to exist. It is known that the strontium transfer reactions are slower than the carbonate solution reactions (Johnson & de Paolo 1997) and full equilibrium may not exist by the time that water flows at the spring.

This technique offers the way towards characterisation of water for water typing and relating towards the aquifer material but more work is required to quantify the reactions involved.

Table 5. Comparison of Sr isotopes between of spring water and dolomite.

Eye	δ Water	δ Rock	δ Difference
BUF	+22.9	+ 5.6	+17.3
DPL	+21.0	+11.5	+ 9.5
MOL	+18.4	+ 3.2	+15.2
OLV	+18.8	+ 0.5	+18.3
RNF	+43.2	+20.0	+23.2

^{87}Sr here is expressed as ‰ deviation from average sea water (ratio 0.7092)

4.8 Chemical Evolution of Dolomite Water

In its simplest form, the chemical make-up of the water in the dolomites consists of calcium and magnesium carbonates dissolved through the action of carbon dioxide of plant origin, in the unsaturated zone above the water table. Additional ions can be presumed to originate from rainfall, from aquifer rock weathering or from local (pollution) sources.

The major feature of chemical variations across the aquifer is the increase of the concentrations of the major ions Ca, Mg and bicarbonate (=alkalinity) westwards (Fig.7a). This increase is paralleled by increases in both the carbon isotopes ^{13}C and ^{14}C (Fig.13). These differences are most pronounced in the Pretoria and Bo-Molopo areas, but also supported, to some extent, by the samples from the West Rand. Recently it has become known that water in the Ghaap Plateau shows the full range of chemical compositions that are found in the rest of the present three study areas (Talma, in preparation).

The major driving force of carbonate dissolution is the carbon dioxide present in the unsaturated zone. There is a direct relationship between the CO_2 partial pressure in the soil and the eventual amount of bicarbonate in the water (Langmuir 1997). The CO_2 partial pressure is, in turn, a function of the plant and root activity in the soil. In its simplest form, this evolution model requires a dramatic increase in biological activity westward. Such a change does not seem likely since the present rainfall and vegetation cover decrease towards the west. It is also not consistent with the ^{13}C increase in the water westward. The simultaneous requirement of increasing ^{13}C and ^{14}C are also incompatible. The usual process of carbonate solution, by whatever process, would cause the ^{14}C content of the water to decrease, i.e. apparent ageing of the water.

The saturation indices for water with respect to calcite or dolomite (Fig. 8b and 8c) provide the clue to the most likely evolution mechanism of the carbonate chemistry of this water. The low alkalinity spring water of the Pretoria area are unsaturated (and have low ^{14}C content) and the relation with tritium (Fig

14) suggests that these waters have not been in contact with sufficient carbonate to reach saturation. This could either be due to short contact time with carbonate, or that (part of the) recharge occurred through a non-carbonaceous rock, for example the quartzite to the north of the Rietvlei compartment (Bredenkamp 2000, Fig 5.4.1.1). This type of carbonate solution is termed ‘closed’ since the solid carbonate is closed to the gaseous CO_2 and there is a low upper limit to the amount of carbonate that can be dissolved (Langmuir 1997, Clark and Fritz 1997). Closed system solution also results in low initial ^{14}C contents for purposes of water age/residence time calculation.

5. TIME SERIES

5.1 Chemistry Time Series

Regular sampling of dolomite spring water by DWAF and analysis of its major elements commenced around 1960. The data that were downloaded from the DWAF database have been assembled in the course of this project. The regular CSIR sampling of springs for isotope samples added some additional data to this data set. The CSIR work was concerned essentially with isotopes and chemical analyses were only added for specific purposes.

The bulk of the 2 500 chemical analyses available on the dolomite spring waters (filename: Spr-flow.dbf) are therefore from the DWAF programme. Appendix F summarises the trends that were evident in the chemical and isotopic time series taken from the springs under consideration.

Details of this monitoring programme, detailed evaluation of the data and the main conclusions that could be drawn therefrom, have been given elsewhere (Bredenkamp 2000, Chapter 11). That report deals with the usefulness of chemistry from natural waters pertaining to:

- characterising aquifers in relation to aquifer types and climatic influences
- indicating mixing between groundwater of different chemical composition
- recharge determination using chloride for those springs that are shown to be uncontaminated.

The major ions (alkalinity, Ca and Mg) remain essentially constant with time (e.g. Fig.21a and 22a). One notices occasional lower values of all parameters, which looks suspiciously like a dilution effect. Levels of the minor ions Cl and SO_4 are more variable (Fig. 21b and 22b): These are likely caused by pollution events in the catchment area of which traces are reaching the springs now.

Two obvious cases of pollution have been identified earlier by Bredenkamp (1995) in Turffontein and Gerhard Minnebron (Fig.4). Rhenosterfontein has been identified as a spring where Cl and SO4 rose significantly in 1980 and then levelled off during the next 10 years (Fig. 23 and Bredenkamp 2000, Fig. 11.3.3.3.1). In spite of this change in chemical composition the changes of ^{14}C , Ca and Mg in this spring water have been minimal.

A feature deserving further investigation is the apparent very gradual increase of some of the chemical parameters with time. This is just noticeable, for example, with NO_3 in BUF and MAL with Cl in MAL (Fig.21 and 22). Pretoria Fountains (PFL) also showed occasional periods (of a few months) of higher Cl and SO_4 increases (Bredenkamp 2000, Fig. 11.5.3.3) above baseline levels. These base line values are however an order of magnitude higher than those for the 1940s (Vegter, 1993 cited in Bredenkamp 2000) and indicate that ‘pollution’ or lower recharge rates, are affecting the chemistry of this spring water and requires further monitoring. A more detailed look at his phenomenon should be made at many other springs and will have to take into account analytical standards and sample preservation practices through the years.

5.2 Spring Flow Rates

Monthly spring flow rate data have been obtained from the DWAF hydrology database from which annual flows were calculated. These can now be used for modelling purposes. A few examples from the four study areas show that individual variations are quite likely (Fig. 21c, 22c and 23c). Detailed discussion of such effects and more data series have also been made elsewhere (Bredenkamp 2000). Van Tonder and Xu have now produced Excel software (Recharge and Springflow) whereby rainfall, spring flow rates and water levels can be used to compute groundwater storage and recharge parameters using SVF, CRD and other methods. The need for spring flow data will therefore increase.

5.3 Radiocarbon

The motivation for repetitive sampling of spring water for isotopes is to discover any possible long term trends, seasonal effects or effects related to sporadic occurrences of a time scale in between these two (e.g. wet/dry sequences, bomb ^{14}C occurrences, etc). Base line levels are necessary to identify possible later changes. The primary impetus for the present project was the observation that since 1968 very little change has occurred in the ^{14}C content of dolomite spring water even though the ^{14}C content of the atmosphere (and vegetation in the area) had undergone a major increase and slow decrease since the 1950's (Fig. 24).

Fig. 26 shows an assemblage of ^{14}C time series for those springs with three or more ^{14}C analyses between 1968 and 1994. The samples are presented where it is certain that the very same spring has been analysed during this time. In many cases there is no obvious trend over the entire period. Appendix E shows a summary of the trends found in these springs.

The following can be noted:

a) Most springs (BUF, PVL, PVU, DPL, TWU, TWL, SFN, GMB, TFL, MAL, MRB?) have only slightly varying radiocarbon contents over the years. The average range of variation is 2½ pmc, which is about four times the standard deviation (1 sigma) of radiocarbon measurements. This variation can be considered just beyond the analytical errors inherent in the measurements.

b) None of the regular flowing springs exhibit the complete bomb ^{14}C rise and fall as one would expect from well-mixed flow patterns having turnover times of 5-10 years (Fig 27). The various sources of Rietgat eye are all fed by a local dam (see also the high ^{18}O value) and this spring is therefore a special case. Wondergat is an open sinkhole with standing water. It is, therefore, likely that atmospheric radiocarbon is directly absorbed by water/air exchange on the surface of the water. The ^{14}C content of the water would then reflect that of the atmosphere with some dilution and delay.

c) Increasing ^{14}C trends are observed in Doornfontein eye (DFN) and Groot Kono Oog (GKO). This could be located on the rising limb of the bomb-^{14}C curve (Fig 27).

d) Decreasing trends are seen at springs that have ^{14}C levels greater than 100% (OLV and WGD). These are then springs with rapid turnover rates on the dropping limb of the bomb-^{14}C curve (Fig 27).

e) Two major springs near Pretoria (Fountains: PFL and Grootfontein, Rietvlei: GFR) show a clear ^{14}C rise since 1990 when more frequent sampling was undertaken. This could well represent the recent inflow of younger water into the spring system and justifies more detailed monitoring in the future.

f) Grootfontein Oog, Bo-Molopo (GFO) represents a case of special interest since it is a strong spring currently heavily pumped for local water supply. Apart from a single low ^{14}C value in 1968, all subsequent ^{14}C analyses have been within the range of 83 to 87 pmc. This spring deserves more detailed attention since it has been well studied (van Rensburg *et al.* 1992) and is a major water supply for nearby Mmabatho.

In the past isotope samples had been taken on an ad-hoc basis as interest and resources allowed. In the present project it was attempted to sample at periods of low and of high flow in order to 'force' variability on the time series, if it were to be related to flow rate anyway. Viewing those springs where, for the period 1991 to 1994, there were ^{14}C variations greater than 1 % showed that only in the case of Gerrit Minnebron could a relation with flow be seen in the form of lower ^{14}C content during the period November 1992 to August 1993 when flow was also lower.

The isotope variations of flow from the Kuruman springs have been discussed elsewhere (Bredenkamp *et al.* 1992,1995 and Bredenkamp 2000). It was shown that a relation between flow and ^{14}C exists following the high recharge event of 1976 (see also Fig. 25). These variations were interpreted as mixing from a two-box model: a quick response of flow from recharge of the Asbestos Mountains followed by delayed response of the actual (high ^{14}C) water reaching the spring. The return of ^{14}C levels to the earlier baseline level follows from the return to low-flow conditions from the larger (and older) water compartment. In none of the other springs was this evident and it must be concluded that, in the short term of a few years, in none other than the Kuruman springs, is a flow relation evident on the short (few months) timescale.

6. CONCLUSIONS

6.1 Hydrochemical development of dolomite water

The main chemical constituents of the water in the Dolomites (Ca, Mg and HCO_3) are the products of solution of dolomite (Ca-Mg-CO_3) due to the acidity produced by the solution of carbon dioxide in water. This solution process occurs in the vadose and in the saturated zones (Vogel and Ehhalt 1963, Clark and Fritz 1997). The solution equilibria of calcite, dolomite, carbonate, bicarbonate and carbon dioxide (dissolved and gaseous) pose limits to the quantities of carbonate that can be dissolved (Deines and Langmuir 1974). The main control is imposed by the partial pressure of carbon dioxide in the vadose zone (Figure 28). Variations of these parameters can subsequently be effected by processes involving any of the components of this chemical equilibrium system (Talma 1981). The calculations of saturation equilibria, based on chemistry and field pH determinations in this area, indicate that most of the spring water in the study area is close to equilibrium with both calcite and dolomite (Fig 8b & 8c). The carbon dioxide partial pressures associated with these equilibria in the present study areas are in the range of 0.3 to 9% (Fig 8a) and are consistent with values produced by vegetation in soils (Brook *et al.* 1983) and are orders higher than that of carbon dioxide in the atmosphere (0.03%). The equilibrium with dolomite probably governs the amount that can be dissolved while the calcite equilibrium controls the potential of carbonate precipitation from the water.

Quantification of the progress of carbonate solution process requires consideration of the solution mechanism (Deines *et al*. 1974). In the simplest case, equilibrium exists between the three phases: gaseous carbon dioxide in the vadose zone, the dissolved species in water (CO_2, HCO_3 and CO_3) and the solid carbonate of the soil or aquifer material (dolomite). In this ‘open’ solution model the maximum amount of carbonate for a given carbon dioxide level in the soil atmosphere will be dissolved (Fig 28). For the ‘closed’ model, it is assumed that as a first step, carbon dioxide dissolves in soil water to its maximum extent and that subsequently this CO_2-saturated water flows towards solid carbonate where dissolution to yield HCO_3 and CO_3 occurs. The closed model results in a lower limit to the quantity of carbonate that can be dissolved for a given soil CO_2 content (Fig 28) (Vogel and Ehhalt 1963, Deines and Langmuir 1974). In nature the real process will be somewhere between these two models.

It seems likely that the low alkalinity values encountered in the Pretoria region are caused by closed system solution. The fact that some of the samples show under-saturation underscores the lack of progress towards saturation. These under-saturated spring waters (Elandsfontein, Grootfontein Rietvlei and Erasmus spring, Appendix D) are located on the edge of the Pretoria aquifer. It is possible that the water was recharged through the adjacent quartzites and was limited in its contact with dolomite (Bredenkamp 2000).

Apart from imposing limits on the alkalinity of groundwater, the open and closed models of solution also determine the initial ^{14}C and ^{13}C content of the water that develops (Deines et al 1974). Open system carbonate solution produces groundwater with a ^{14}C content of 100 pmc in the dissolved carbonate species, since there is ample opportunity for isotopic exchange between soil CO_2 and water. This serves as the initial ^{14}C content from which radioactive decay will cause reduction with increasing age. The closed model, however, produces TIC with an initial ^{14}C content of 50 pmc since half the carbon in solution is derived from soil CO_2 and the other half from carbonate (Vogel and Ehhalt 1963). Various methods are used to assess the initial ^{14}C content (Clark & Fritz 1997). The usual approach in hydrology is to use the parallel behaviour of ^{13}C to estimate the extent of open/closed behaviour. To do this, the ^{13}C content of soil CO_2 needs to be known. The isotope composition of soil CO_2 depends on the isotope composition of the vegetation from which it is derived. In the South African case, this is difficult to estimate since grasses and other plants in the interior of the country have widely different ^{13}C contents (Vogel *et al.* 1978). The ^{13}C content of soil CO_2 actually depends on the relative contribution of grass and other plants to the total biomass turnover in the recharge area, which is hardly ever known. For this reason it has become more practical to use the relation between tritium and ^{14}C to estimate the initial ^{14}C content of groundwater (Verhagen *et al*. 1974). This data, in so far as it exists for the Dolomite water (Fig 14), suggests a lower initial ^{14}C content for the samples from the Pretoria aquifer compared to the aquifers to the west. More tritium measurements are certainly required to constrain this aspect.

6.2 A Conceptual Flow Model

In order to evaluate data presented above some conceptual model must be used and tested to explain the variations noticed. Only thereafter can useful numbers be derived from such a model.

There are usually two types of models used to test the response of aquifers to the input of a time variable input function such as the atmospheric radiocarbon content (Malochewski and Zuber 1982). In the piston-flow model applicable for confined aquifers, groundwater flows as a piston through a pipe (with possibly some dispersion) and the input function will appear at the outlet at some or other time, perhaps reduced or smoothed to some extent (Fig 28). This is the classic form of 'dating' of water and resembles the radio-active dating of artefacts. In the case where the input tracer concentration remains constant in time, the reduction of tracer concentration at the outlet of the aquifer can be used to calculate the flow rate of water through the aquifer. When the input tracer concentration varies with time, such as the atmospheric bomb-^{14}C or tritium peaks in the atmosphere, this pulse will also be observable at the outlet of the aquifer. Depending on the dispersion, there may be some smoothing of the peak or tailing off after passage of the peak maximum.

In the exponential (or mixed box) flow model, the water input enters the water table over the entire area and represents a phreatic aquifer (Fig 29). In this case the spring will deliver a mixture of recharge water with a range of delay times (Vogel 1967). The distribution of delay times is exponential

(Verhagen *et al*. 1991). The computation method is the same as is the case of water entering a box and being well mixed. The calculated 'age' of the outlet water (the spring for instance) when there is a constant input of tracer equals the average residence time of water in the aquifer. This model was used in the original investigations in the Bo-Molopo area (Bredenkamp and Vogel 1970). When the input of tracer into the aquifer is variable then a smoothed tracer response will emerge from the spring of which the amplitude and shape will depend on the mean residence time of water in the aquifer (Fig. 29).

The expectation of the application of these models is that some signs of bomb ^{14}C and tritium should be visible in most spring water in the course of time. The transfer of the bomb-^{14}C pulse through the dolomite compartments only occurred in a few cases of the smaller compartments (see section 5.3 and Fig 26). For the larger compartments in the Dolomites (e.g. Grootfontein Bo-Molopo, Pretoria Fountains, Grootfontein Rietvlei) the flow systems appear to be large enough that the bulk of the ^{14}C input is not visible. At the same time, some elements of contamination (SO_4, Cl) have clearly already appeared in Gerrit Minnebron and Turffonteinoog (Fig. 4b) in spite of stable and not too high ^{14}C content (73 and 90 pmc). It thus seems likely that there should be more elements of a linear nature in these systems than originally supposed. A possible explanation could be that local agriculture withdraws substantial amounts of water by pumping and thereby reducing the effective present day recharge.

This complexity can be illustrated by the ^{14}C response of the Grootfontein (Bo-Molopo) spring (Fig 26, GFO). A rise of 8 pmc within one year (1968-1969) indicates a very small aquifer with rapid turnover time of the order a just a few years (see Fig 27). All subsequent ^{14}C values for the next 25 years are between 83.2 and 86.4pmc, which suggests a long turnover time (in the order of 50 to 100 years). The known data of this aquifer indicate that the average depth of fracturing is between 50 and 100 metre (Bredenkamp 2000). Earlier water level modelling indicates that the storativity is 2% implying that the aquifer contains 75*0.02=1.5 meter water. Various recharge determinations based on springflows and water level variations indicate annual recharge amounts of 22 to 49mm (Table 12.2 in Bredenkamp et al 1995). These two pieces of information suggest that the turnover time of water in the aquifer could be 1500/35=43 years. Turnover times of water in the aquifer of this size would have produced more ^{14}C change between 1969 and 1994 (Fig 27) than has in fact been observed (Fig. 26).

The opposite behaviour is noted at Paardevallei Lower Eye (Fig 26) where the spring water has maintained a ^{14}C content above the pre-bomb value (of 90pmc or less) for a period of close to 20 years. If there was a rise to 100pmc between 1965 and 1976 (of at least 10pmc) then it would be expected that the next 25 years would see either a further rise or a depletion as the bomb pulse would pass. Similar behaviour can be seen in Buffelshoek and Doornplaatoog.

A feature of the exponential mixing model is that the ^{14}C content of the spring water should be independent of the aquifer size. The data accumulated for part of the Bo-Molopo area (Fig.11) indicate that lower ^{14}C values (greater age) are associated with larger catchment size and that travel times then become relevant. The exponential model in its simplest form is therefore not directly applicable in these aquifers.

The Kuruman upper (A) spring is an exception in that evaluation of the more detailed ^{14}C record of this spring has revealed a distinct two-box behaviour during the large flow episodes of 1976 (Fig 25). Bredenkamp et al (1995) have shown that this can successfully be explained as the varying inflow of water from two separate boxes of widely different residence times. The high recharge of the 1976 rainfall season introduced high ^{14}C in the water, which soon receded and was replaced by water with lower ^{14}C content. Some similar behaviour may be present in some of the other springs where ^{14}C time series exhibit minor ‘spiky’ behaviour (Fig 26).

There is however a fundamental difference between flow response to recharge and that of any of the tracers, be they isotopic or chemical. The flow rate of a spring and the water level in an aquifer are both responses to the piezometric pressure of water and the responses to recharge can be transferred rapidly throughout an aquifer. Water levels are known to responds fairly rapidly to recharge since it is pressure that is transmitted through the aquifer. For a tracer to appear in a borehole or spring water, the water should actually travel from recharge area to the observation point and this may take considerable time, which is reflected in the ‘age’ or ‘residence time’ of water in the aquifer. Tracer response can therefore lag significantly behind flow variations (Bredenkamp 2000).

6.3 Recharge and Storage Estimates

The data presented above indicate that there is no single generic model that can be applied to explain the time dependent behaviour of various tracers in every one of the springs. Some of the smaller springs (e.g. Rietgat oog, Olievendraai oog, Welgedacht oog) can be described by short turnover rates of bomb-^{14}C through the aquifers. With some parameter adjustment (delay in appearance of bomb ^{14}C and dilution amount by aquifer carbonate), it will be possible to match the MRT curves of Fig 27 to each of the simpler ^{14}C curves of these springs (Fig 26). The larger ones either exhibit little change over time or show patterns inconsistent with simple single box flow models. For these simple box models one can then use the relation

$$\mathrm{MRT} = S/R$$

With S= storage as depth of water in the aquifer and R=recharge as depth of water annually recharged.

The ^{14}C data indicate that residence times of the groundwater in the major compartments of the dolomites can be at least a hundred years old. This is indicated by the low and reasonably constant radiocarbon content of much of the water and the negligible influence of bomb ^{14}C on the major water sources in the area. Even if models, such as in Kuruman, indicate a young component, then there remains a significant low ^{14}C contribution. The few tritium results available support the ^{14}C data (Fig 14). The exact calculation of turnover times is made difficult by the uncertainty in the extent of dilution of the ^{14}C by soil/aquifer carbonate.

6.4 Recommendations

The data available do not allow unequivocal interpretation of the processes recharge, turnover time flow patterns etc of the groundwater in the Dolomite compartments. In most cases the situations are more complex than perceived in the pioneering work of the seventies (Bredenkamp and Vogel 1970). The main shortcoming lies in the development of concepts of flow (what sort of model to use), the uncertainty of the existence of deep water (how old?) and the confirmation of age/mean residence time of the water in each compartment.

It is therefore recommended that
- studies of compartments be undertaken individually and be targeted on those catchments that are of importance for water supply,
- these surveys include chemistry, isotopes, water levels and flow patterns from both boreholes and springs to clarify the processes within each compartment,
- a wider spectrum of the age related parameters are applied to confirm age patterns in the water, e.g. tritium, CFC, T/He, ^{36}Cl.
- detailed modelling of water and pressure flow in each compartment be undertaken,
- the application of trace metals and radiogenic isotopes (e.g. strontium) be investigated as these have real potential to characterise the kinetics of the interaction between water and aquifer rock.

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APPENDICES

APPENDIX A: Spring localities, maps used and DWAF references

Label	Area	Spring Name	Latitude	Longitude	Map Ref	DWA_NO
ASL	BM	ASLAAGTE OOG	260713	261117	2626AA	
BTS	GH	BOETSAP EYE	275615	242414	2724CD	
BOT	GH	BOTHETHELETSE	272345	234800	2723BD	D4H010
BUF	BM	BUFFELSHOEK OOG	254145	260030	2526CA	A3H009
CTO	GH	COMPTON OOG	272930	233045	2723BC	
CUT	PT	CUTTINGS	255217	281747	2528CD	
DAN	GH	DANIELSKUIL OOG	281200	233000	2823AA	
DKL	BM	DINOKANE LOWER	252600	255200	2525BD	A1H002
DKU	BM	DINOKANE UPPER	252721	255114	2525BD	A1H001
DFN	BM	DOORNFONTEIN OOG	253815	255545	2525DB	A3H015
DPL	BM	DOORNPLAATOOG	254600	255930	2525DD	A3H026
ELF	PT	ELANDSFONTEIN	255906	281954	2528CD	A2H008
ERR	PT	ERASMUS SPRING	255415	282110	2528CD	
GMB	WR	GERRIT MINNEBRON	262845	270900	2627AC	C2H011
GOP	BM	GOPANE SPRING	251942	254518	2525BD	
GFO	BM	GROOTFONTEIN OOG	255500	255130	2525DD	D4H004
GFR	PT	GROOTFONTEIN RIETVLE	255450	282042	2528CD	
GKO	GH	GROOTKONO OOG	274000	233645	2723DA	D4H009
KLL	BM	KAALOOG (Grootfontein Marico) BRIDGE	254700	262220	2526CD	
KLU	BM	KAALOOG (Grootfontein Marico) UPPER	254727	262212	2526CD	
KKL	BM	KAFFERSKRAAL OOG	253845	255700	2525DB	A3H013
KRB	BM	KAREEBOS OOG	255000	255900	2525DD	A3H020
KSO	BM	KLAARSTROOM OOG	253310	255945	2525DB	A3H012
KVF	GH	KLEIN VLAKFONTEIN	273950	240706	2724CA	
KFN	BM	KLEINFONTEIN OOG	255440	255211	2525DD	
KKO	GH	KLEINKONO OOG	273930	233445	2723DA	D4H008
KU1	GH	KURUMAN OOG 1	272730	232615	2723AD	D4H005
KU2	GH	KURUMAN OOG 2	272715	232745	2723AD	D4H006
LBO	BM	LICHTENBURG OOG	260645	261019	2626AA	
MMU	BM	MALMANI INFLOW	254930	260345	2526CC	A3H023
MML	BM	MALMANI WEIR	254845	260300	2526CC	A3H018
MAL	WR	MALONEY'S EYE	260130	273345	2627BA	A2H010
MAY	GH	MAYEDING OOG	273000	234130	2723BA	D4H007
MOL	BM	MOLOPO OOG	255300	260115	2526CC	D4H014
MMF	BM	MOOIMEISIESFONTEIN	255801	255054	2525DD	
MRB	WR	MOOIRIVIER BO	261145	270955	2627AA	
OLV	BM	OLIEVENDRAAI	255115	255230	2525DD	D4H017
PVL	BM	PAARDEVALLEI OOG LOW	253742	260003	2526CA	A3H022
PVU	BM	PAARDEVALLEI OOG UPP	253756	255930	2525DB	A3H021
POL	BM	POLFONTEIN OOG	260345	255130	2625BB	D4H019
PFL	PT	PRETORIA FOUNTAINS L	254649	281141	2528CC	
PFU	PT	PRETORIA FOUNTAINS U	254649	281200	2528CC	
RNF	BM	RHENOSTERFONTEIN	254315	260815	2526CA	A3H017
RGO	BM	RIETGAT OOG	255709	254742	2525DD	
RGB	BM	RIETGAT OOG OOS BH	255709	254743	2525DD	

Label	Area	Spring Name	Latitude	Longitude	Map Ref	DWA_NO
RGW	BM	RIETGAT WEST BH	255709	254740	2525DD	
SSW	WR	SCHOONSPRUIT OOG DWA	261700	265130	2626BD	C2H064
SSL	WR	SCHOONSPRUIT OOG LOW	261636	265201	2626BD	
SSS	WR	SCHOONSPRUIT OOG SOU	261632	265152	2626BD	
SSU	WR	SCHOONSPRUIT OOG UPP	261510	265358	2626BD	
STF	PT	STERKFONTEIN SPRING	255610	281445	2528CC	
SBL	BM	STINKHOUTBOOMOOG LOW	253858	255947	2525DB	A3H010
SBU	BM	STINKHOUTBOOMOOG UPP	253906	255928	2525DB	
STO	BM	STRYDFONTEIN OOG	254600	260648	2526CC	
TBN	GH	THABA SIKWE NORTH	273618	243609	2724DA	C3H010
TBS	GH	THABA SIKWE SOUTH	273638	243609	2724DA	
TRD	BM	TREKDRIF OOG	255736	260205	2526CC	
TSI	GH	TSINENG OOG	270508	230431	2723AA	D4H011
TFL	WR	TURFFONTEIN LOWER	262415	271030	2627AC	C2H013
TFU	WR	TURFFONTEIN UPPER	262400	271050	2627AC	
TWL	BM	TWEEFONTEIN LOWER	253230	255645	2525DB	A1H004
TWU	BM	TWEEFONTEIN UPPER	253245	255630	2525DB	A1H003
VRR	PT	V REENEN SPRING	255237	281749	2528CD	
VGD	BM	VERGENOEGD OOG	253615	255930	2525DB	A3H011
VKF	GH	VLAKFONTEIN OOG	273945	240515	2724CA	
WGD	BM	WELGEDACHTOOG	254915	255800	2525DD	D4H016
WTV	BM	WELTEVREDE OOG	255210	255147	2525DD	
WIL	PT	WILLOW SPRING	255131	281800	2528CD	
WFN	WR	WONDERFONTEIN OOG	255020	261105	2526CC	
WGT	BM	WONDERGAT	255210	255335	2525DD	

APPENDIX B: Sampling site descriptions

This section contains details of the sources sampled in the course of the present sampling campaign. The samples indicated as WR were collected by Siep Talma from the Bo-Molopo, West Rand and Pretoria areas and consequently the locations and details are better defined. Other samples were collected by DWAF personnel and are presumed to be from the sites as described below. Names of the sources are derived from available 1:50 000 maps (Appendix A) on which most of the springs are indicated.

PRETORIA AREA

CUT: Cuttings (WR35)

One of a group of three covered springs that were flowing directly into Rietvlei dam. Flow ceased during the 1980's. Samples were taken from a weir at the collection point.

ELF: Elandsfontein (WR75)

Samples were collected at the outflow point in a sandy pool just below a bend in the gravel road. This spring has a special significance for the local members of the Zion Christian Church.

ERR: Erasmus spring **(WR14)**

Direct outflow in a roofed-over outcrop west of Grootfontein spring.

GFR: Grootfontein Rietvlei (WR13)

Samples were collected from a pool at the outflow point of the municipal owned spring.

PFL: Pretoria Fountains Lower spring (WR10)

Water was collected from an outflow point under cover, across the road from the old pumping station in Fountains Valley.

PFU: Pretoria Fountains Upper spring (WR72)

Water was samples at the collection station of three water sources in Fountains valley located northwest of WR10.

STF: Sterkfontein Spring (WR15)

The spring is covered over. Samples were taken at the collection and gauging house.

VRR: Van Reenen (WR12)

One of a group of three covered springs that were flowing directly into Rietvlei dam. Flow ceased during the 1980's. Samples were taken from a weir at the collection point.

WIL: Willows (WR11)

One of a group of three covered springs that were flowing directly into Rietvlei dam. Flow ceased during the 1980's. Samples were taken from a weir at the collection point.

BO-MOLOPO AREA

ASL: Aslaagte Oog (WR44)

The spring is located on land belonging to the cement factory. The sample was taken from the open pool with lots of floating debris. No longer flowing in 1992.

BUF: Buffelshoek Oog (WR53)

Samples were collected at the outflow point of water in a pool just above DWAF weir.

DFN: Doornfontein Oog (WR58)

Large reed covered outflow point. Samples were taken at the DWAF weir.

DKL: Dinokane Lower Eye (WR77)

Small pool of water in Dinokane village. Samples were taken at a water outflow point.

DKU: Dinokane Upper Eye (WR78)

Extensive pool supplied by a few eyes. Samples were taken at the eastern-most eye where clear outflow could be observed.

DPL: DoornplaatOog (WR52)

Small pool supplied by single eye. Samples were taken at the outflow point. The spring has now been opened up and fitted with a pump for the supply of bottled water.

GFO: Grootfontein Oog (WR22,WR63)

Sample WR22 was initially collected at the DWAF outflow weir where it drained the natural reed-covered eye area. Since 1984 (WR63) samples were taken from whichever one of the main boreholes drilled within 10 meters of the perimeter of the original eye was running at the time of sampling.

GOP: Gopane Spring (WR80)

Small spring near village. Samples were taken at the inflow point.

KLF: Kleinfontein Oog

Intermittent flow in 1967 and 1975-80.

KLL: Kaaloog Bridge (WR68)

Samples were taken from the stream at the road bridge. This water drains the entire spring area and feeds the Marico river.

KLU: Kaaloog Upper (WR69)

The entire eye is a large area covered with floating reeds with numerous inflow points. The samples were taken from the surface of the diving platform belonging to Mr Z Palm. This is close to a distinctive inflow point.

KRB: Kareebos Oog (WR50)

Sample taken at DWAF gauging weir.

LBO: Lichtenburg Oog (WR43)

Sample taken from a spring from a dolomite outcrop located in the Caravan Park. Flow has now ceased.

MML: Malmani Weir (WR61)

Sample collected 200m upstream from the road bridge.

MMU: Malmani inflow (WR62)

The area contains many small eyes that feed a large reed covered area. Water samples were taken at one of the smaller eyes that were accessible on the east side, close to the DWAF weir.

MOL: Molopo Oog (Bosman) (WR49)

Samples were taken at the jetty of Bosman on the west side of the area, close to one of several distinctive inflow points on the bottom of the pool.

OLV: Olievendraai (WR66)

Sample taken at inflow point.

POL: Polfontein Oog (WR45)

Large red-covered area with lots of mud and cattle. The sample was taken from a channel on the south side of the spring.

PVL: Paardevallei Lower Eye (WR57)

Small dam with V-notch

PVU: Paardevallei Upper Eye (WR56)

Distinct inflow point, Small pool with V-notch, 1 km upstream from PVL.

RGB: Rietgat Eastern Borehole (WR47)

Borehole 20m east of RGO

RGO: Rietgat Oog (WR46)

On farm Spring Valley of Rooigrond prison. The eye consists of standing water in small sinkhole that is fitted with a pump and regularly used. Probably recharged from the nearby dam that was at one time used as fish hatchery.

RGW: Rietgat Oog Western Borehole (WR82)

Borehole west of RGO.

RNF: Rhenosterfontein (WR60)

Sampled directly from eye that is feeding the pool.

SBL: Stinkhoutboom Lower Eye (WR54)

Small spring with clear inflow point, 200m upstream of DWAF weir.

SBU: Stinkhoutboom Upper Eye (WR55)

Large spring with clear water flow point, 1 km upstream of SBL.

TWL: Tweefontein Lower Eye (WR59)

Drainage from a reed covered area that is fed by eyes below the reeds. Samples were taken at the DWAF weir directly accessible from the road.

TWU: Tweefontein Upper Eye (WR70)

Sampled from one of many small eyes that feed a stream near the farm house.

VGD: Vergenoegd Oog (WR73)

Open spring. Ceased flowing in 1993.

WGD: Welgedacht Oog (WR51)

Spring located in the front garden of the farm house. Centrifugal pump fitted on shallow borehole to augment water supply.

WGT: Wondergat (WR 40)

Samples were taken at the water surface in the sinkhole.

WTV: Weltevrede Oog (WR48)

Borehole used to be artesian. A furrow has been excavated 1m metre deep, to maintain flow.

WEST RAND AREA

GMB: Gerrit Minnebron (WR5)

Large pool fed my strong inflow. Samples were collected at the pump on the NW side of the pool.

MAL: Maloneys Eye (WR8)

Many small eyes contributing to a large pool that supplied water for a trout hatchery. Samples were taken from one of the eyes on the upstream side of the pool. Access was found from the road leading towards the homestead on the hill.

MRB: Mooirivier Boonste Oog (WR7)

Sample taken at inflow point on the east side of the pool.

SSL: Schoonspruit Oog (WR6)

Samples were collected from a low water bridge crossing the drainage from a large reed covered eye.

SSU: Schoonspruit Oog upper (WR 79)

One-off sample was collected from a windmill close the most northerly eye indicated on the 1:50 000 map of the area.

SSW: Schoonspruit Oog DWAF

The samples collected by DWAF were *presumably* collected at the DWAF gauging weir further downstream from which the Ventersdorp water supply is also abstracted.

SSS: Schoonspruit Oog South (WR83)

Samples were collected from a standing water pool located to the south of the road leading to SSL and SSU.

TFL: Turffontein lower Eye (WR76)

Drainage from large reed coverd area. Near DWAF weir.

TFL: Turffontein upper Eye (WR4)

Outflow from dolomite outcrop, upstream of TFL.

APPENDIX C: Field data pH, temperature and saturation indices of some spring water.

Open water is defined as springs where samples were taken after the water had been exposed to the atmosphere

EYE	AREA	Sample	Date	Open water?	T	pH	Ca	Mg	TAL	log pCO_2	SI Calcite	SI Dolomite	SI Gypsum
BUF	BM	BUFFELSHOEK OOG	Dec-84		21		58	31	242				-2.7
BUF	BM	BUFFELSHOEK OOG	Jul-93		20.3	7.05	58	31	249	-1.6	-0.2	-0.2	-3.6
BUF	BM	BUFFELSHOEK OOG	Jun-94		21.2	7.5	54	32	262	-2.0	0.2	0.7	-2.7
DFN	BM	DOORNFONTEIN OOG	Jul-93	O	10.3	7.55	76	41	331	-1.9	0.5	1.2	-3.0
DKL	BM	DINOKANE LOWER	Jul-93		21.3	6.87	56	32	251	-1.4	-0.4	-0.6	-3.0
DKU	BM	DINOKANE UPPER	Jul-93		21.3	7.01	51	28	219	-1.6	-0.3	-0.5	-2.9
DPL	BM	DOORNPLAATOOG	Dec-84		20		60	33	245				-3.0
DPL	BM	DOORNPLAATOOG	Jul-93		19.8	6.85	56	30	239	-1.4	-0.4	-0.7	-2.9
DPL	BM	DOORNPLAATOOG	May-94		20.1	7.04	54	31	257				
GFO	BM	GROOTFONTEIN OOG	Aug-93		19.9	6.85	75	32	282	-1.3	-0.2	-0.4	-3.0
GFO	BM	GROOTFONTEIN OOG	Jun-94		20.4	7.05	68	34	289	-1.5	-0.1	-0.0	-2.9
MLW	BM	MOLOPO OOG WEIR	May-94	O	14.1	7.88	40	26	205	-2.5	0.4	1.1	-3.2
MOL	BM	MOLOPO OOG BOSMAN	Jul-93		18.8	7.3	49	26	212	-1.9	-0.1	-0.0	-3.0
MOL	BM	MOLOPO OOG BOSMAN	May-94		19.1	7.73	45	26	222				
OLV	BM	OLIEVENDRAAI OOG	Jul-93		20	6.82	73	41	319	-1.2	-0.2	-0.3	-2.6
OLV	BM	OLIEVENDRAAI OOG	Jun-94		21	7.04	69	42	334	-1.4	-0.0	0.1	-2.7
PVL	BM	PAARDEVALLEI OOG LOWER	Dec-84		21		81	33	296				-2.5
PVL	BM	PAARDEVALLEI OOG LOWER	Jul-93		19.6	6.89	70	37	297	-1.3	-0.2	-0.3	-2.5
PVL	BM	PAARDEVALLEI OOG LOWER	May-94		19.9	6.96	67	40	321	-1.4	-0.1	-0.1	-2.5
RGB	BM	RIETGAT OOG OOS BH	Jul-93		21.3	6.96	80	41	289	-1.4	-0.1	-0.1	-2.1
RGB	BM	RIETGAT OOG OOS BH	Jun-94		20.3	7.22	79	39	275	-1.7	0.1	0.4	-2.1
RGO	BM	RIETGAT OOG	Jul-93			6.89	69	38	261	-1.4	-0.3	-0.4	-2.3
RGW	BM	RIETGAT WEST BH	Jun-94		20.1	7.18	82	35	277	-1.7	0.1	0.3	-2.0
RNF	BM	RHENOSTERFONTEIN	Jul-93		20.8	7.6	43	27	185	-2.2	0.1	0.4	-2.7
RNF	BM	RHENOSTERFONTEIN	May-94		21.1	7.52	49	27	219	-2.1	0.1	0.5	-2.6
SBL	BM	STINKHOUTBOOMOOG LOWER	Jul-93		20.2	6.8	58	31	247	-1.3	-0.5	-0.7	-3.6
SBL	BM	STINKHOUTBOOMOOG LOWER	Jun-94		20.2	7.09	53	32	255	-1.6	-0.2	-0.2	-2.6
SBU	BM	STINKHOUTBOOMOOG UPPER	Dec-84		21.5		79	27	255				-2.3
TWL	BM	TWEEFONTEIN LOWER	May-94	O	17.8		51	30	247				-3.0
TWU	BM	TWEEFONTEIN UPPER	May-94		20.5	7.37	40	24	195	-2.0	-0.1	-0.0	-3.1
WGD	BM	WELGEDACHTOOG	Dec-84		21		77	31	276				-2.6
WGT	BM	WONDERGAT	Jul-80	O	18.4	7.58	56	35	270	-2.1	0.3	0.9	-3.4
BTS	GH	BOETSAP EYE	Jul-93	O		7.73	72	113	593	-1.9	0.9	2.3	-2.2
DAN	GH	DANIELSKUIL OOG	Jul-93			7.18	43	11	147	-1.9	-0.4	-0.9	-2.8
GKO	GH	GROOTKONO OOG	Jul-93			7.07	70	29	256	-1.6	-0.1	-0.1	-2.8
KKO	GH	KLEINKONO OOG	Jul-93			6.96	74	40	313	-1.4	-0.1	-0.1	-2.7
KU1	GH	KURUMAN OOG 1	Jul-93			7.14	44	15	162	-1.8	-0.4	-0.8	-2.9
KU2	GH	KURUMAN OOG 2	Jul-93			7.65	54	23	218	-2.2	0.3	0.7	-2.9
MAY	GH	MAYEDING OOG	Jul-93	O		7.56	64	36	279	-2.0	0.4	1.0	-2.8
VKF	GH	VLAKFONTEIN EYE	Jul-93	O		7.35	69	39	287	-1.8	0.2	0.6	-2.8
ELF	PT	ELANDSFONTEIN	Nov-92			6.8	27	16	134	-1.6	-1.0	-1.8	-3.6
ELF	PT	ELANDSFONTEIN	Aug-93		19.5	7.17	28	16	134	-2.0	-0.6	-1.0	-3.2
ELF	PT	ELANDSFONTEIN	Aug-94		19.4	7.17							
ERR	PT	ERASMUS SPRING	Jul-79		19.5	7.47	20	13	106	-2.4	-0.5	-0.8	-3.2
ERR	PT	ERASMUS SPRING	Aug-93		19	7.36	23	12	112	-2.2	-0.6	-1.0	-3.1
ERR	PT	ERASMUS SPRING	Aug-94		19.3	7.35	22	15	112	-2.2	-0.6	-0.9	-3.1

EYE	**AREA**	**Sample**	**Date**	**Open water?**	**T**	**pH**	**Ca**	**Mg**	**TAL**	**log pCO_2**	**SI Calcite**	**SI Dolomite**	**SI Gypsum**
GFR	PT	GROOTFONTEIN RIETVLEI	Jul-79		19.1	7.7	23	14	123	-2.5	-0.2	-0.2	-6.9
GFR	PT	GROOTFONTEIN RIETVLE	Nov-92			7.1	24	14	120	-1.9	-0.8	-1.4	-6.9
GFR	PT	GROOTFONTEIN RIETVLEI	Aug-93		19.3	7.67	25	13	114	-2.5	-0.2	-0.3	-3.0
GFR	PT	GROOTFONTEIN RIETVLEI	Aug-94		19.4	7.37	24	14	114	-2.2	-0.5	-0.9	-2.9
PFL	PT	PRETORIA FOUNTAINS LOWER	Jul-79		20.6	7.59	46	27	180	-2.2	0.1	0.4	-2.7
PFL	PT	PRETORIA FOUNTAINS LOWER	Nov-92			6.9	47	26	196	-1.5	-0.5	-0.9	-2.6
PFL	PT	PRETORIA FOUNTAINS LOWER	Aug-93		20.8	7.14	44	26	178	-1.8	-0.4	-0.5	-2.7
PFL	PT	PRETORIA FOUNTAINS LOWER	Aug-94		20.8	7.07	41	25	192	-1.7	-0.4	-0.6	-2.6
PFU	PT	PRETORIA FOUNTAINS UPPER	Nov-92			7.1	41	24	191	-1.7	-0.4	-0.6	-2.9
PFU	PT	PRETORIA FOUNTAINS UPPER	Aug-93		20.8	7.17	42	23	182	-1.8	-0.3	-0.5	-3.7
PFU	PT	PRETORIA FOUNTAINS UPPER	Aug-94		20.7	6.95							
STF	PT	STERKFONTEIN SPRING	Jul-79		22	7.4	37	24	189	-2.0	-0.1	-0.0	-2.9
STF	PT	STERKFONTEIN SPRING	Nov-92		20	7	39	25	191	-1.6	-0.5	-0.8	-2.9
STF	PT	STERKFONTEIN SPRING	Aug-93		19.8	7.14	40	24	180	-1.8	-0.4	-0.6	-2.7
STF	PT	STERKFONTEIN SPRING	Aug-94		19.8	7.23	39	26	188	-1.9	-0.3	-0.3	-2.7
VRR	PT	V REENEN SPRING	Jul-79		18.2	7.41	25	17	138	-2.2	-0.4	-0.6	-6.9
WIL	PT	WILLOW SPRING	Jul-79		18.4	7.56	22	15	125	-2.4	-0.3	-0.4	-7.0
GMB	WR	GERRIT MINNEBRON	Jul-79		20.1	7.29	55	33	201	-1.9	-0.1	0.0	-2.0
GMB	WR	GERRIT MINNEBRON	Nov-92		20	7.1	63	37	208	-1.7	-0.2	-0.2	-1.6
GMB	WR	GERRIT MINNEBRON	Aug-93			7.48	60	38	201	-2.1	0.1	0.5	-1.7
GMB	WR	GERRIT MINNEBRON	Jun-94		19.9	7.13	63	40	208	-1.7	-0.2	-0.2	-1.6
MAL	WR	MALONEY'S EYE	Jun-79		19.5	7.72	26	16	124	-2.5	-0.1	-0.0	-6.9
MAL	WR	MALONEY'S EYE	Nov-92		19.8	7.7	28	17	135	-2.5	-0.1	0.0	-3.4
MAL	WR	MALONEY'S EYE	Aug-93			7.65	24	16	129	-2.5	-0.2	-0.2	-3.1
MAL	WR	MALONEY'S EYE	Jun-94		19.6	7.67	25	17	132	-2.5	-0.2	-0.1	-3.3
MRB	WR	MOOIRIVIER BOONSTE OOG	Jun-79		18.6	7.2	48	28	224	-1.8	-0.2	-0.1	-3.0
MRB	WR	MOOIRIVIER BO BOONSTE OOG	Dec-84		21		69	25	245				-2.7
MRB	WR	MOOIRIVIER BOONSTE OOG	Nov-92		20	6.8	47	28	231	-1.4	-0.6	-0.9	-3.4
MRB	WR	MOOIRIVIER BOONSTE OOG	Aug-93			7.6	44	27	219	-2.2	0.2	0.6	-3.1
MRB	WR	MOOIRIVIER BOONSTE OOG	Jun-94		20.1	7.17	47	27	223	-1.7	-0.2	-0.2	-3.4
SSL	WR	SCHOONSPRUIT OOG LOWER	Dec-84	O	19		77	34	295				-2.6
SSL	WR	SCHOONSPRUIT OOG LOWER	Nov-92	O		7.4	43	44	270	-1.9	0.0	0.5	-2.1
SSU	WR	SCHOONSPRUIT OOG UPPER	Aug-93	O		7.8	55	34	267	-2.3	0.6	1.3	-3.1
TFL	WR	TURFFONTEIN LOWER	Nov-92	O	19.8	6.9	99	58	210	-1.5	-0.3	-0.4	-1.1
TFU	WR	TURFFONTEIN UPPER	Jun-79	O	18.5	7.3	75	43	212	-1.9	0.1	0.3	-1.6
TFU	WR	TURFFONTEIN UPPER	Nov-92	O	21.2	7.1	96	53	206	-1.7	-0.1	-0.0	-1.1
TFU	WR	TURFFONTEIN UPPER	Aug-93	O		7.19	90	56	204	-1.8	-0.0	0.1	-1.2

APPENDIX D: Isotope data of samples collected during 1992-1994

Eye	Area	Name of spring	Date	Temperature	^{14}C pmc	^{14}C error	^{13}C ‰PDB	^{18}O ‰SMOW
BUF	BM	BUFFELSHOEK OOG	Aug-92		91.40	0.57	-8.7	-3.90
BUF	BM	BUFFELSHOEK OOG	Jul-93	20.3	90.65	0.76	-8.7	-4.16
BUF	BM	BUFFELSHOEK OOG	Jun-94	21.2	90.72	0.76	-8.7	-4.11
DFN	BM	DOORNFONTEIN OOG	Sep-92		102.40	0.47	-5.0	-4.44
DFN	BM	DOORNFONTEIN OOG	Jul-93	10.3	102.86	0.84	-6.2	-4.34
DKL	BM	DINOKANE LOWER	Jul-93	21.3	95.25	0.56	-7.2	-5.11
DKU	BM	DINOKANE UPPER	Jul-93	21.3	86.09	0.54	-7.0	-5.16
DPL	BM	DOORNPLAATOOG	Aug-92		94.61	0.72	-7.7	-3.84
DPL	BM	DOORNPLAATOOG	Jul-93	19.8	93.24	0.77	-8.3	-4.21
DPL	BM	DOORNPLAATOOG	May-94	20.1	94.83	0.55	-6.5	-4.11
GFO	BM	GROOTFONTEIN OOG	Sep-92		86.04	0.78	-7.0	-4.30
GFO	BM	GROOTFONTEIN OOG	Aug-93	19.9	86.29	0.54	-6.5	-4.67
GFO	BM	GROOTFONTEIN OOG	Jun-94	20.4	84.52	0.79	-6.5	-4.53
GOP	BM	GOPANE SPRING	Dec-93		86.51	0.53	-6.3	-5.88
MLW	BM	MOLOPO OOG WEIR	May-94	14.1	81.89	0.49	-5.7	-4.92
MOL	BM	MOLOPO OOG BOSMAN	Sep-92		82.41	0.52	-5.8	-5.16
MOL	BM	MOLOPO OOG BOSMAN	Jul-93	18.8	81.44	0.72	-5.6	-5.06
MOL	BM	MOLOPO OOG BOSMAN	May-94	19.1	80.71	0.51	-6.6	-5.02
OLV	BM	OLIEVENDRAAI OOG	Sep-92		104.39	0.57	-8.5	-3.67
OLV	BM	OLIEVENDRAAI OOG	Jul-93	20.0	103.85	0.86	-9.4	-4.07
OLV	BM	OLIEVENDRAAI OOG	Jun-94	21.0	105.44	0.84	-4.2	-3.88
PVL	BM	PAARDEVALLEI OOG LOWER	Sep-92		99.68	0.57	-8.3	-3.40
PVL	BM	PAARDEVALLEI OOG LOWER	Jul-93	19.6	100.98	0.68	-8.6	-3.71
PVL	BM	PAARDEVALLEI OOG LOWER	May-94	19.9	98.63	0.83	-10.2	-3.63
RGB	BM	RIETGAT OOG OOS BH	Sep-92		103.58	0.92	-5.9	-2.17
RGB	BM	RIETGAT OOG OOS BH	Jul-93	21.3	106.38	0.59	-7.0	-2.07
RGB	BM	RIETGAT OOG OOS BH	Jun-94	20.3	102.87	0.59	-7.2	-2.10
RGO	BM	RIETGAT OOG	Jul-93		99.45	0.87	-5.4	-1.46
RGO	BM	RIETGAT OOG	Jun-94					-1.47
RGW	BM	RIETGAT WEST BH	Jun-94	20.1	103.22	0.60	-7.1	-1.73
RNF	BM	RHENOSTERFONTEIN	Sep-92		71.97	0.49	-7.5	-5.19
RNF	BM	RHENOSTERFONTEIN	Jul-93	20.8	72.74	0.69	-7.6	-5.30
RNF	BM	RHENOSTERFONTEIN	May-94	21.1	70.62	0.68	-8.1	-5.24
SBL	BM	STINKHOUTBOOMOOG LOWER	Aug-92		91.19	0.78	-10.3	-3.99
SBL	BM	STINKHOUTBOOMOOG LOWER	Jul-93	20.2	90.86	0.77	-9.9	-4.20
SBL	BM	STINKHOUTBOOMOOG LOWER	Jun-94	20.2	90.52	0.76	-7.4	-3.80
TWL	BM	TWEEFONTEIN LOWER	Aug-92		91.10	0.55	-9.4	-5.03
TWL	BM	TWEEFONTEIN LOWER	May-94	17.8	92.66	0.59	-9.4	-4.97
TWU	BM	TWEEFONTEIN UPPER	Aug-92		85.74	0.54	-7.7	-5.36
TWU	BM	TWEEFONTEIN UPPER	May-94	20.5	86.78	0.53	-6.2	-5.15
VGD	BM	VERGENOEGD OOG	Aug-92		92.72	0.78	-8.0	-4.42
VGD	BM	VERGENOEGD OOG	May-94					-4.24
WGD	BM	WELGEDACHTOOG	Aug-92		94.68	0.77	-7.9	-4.01
WGT	BM	WONDERGAT	Aug-92		104.84	0.81	-6.8	-3.59
WGT	BM	WONDERGAT	Jul-93		101.32	0.58	-7.8	-3.94
WGT	BM	WONDERGAT	Jun-94		101.28	0.57	-7.5	-3.77
BTS	GH	BOETSAP EYE	Jul-93					-4.44
DAN	GH	DANIELSKUIL OOG	Jul-93		69.75	0.48	-11.0	-6.35

Eye	Area	Name of spring	Date	Temperature	^{14}C pmc	^{14}C error	^{13}C ‰PDB	^{18}O ‰SMOW
GKO	GH	GROOTKONO OOG	Jul-93		101.58	0.55	-9.4	-6.29
KKO	GH	KLEINKONO OOG	Jul-93		108.37	0.59	-10.6	-6.04
KU1	GH	KURUMAN OOG 1	Jan-92		68.86	0.79	-8.7	-6.30
KU1	GH	KURUMAN OOG 1	Feb-92		68.16	0.51	-8.9	-6.20
KU1	GH	KURUMAN OOG 1	May-92		67.71	0.41	-8.8	-6.11
KU1	GH	KURUMAN OOG 1	Aug-92		68.43	0.49	-8.8	-6.49
KU1	GH	KURUMAN OOG 1	Oct-92		68.14	0.66	-8.9	-6.57
KU1	GH	KURUMAN OOG 1	Feb-93		67.79	0.68	-8.5	-5.94
KU1	GH	KURUMAN OOG 1	Apr-93		68.34	0.48	-8.6	-5.94
KU1	GH	KURUMAN OOG 1	Jul-93		67.37	0.66	-8.6	-6.43
KU1	GH	KURUMAN OOG 1	Aug-93		67.23	0.65	-8.6	-5.83
KU1	GH	KURUMAN OOG 1	Jan-94		69.18	0.50	-8.8	-6.16
KU1	GH	KURUMAN OOG 1	May-94		67.89	0.67	-9.1	-6.20
KU2	GH	KURUMAN OOG 2	Jan-92		82.64	0.73	-9.1	-6.01
KU2	GH	KURUMAN OOG 2	Feb-92		82.05	0.44	-9.8	-6.00
KU2	GH	KURUMAN OOG 2	May-92		82.93	0.53	-10.1	-5.93
KU2	GH	KURUMAN OOG 2	Aug-92		83.26	0.52	-8.2	-6.27
KU2	GH	KURUMAN OOG 2	Oct-92		83.34	0.74	-9.1	-6.16
KU2	GH	KURUMAN OOG 2	Feb-93		83.48	0.79	-9.5	-5.86
KU2	GH	KURUMAN OOG 2	Apr-93		82.08	0.52	-9.0	-5.76
KU2	GH	KURUMAN OOG 2	Jul-93		82.14	0.75	-8.9	-6.18
KU2	GH	KURUMAN OOG 2	Aug-93		82.61	0.71	-9.1	-6.26
KU2	GH	KURUMAN OOG 2	Jan-94		82.21	0.58	-10.3	-6.07
KU2	GH	KURUMAN OOG 2	May-94		81.60	0.55	-8.8	-5.97
MAY	GH	MAYEDING OOG	Jul-93		101.91	0.60	-5.9	-5.74
TAM	GH	TAMASIKWA	Oct-92		114.83	0.60	-9.4	-0.60
VKF	GH	VLAKFONTEIN EYE	Jul-93					-5.46
ELF	PT	ELANDSFONTEIN	Feb-92		56.35	0.48	-9.9	-4.08
ELF	PT	ELANDSFONTEIN	Nov-92		88.14	0.53	-9.6	-4.43
ELF	PT	ELANDSFONTEIN	Aug-93	19.5	55.81	0.44	-10.0	-4.26
ELF	PT	ELANDSFONTEIN	Aug-94	19.4	55.91	0.87	-7.7	-4.21
ERR	PT	ERASMUS SPRING	Nov-92		55.09	0.73	-9.6	-5.05
ERR	PT	ERASMUS SPRING	Aug-93	19.0	54.09	0.43	-7.7	-4.82
ERR	PT	ERASMUS SPRING	Aug-94	19.3	52.34	0.68	-7.5	-4.69
GFR	PT	GROOTFONTEIN RIETVLEI	Feb-92		58.88	0.61	-9.7	-4.31
GFR	PT	GROOTFONTEIN RIETVLEI	Nov-92		59.27	0.65	-8.9	-4.71
GFR	PT	GROOTFONTEIN RIETVLEI	Aug-93	19.3	59.58	0.64	-8.9	-4.51
GFR	PT	GROOTFONTEIN RIETVLEI	Aug-94	19.4	59.17	0.65	-7.9	-4.40
PFL	PT	PRETORIA FOUNTAINS LOWER	Feb-92		81.65	0.74	-8.7	-3.70
PFL	PT	PRETORIA FOUNTAINS LOWER	Nov-92		80.89	0.74	-9.0	-3.77
PFL	PT	PRETORIA FOUNTAINS LOWER	Aug-93	20.8	81.40	0.72	-8.7	-3.74
PFL	PT	PRETORIA FOUNTAINS LOWER	Aug-94	20.8	80.99	0.52	-5.0	-4.23
PFU	PT	PRETORIA FOUNTAINS UPPER	Feb-92		73.59	0.46	-8.4	-4.23
PFU	PT	PRETORIA FOUNTAINS UPPER	Nov-92		72.85	0.68	-10.1	-4.54
PFU	PT	PRETORIA FOUNTAINS UPPER	Aug-93	20.8	74.35	0.99	-5.9	-4.30
PFU	PT	PRETORIA FOUNTAINS UPPER	Aug-94	20.7	72.94	0.48	-8.4	-3.48
STF	PT	STERKFONTEIN SPRING	Feb-92		78.49	0.52	-8.0	-3.93
STF	PT	STERKFONTEIN SPRING	Nov-92	20.0	79.47	0.76	-7.6	-4.13
STF	PT	STERKFONTEIN SPRING	Aug-93	19.8	80.56	0.72	-8.1	-4.00
STF	PT	STERKFONTEIN SPRING	Aug-94	19.8	80.56	0.72	-5.7	-3.87

Eye	**Area**	**Name of spring**	**Date**	**Tempe-rature**	**^{14}C pmc**	**^{14}C error**	**^{13}C ‰PDB**	**^{18}O ‰SMOW**
GMB	WR	GERRIT MINNEBRON	Feb-92		73.55	0.50	-8.9	-3.28
GMB	WR	GERRIT MINNEBRON	Nov-92	20.0	72.78	0.81	-7.3	-3.20
GMB	WR	GERRIT MINNEBRON	Aug-93		72.48	0.71	-8.3	-3.64
GMB	WR	GERRIT MINNEBRON	Jun-94	19.9	73.75	0.75	-7.6	-3.57
MAL	WR	MALONEY'S EYE	Nov-92	19.8	57.52	0.75	-7.7	-4.32
MAL	WR	MALONEY'S EYE	Aug-93		55.88	0.71	-8.0	-4.81
MAL	WR	MALONEY'S EYE	Jun-94	19.6	57.48	0.56	-7.5	-4.58
MRB	WR	MOOIRIVIER BO	Nov-92	20.0	75.09	0.70	-7.1	-4.40
MRB	WR	MOOIRIVIER BO	Aug-93		74.50	0.67	-6.1	-4.90
MRB	WR	MOOIRIVIER BO	Jun-94	20.1	72.86	0.52	-6.5	-4.76
SSL	WR	SCHOONSPRUIT OOG LOWER	Nov-92		117.49	0.88	-14.0	-3.20
SSS	WR	SCHOONSPRUIT OOG SOUTH	Feb-94		91.58	0.54	-6.4	-4.40
SSU	WR	SCHOONSPRUIT OOG UPPER	Aug-93		95.67	0.81	-6.2	-4.56
TFL	WR	TURFFONTEIN LOWER	Nov-92	19.8	88.17	0.79	-8.3	-2.46
TFU	WR	TURFFONTEIN UPPER	Nov-92	21.2	87.83	1.10	-7.5	-2.37
TFU	WR	TURFFONTEIN UPPER	Aug-93		86.51	0.75	-8.9	-2.85
TFU	WR	TURFFONTEIN UPPER	Jun-94	19.1	91.28	0.53	-8.2	-1.91

APPENDIX E: Summary of trends of ^{14}C and chemistry in spring water (Partly from Bredenkamp 2000).

Area	Eye	Name of spring	Number of samples	First year	Last year	Range of ^{14}C results	^{14}C Trend	Chemistry trend
BM	ASL	Aslaagte Oog	2	1976	1984	108.2-101.5	Decreasing, now dry	
BM	BUF	Buffelshoek Oog	7	1976	1994	89.4-91,4	Stable	Pristine spring
BM	DFN	Doornfontein Oog	5	1976	1993	96.5-102.9	Increasing	
BM	DPL	Doornplaatoog	5	1975	1994	92.7-94.8	Stable	
BM	GFO	Grootfontein Oog	17	1969	1994	83.2-86.3	Generally stable	
BM	KFN	Kleinfontein Oog	3	1975	1977	85.6-88.5	Stable, now dry	
BM	KKL	Kafferskraal Oog	2	1976	1977	101.6-97.6	Stable, now dry	
BM	KLL	Kaaloog Bridge	3	1990	1991	75.8-79.6	Variable	
BM	LBO	Lichtenburg Oog	3	1976	1984	100.1-102.5	Stable, now dry	
BM	MAY	Mayeding Oog	2	1991	1993	104.1-101.9	Stable	
BM	MMF	Mooimeisiesfontein	3	1969	1980	104.5-118.8	Variable, now dry	
BM	MMU	Malmani Inflow	3	1976	1990	69.6-70.8	Stable, unsamplable	
BM	MOL	Molopo Oog	8	1976	1994	79.6-85.1	Slow decrease	No evident contamination
BM	OLV	Olievendraai	6	1976	1994	103.8-111.4	Decreasing	
BM	POL	Polfontein Oog	2	1968	1984	91.1-91.0	Stable	
BM	PVL	Paardevallei Oog Lower	5	1976	1994	98.6-101.0	Stable	
BM	PVU	Paardevallei Oog Upper	3	1976	1984	93.3-95.7	Stable,now dry	
BM	RGB	Rietgat Oog Borehole	4	1984	1993	102.9-108.9	Variable	Supplied by nearby, evaporated dam water
BM	RGO	Rietgat Oog	6	1969	1993	98.4-128.6	Bomb ^{14}C peak 1976	
BM	RNF	Rhenosterfontein	7	1976	1994	70.6-74.5	Minor decrease	Non-dolomtic chemistry, polluton peak in 1982
BM	SBL	Stinkhoutboomoog Lower	6	1976	1994	89.4-91.7	Stable, peak 1991?	
BM	TWL	Tweefontein Lower	5	1984	1994	91.1-93.0	Stable	
BM	TWU	Tweefontein Upper	3	1991	1994	85.7-87.5	Increasing	
BM	VGD	Vergenoegd Oog	4	1976	1992	92.8-95.7	Stable,peak 1990?	Pristine spring
BM	WFN	Wonderfontein Oog	2	1976	1977	71.5-69.9	Stable, now dry	
BM	WGD	Welgedachtoog	4	1976	1992	108.9-94.7	Decrease 1976/84,dry	
BM	WGT	Wondergat	7	1976	1994	101.3-112.7	Open water, decrease	
BM	WTV	Weltevrede Oog	2	1968	1984	109.4-100.4	Decrease, now dry	
NC	GKO	Grootkono Oog	4	1969	1993	90.8-104.0	Increase? variable	Pristine
NC	KKO	Kleinkono Oog	3	1976	1993	103.9-108.4	Increase 1976/91	
NC	KU1	Kuruman Oog 1	26	1969	1994	67.2-78.6	Variable, peak 76/91	Two source recharge
NC	KU2	Kuruman Oog 2	20	1976	1994	79.5-87.4	Peak 76/91	
PT	ELF	Elandsfontein	4	1992	1994	55.8-56.4	Stable	Low HCO_3
PT	ERR	Erasmus Spring	5	1984	1994	51.4-58.2	variable? peak 1991?	Low HCO_3

Area	**Eye**	**Name of spring**	**Number of samples**	**First year**	**Last year**	**Range of ^{14}C results**	**^{14}C Trend**	**Chemistry trend**
PT	GFR	Grootfont'n Rietvlei	8	1970	1994	57.3-59.6	Stable, recently up	Low HCO_3
PT	PFL	Pta Fountains Lower	8	1970	1994	77.6-81.8	Peak since 1991	Rising Cl?
PT	PFU	Pta Fountains Upper	5	1991	1994	72.7-74.7	Stable	
PT	STF	Sterkfontein Spring	8	1979	1994	78.5-80.6	Stable	
PT	VRR	V Reenen Spring	2	1979	1984	74.3-69.6	Decrease, now dry	Low HCO_3
PT	WIL	Willow Spr. Rietvlei	3	1970	1984	68.4-55.2	Decrease, now dry	Low HCO_3
PT	CUT	Cuttings Rietvlei	2	1970	1984	55.0-67.3	Variable	
WR	GMB	Gerrit Minnebron	9	1969	1994	71.4-74.2	Stable	Low HCO_3, high SO_4
WR	MAL	Maloney's Eye	8	1976	1994	55.9-58.6	Stable	Slight SO_4 pollution
WR	MRB	Mooirivier Bo	9	1973	1994	72.4-76.1	Stable	
WR	SSW	Schoonspruit Oog DWA	3	1976	1991	88.7-93.9	Decrease	
WR	SSL	Schoonspruit Oog Low	3	1979	1992	92.9-117.7	High ^{14}C when it started drying up	
WR	TFL	Turffontein Lower	3	1973	1992	88.2-89.7	Stable	
WR	TFU	Turffontein Upper	4	1976	1994	87.8-91.3	Stable, recently up	High SO_4 pollution

APPENDIX F: Strontium isotope measurements of the dolomite water and outcrop rocks.

Analyses by B M Eglington and J M Auret (then of Ematek, CSIR, Pretoria).

Eye	Area	Name	Sample	Date	Sr concentration (mg/L)	δ ^{87}Sr	^{87}Sr/^{86}Sr	Ratio error
BTS	NC	BOETSAP EYE	Water	Jul-93	0.156	16.7	0.721056	0.000018
BUF	BM	BUFFELSHOEK OOG	Water	Aug-92		22.9	0.725464	0.000011
BUF	BM	BUFFELSHOEK EYE	Rock		4.860	5.6	0.713139	0.000035
DAN	NC	DANIELSKUIL OOG	Water	Jul-93	0.046	22.7	0.725314	0.000010
DFN	BM	DOORNFONTEIN OOG	Water	Sep-92		23.7	0.725998	0.000014
DKL	BM	DINOKANE LOWER	Water	Jul-93	0.020	29.6	0.730162	0.000012
DKU	BM	DINOKANE UPPER	Water	Jul-93	0.015	28.3	0.729260	0.000014
DPL	BM	DOORNPLAATOOG	Water	Aug-92		21.1	0.724143	0.000024
DPL	BM	DOORNPLAATOOG	Water	Jul-93	0.018	21.0	0.724089	0.000012
DPL	BM	DOORNPLAATOOG	Rock		4.430	11.5	0.717336	0.000066
ELF	PT	ELANDSFONTEIN	Water	Nov-92	0.020	21.4	0.724354	0.000023
ERR	PT	ERASMUS SPRING	Water	Nov-92	0.013	22.2	0.724965	0.000054
ERR	PT	ERASMUS SPRING	Water	Aug-93	0.013	22.3	0.725039	0.000013
GFO	BM	GROOTFONTEIN OOG	Water	Sep-92		18.6	0.722421	0.000014
GFR	PT	GROOTFONTEIN RIETVLEI	Water	Nov-92	0.018	17.8	0.721806	0.000021
GFR	PT	GROOTFONTEIN RIETVLEI	Water	Aug-93	0.018	18.0	0.721996	0.000011
GKO	NC	GROOTKONO OOG	Water	Jul-93	0.038	15.1	0.719926	0.000010
GMB	WR	GERRIT MINNEBRON	Water	Nov-92	0.037	25.4	0.727231	0.000016
GMB	WR	GERRIT MINNEBRON	Water	Aug-93	0.037	25.3	0.727174	0.000011
KKO	NC	KLEINKONO OOG	Water	Jul-93	0.037	15.4	0.720150	0.000010
KU1	NC	KURUMAN OOG 1	Water	Jul-93	0.480	20.1	0.723462	0.000011
KU2	NC	KURUMAN OOG 2	Water	Jul-93	0.041	18.4	0.722248	0.000012
MAL	WR	MALONEY'S EYE	Water	Nov-92	0.020	45.9	0.741761	0.000032
MAL	WR	MALONEY'S EYE	Water	Aug-93	0.020	45.2	0.741233	0.000013
MAY	NC	MAYEDING OOG	Water	Jul-93	0.035	15.8	0.720427	0.000011
MOL	BM	MOLOPO OOG BOSMAN	Water	Sep-92		18.6	0.722416	0.000014
MOL	BM	MOLOPO OOG BOSMAN	Water	Jul-93	0.019	18.4	0.722284	0.000011
MOL	BM	MOLOPO OOG BOSMAN	Rock		10.520	3.2	0.711497	0.000063
MRB	WR	MOOIRIVIER BO	Water	Nov-92	0.035	33.4	0.732865	0.000018

Eye	**Area**	**Name**	**Sample**	**Date**	**Sr concentration (mg/L)**	**δ ^{87}Sr**	**^{87}Sr/^{86}Sr**	**Ratio error**
OLV	BM	OLIEVENDRAAI OOG	Water	Sep-92		18.8	0.722511	0.000011
OLV	BM	OLIVENDRAAI OOG	Rock		4.470	0.5	0.709538	0.000032
PFL	PT	PRETORIA FOUNTAINS LOWER	Water	Nov-92	0.033	24.9	0.726856	0.000012
PFL	PT	PRETORIA FOUNTAINS LOWER	Water	Aug-93	0.032	25.1	0.727025	0.000012
PFU	PT	PRETORIA FOUNTAINS UPPER	Water	Nov-92	0.024	25.7	0.727444	0.000015
PFU	PT	PRETORIA FOUNTAINS UPPER	Water	Aug-93	0.023	26.2	0.727760	0.000012
PVL	BM	PAARDEVALLEI OOG LOWER	Water	Sep-92		23.8	0.726049	0.000017
RGB	BM	RIETGAT OOG OOS BH	Water	Sep-92		23.9	0.726137	0.000016
RGB	BM	RIETGAT OOG OOS BH	Water	Jul-93	0.045	24.7	0.726713	0.000010
RGO	BM	RIETGAT OOG	Water	Jul-93	0.036	25.0	0.726910	0.000010
RNF	BM	RHENOSTERFONTEIN	Water	Sep-92		43.2	0.739807	0.000017
RNF	BM	RHENOSTERFONTEIN	Water	Jul-93	0.017	43.2	0.739861	0.000013
RNF	BM	RHENOSTERFONTEIN	Rock		3.140	20.0	0.723364	0.000043
SBL	BM	STINKHOUTBOOMOOG LOWER	Water	Aug-92		25.2	0.727084	0.000015
SSU	WR	SCHOONSPRUIT OOG UPPER	Water	Aug-93	0.029	21.9	0.724710	0.000011
STF	PT	STERKFONTEIN SPRING	Water	Nov-92	0.025	25.6	0.727390	0.000015
TFL	WR	TURFFONTEIN LOWER	Water	Nov-92	0.072	30.5	0.730805	0.000016
TFU	WR	TURFFONTEIN UPPER	Water	Nov-92	0.084	31.8	0.731785	0.000014
TWL	BM	TWEEFONTEIN LOWER	Water	Aug-92		28.1	0.729150	0.000012
TWU	BM	TWEEFONTEIN UPPER	Water	Aug-92		25.0	0.726934	0.000012
VGD	BM	VERGENOEGD OOG	Water	Aug-92		22.9	0.725417	0.000014
VKF	NC	VLAKFONTEIN EYE	Water	Jul-93	0.032	15.4	0.720094	0.000010
WGD	BM	WELGEDACHTOOG	Water	Aug-92		19.2	0.722834	0.000014
WGT	BM	WONDERGAT	Water	Aug-92		19.0	0.722667	0.000016

Figures

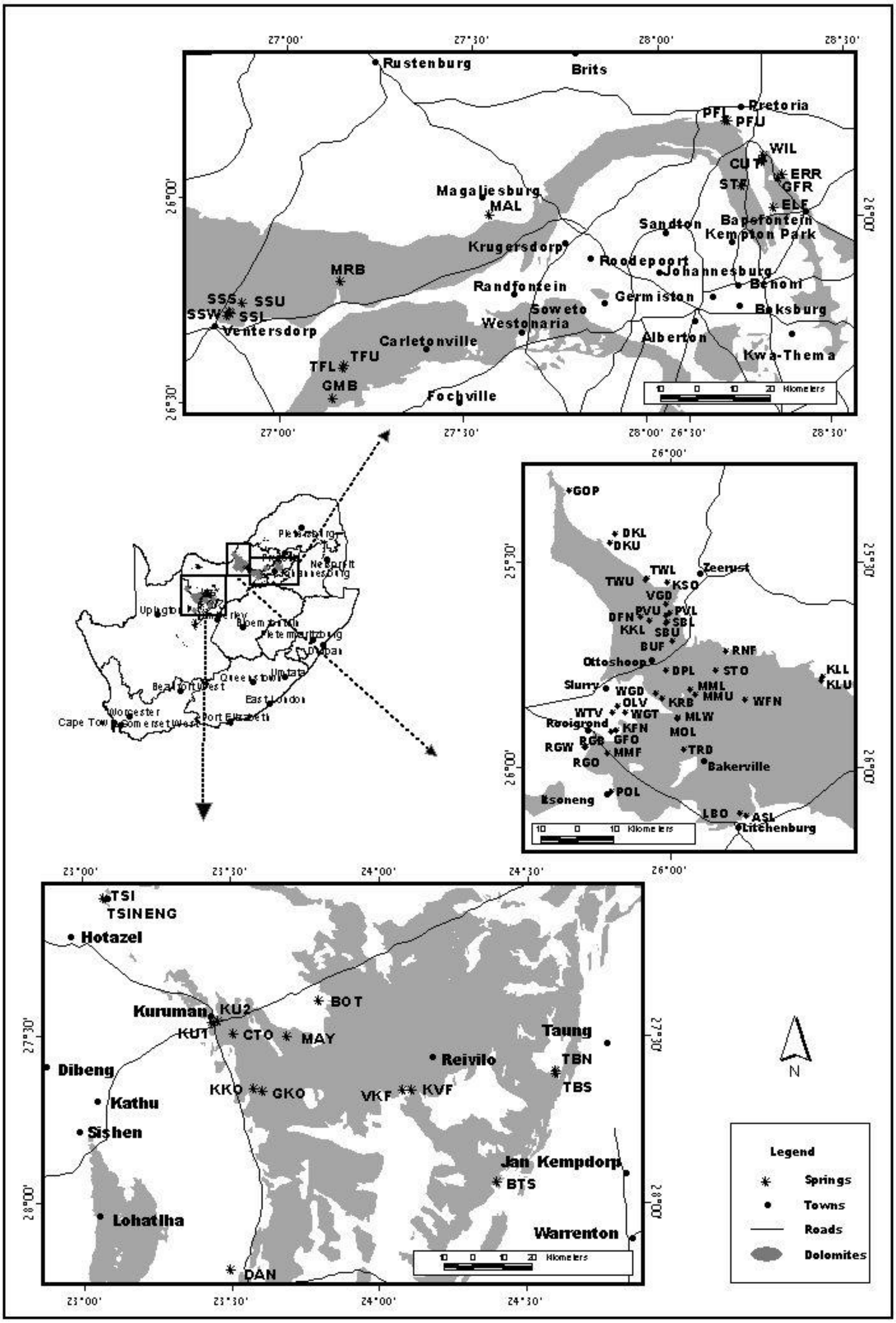


Figure 1. **Map of South Africa with the dolomitic areas indicated. Three study areas are outlined: Pretoria and West Rand, Bo-Molopo and the Ghaap Plateau in the Northern Cape.**

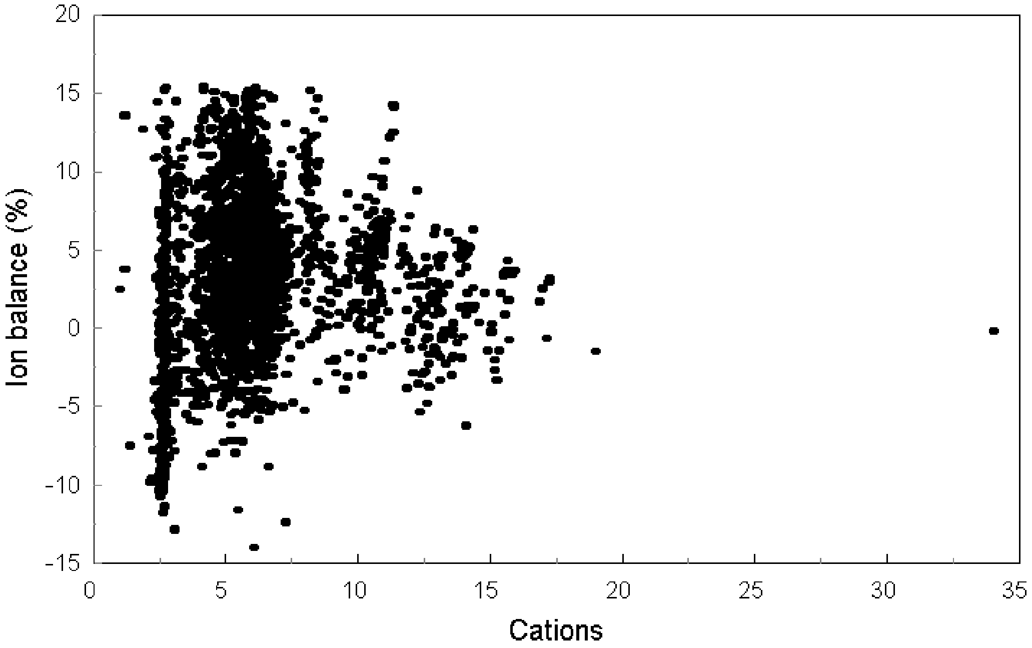


Figure 2. Plot of the ion balance of all the chemistry analyses against cations for all samples

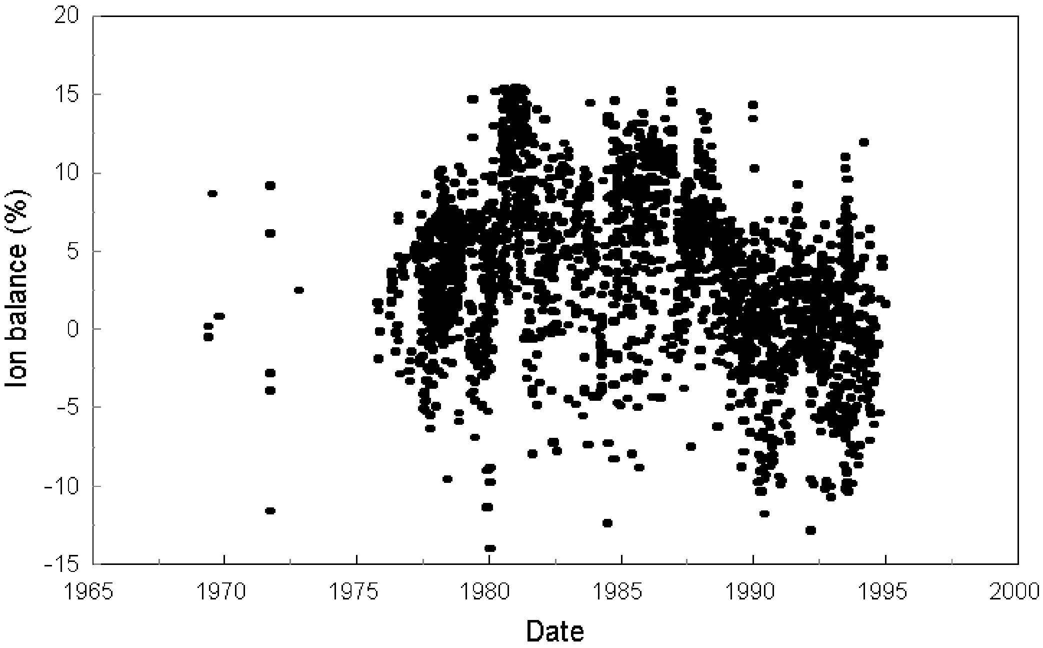


Figure 3. Plot of the ion balance of all chemistry samples against time for all samples

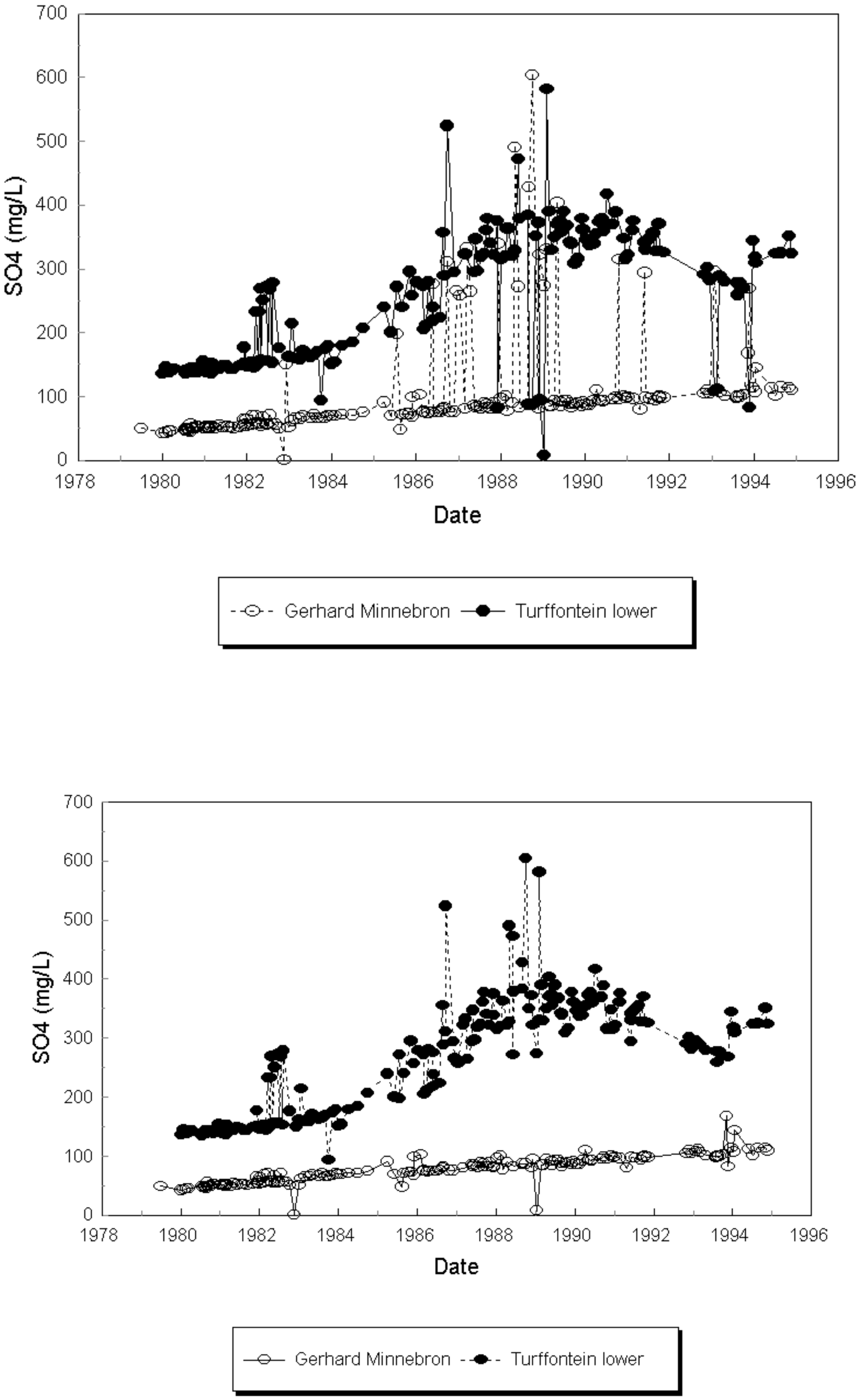


Figure 4. **Time series of sulphate in Gerrit Minnebron and Turffontein lower springs since 1979. a: Raw data as derived from the DWAF data base. b: Corrected data set by eliminating apparent incorrect labelling of sample bottles from the two sources.**

Figure 5. Plot for Ca+Mg (in meq/l) against alkalinity. The open circles represent samples from Gerrit Minnebron and Turffonein lower eye and indicate the additional solution of dolomite due to acid solution. The small closed circles represent the rest of the data set and indicate the normal solution mechanism of dolomite.

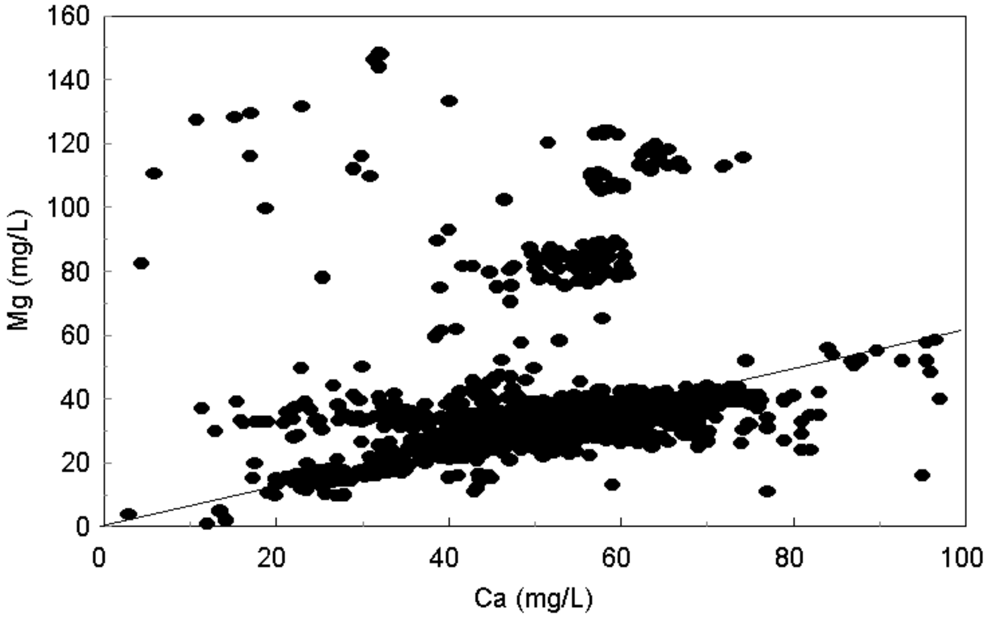


Figure 6. Plot of Mg against Ca for all samples except the polluted TFL and GMB. The line represents the relation of (molar) equal quantities of Ca and Mg by the solution of dolomite. Major deviations from this line (notably higher Mg content) are found in the open waters and those of actively depositing (Ca) carbonate.

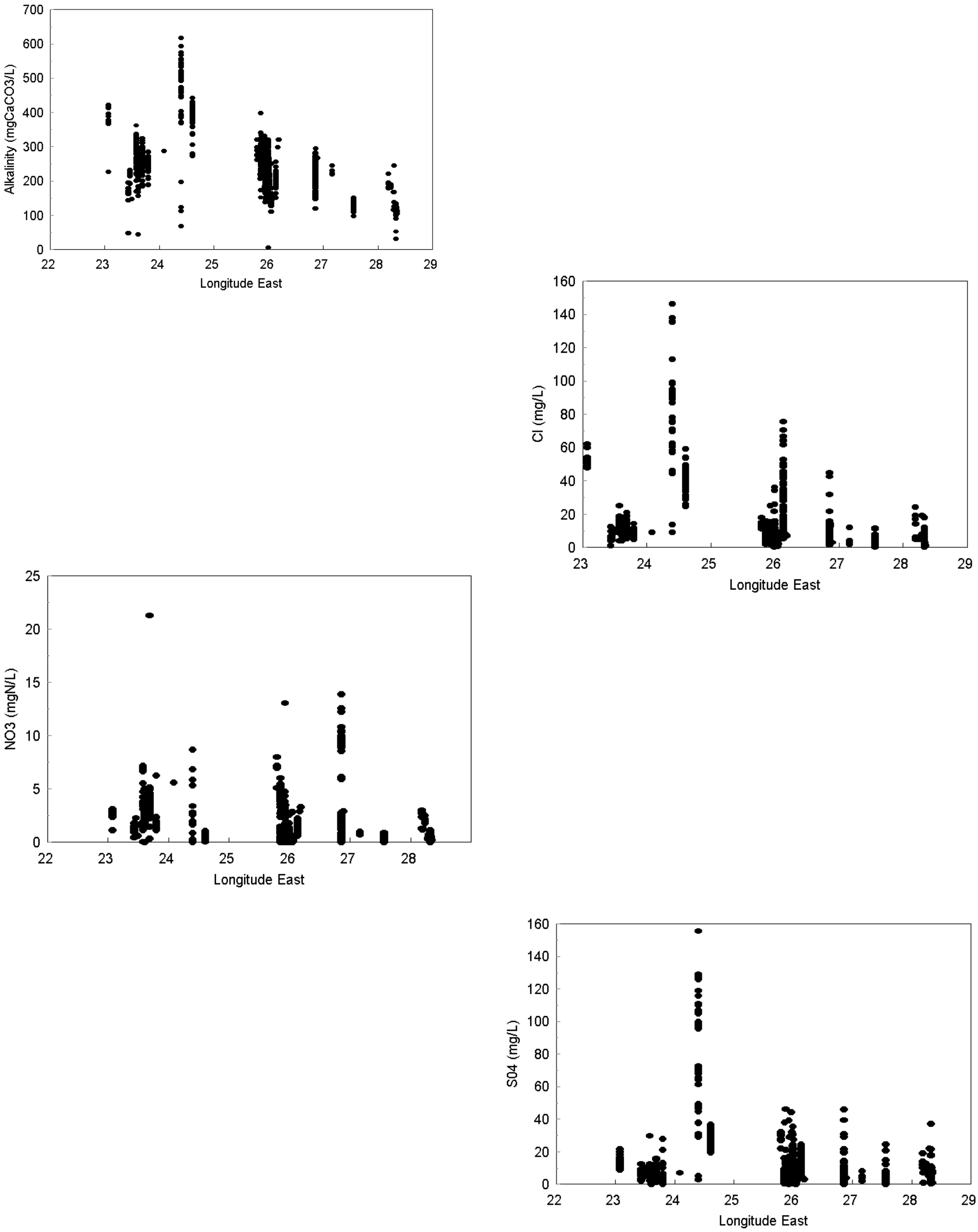


Figure 7. **Dependence of (a) alkalinity, (b) Cl, (c) NO_3 and (d) SO_4 on longitude of sample.**

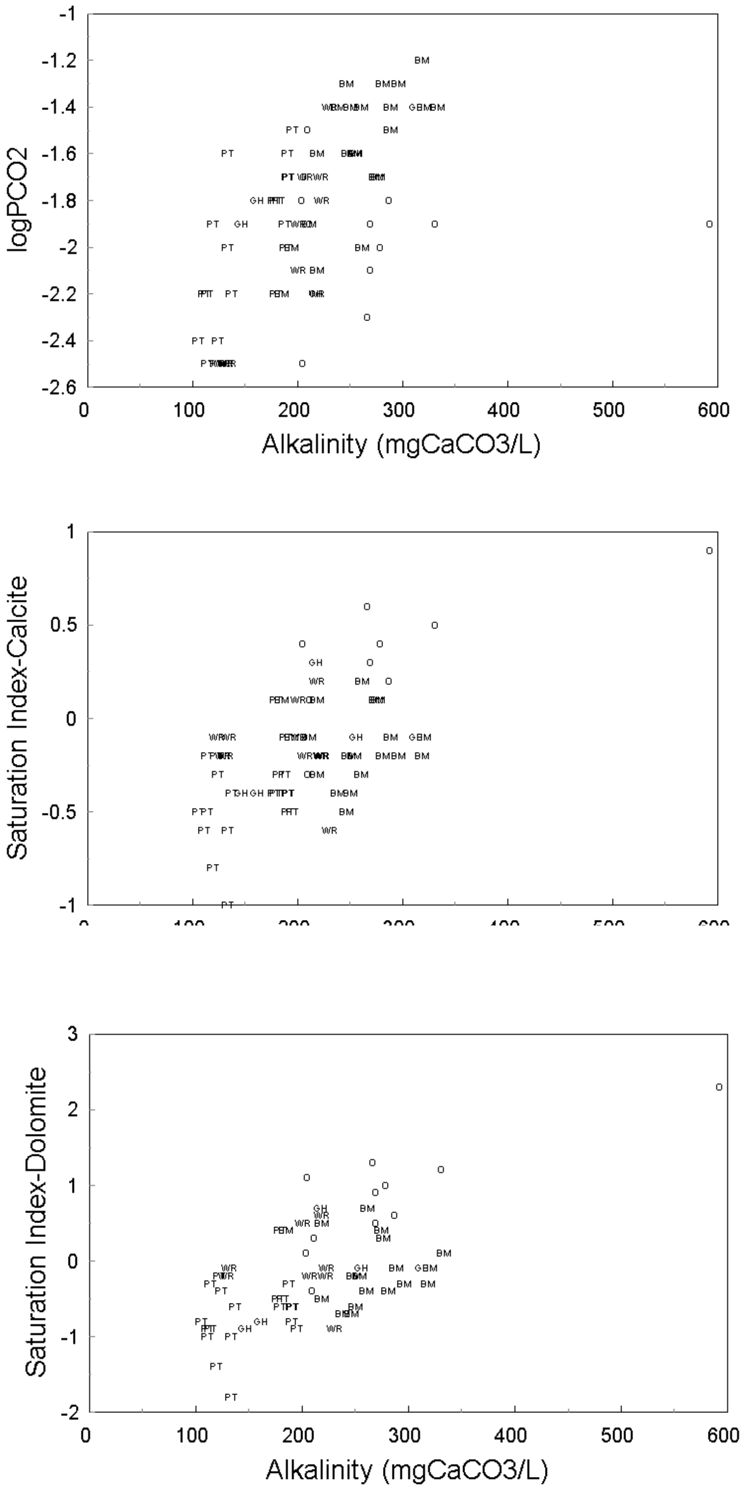


Figure 8. **CO_2 partial pressure (a) and saturation indices of water samples determined from field pH and lab cation measurements, for calcite (b) and dolomite (c). The water origins are indicated. Sources where the spring water has had some contact with**

Figure 9. **Plot of sodium against chloride for all chemistry analyses except TFL and GMB. the dashed line indicates the solution of NaCl.**

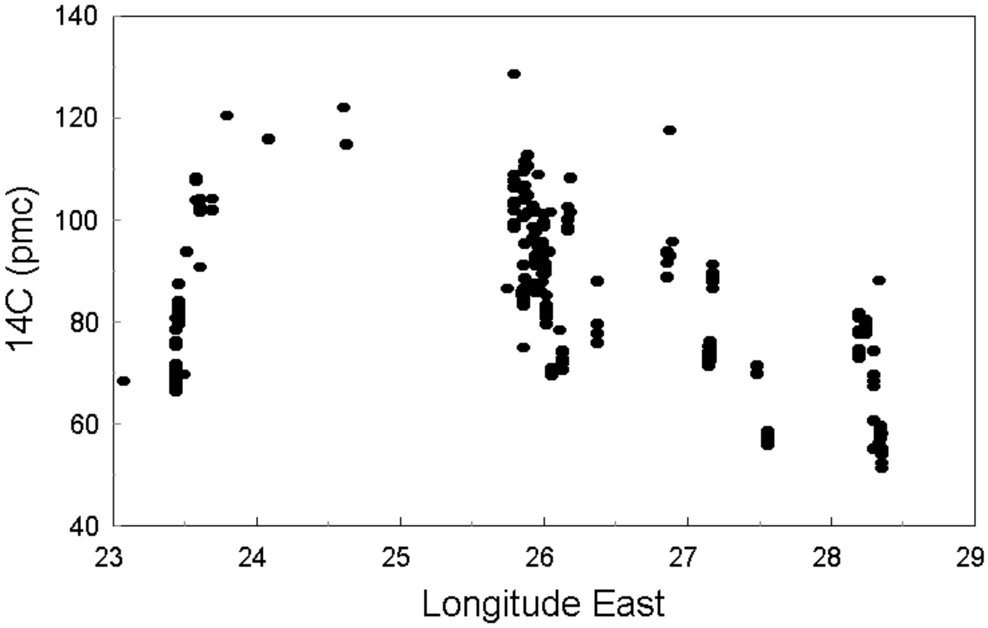


Figure 10. **Dependence of ^{14}C content of spring water on longitude.**

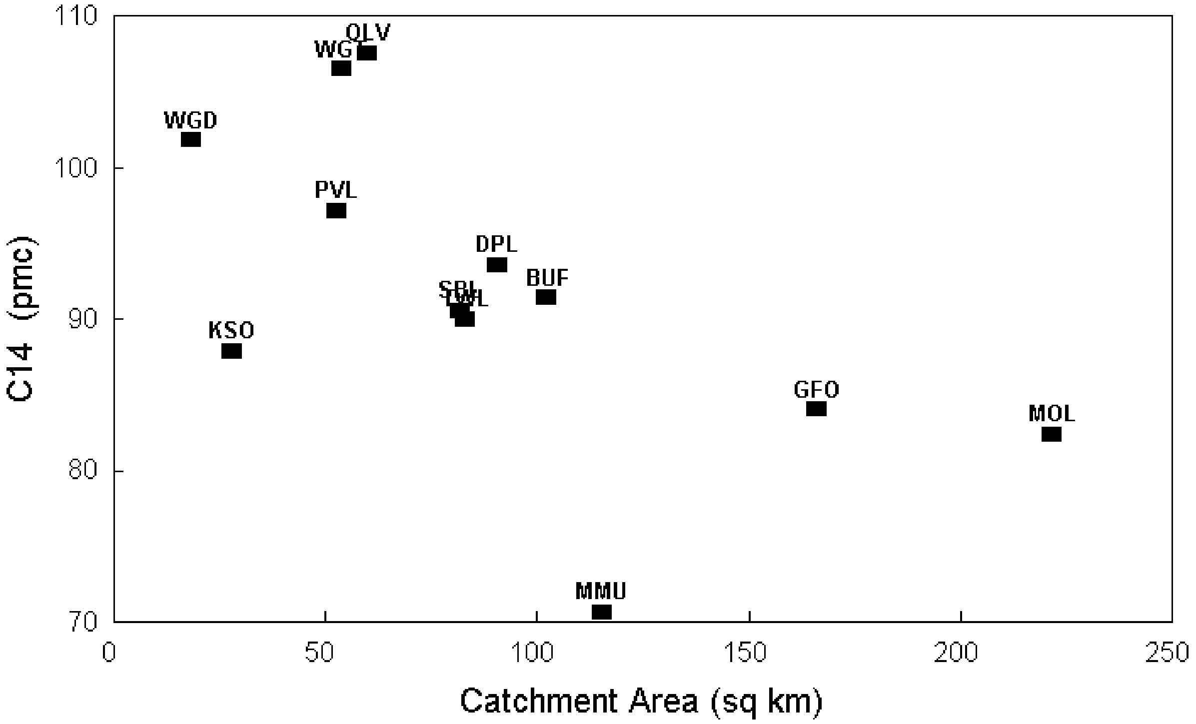


Figure 11. **Dependence of ^{14}C concentration of spring water on compartment size in the Bo-Molopo area.**

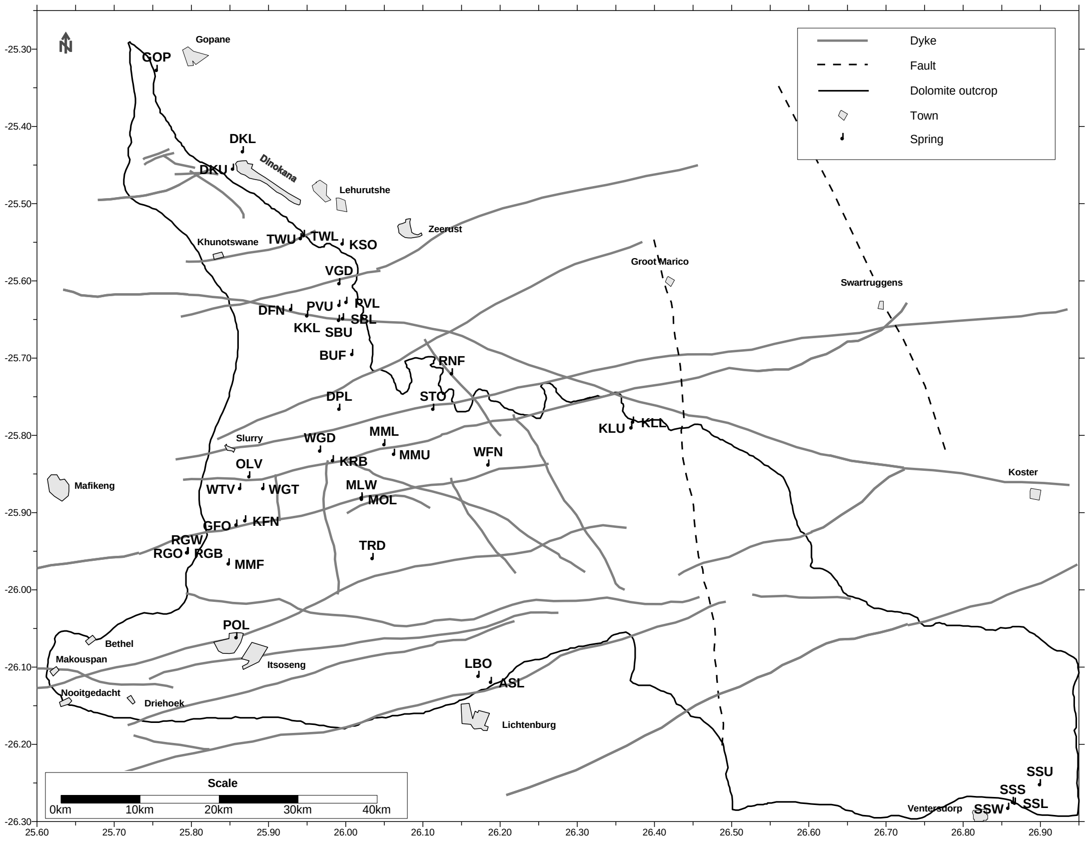


Figure 12. **Map of the Bo-Molopo area indicating the dykes that bound the compartments and the spring locations.**

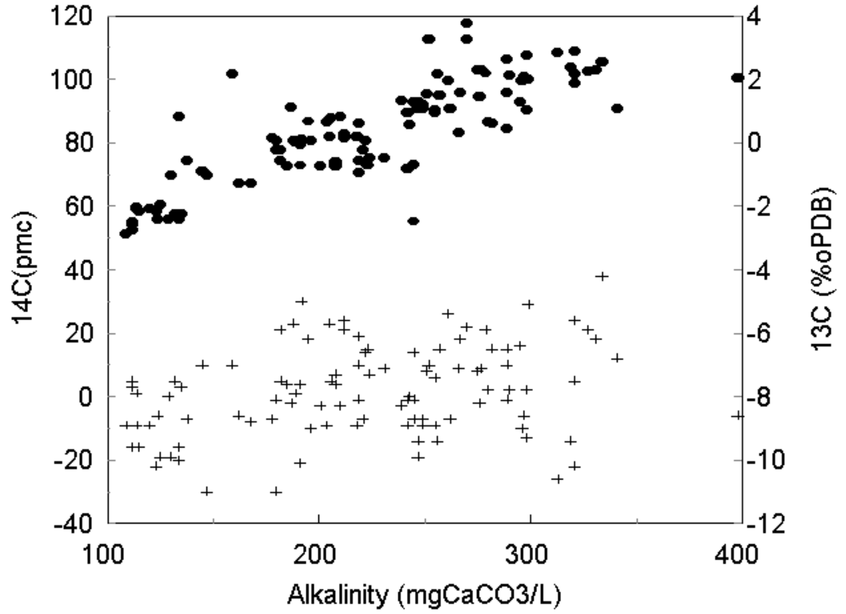


Figure 13. Plot of ^{14}C (solid circles) and ^{13}C (plusses) in spring water against the alkalinity of the water.

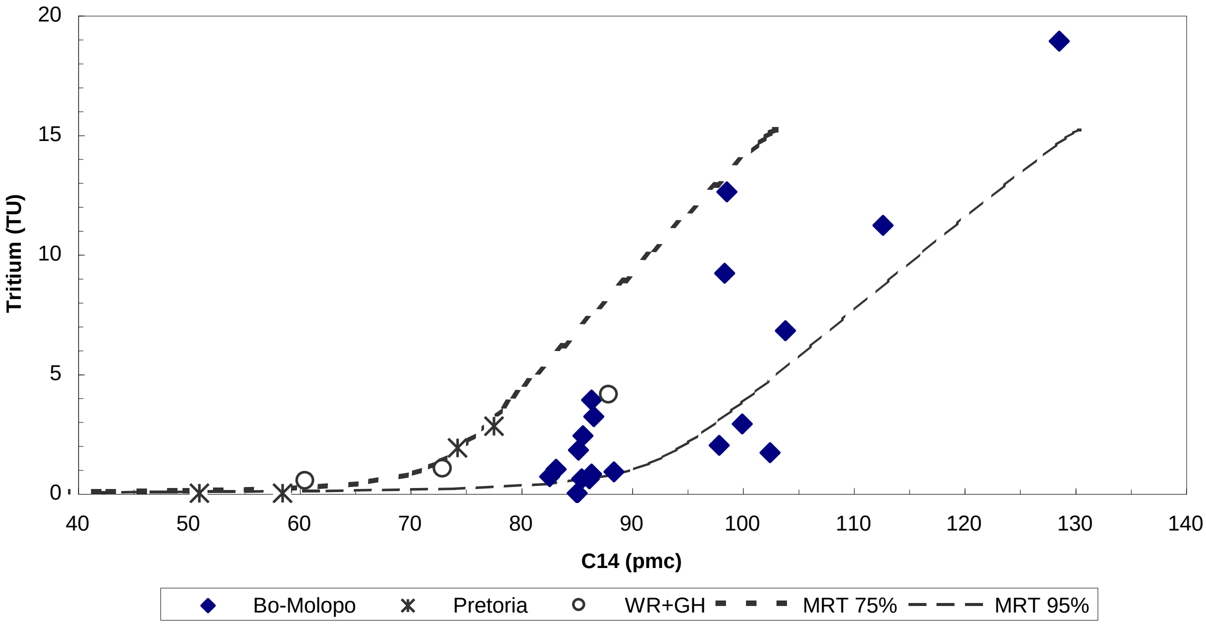


Figure 14. Relations between the tritium content and ^{14}C in spring water. The dashed lines indicate the expected relation between the two parameters for exponential mixing processes using initial ^{14}C contents of 75 and 95 % modern.

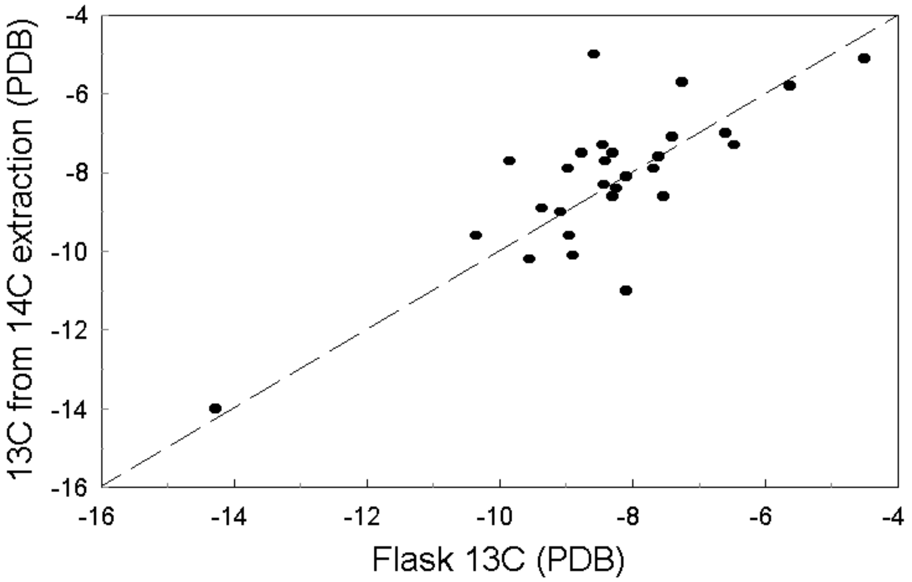


Figure 15. **Plot of the ^{13}C content of water samples extracted for ^{14}C analysis against the (more accurate) ^{13}C content for samples derived from vacuum flask evacuation. The dashed line indicates the expected 1:1 relation.**

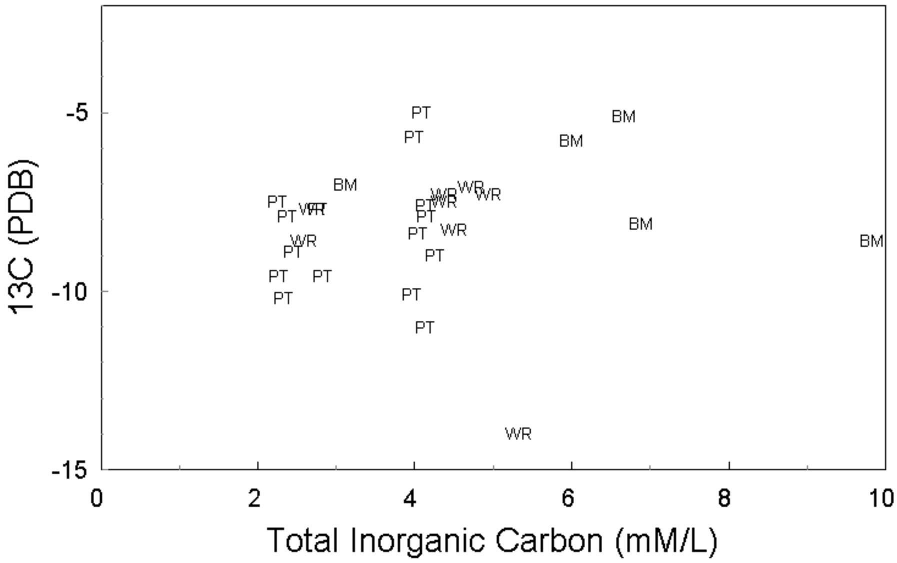


Figure 16. **^{13}C content against the total inorganic carbon content of spring water for which flask samples were taken. The area from which the samples were taken is indicated. Note the low end of the samples from the Pretoria area (PT).**

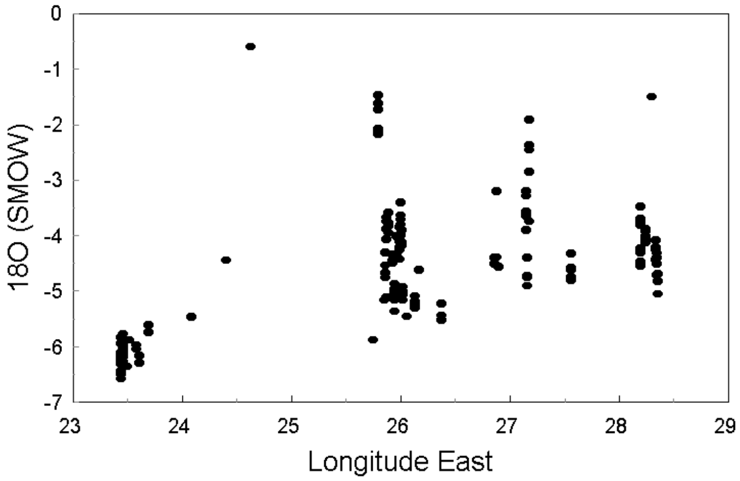


Figure 17 Plot of ^{18}O in the water against longitude to seek regional effects.

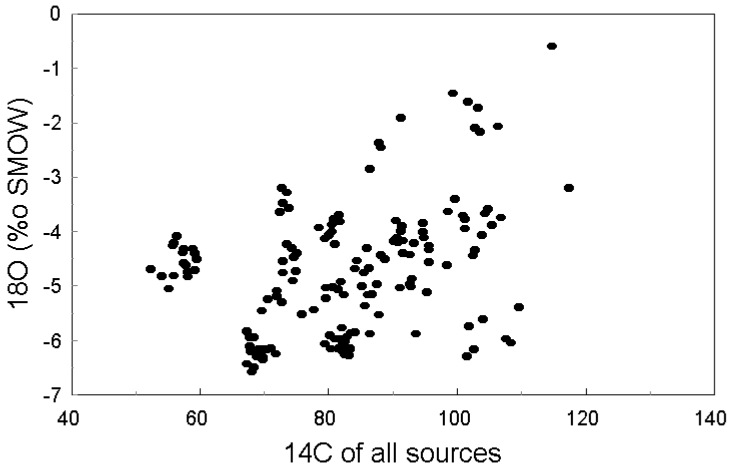


Figure 18. Plot of ^{18}O in water against ^{14}C content to seek regional effects.

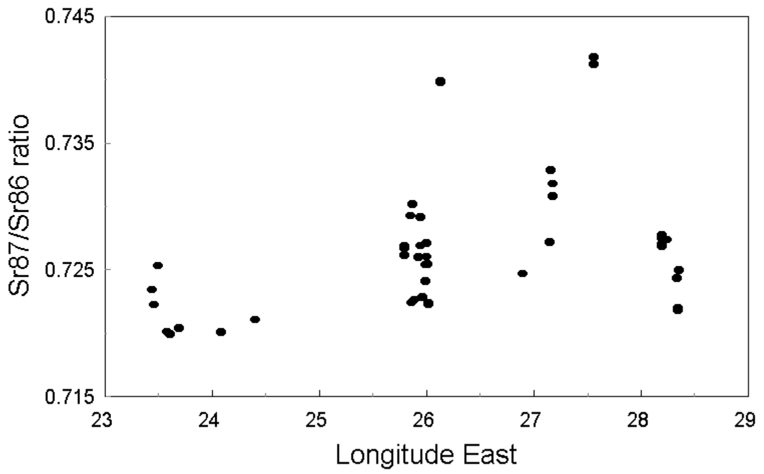
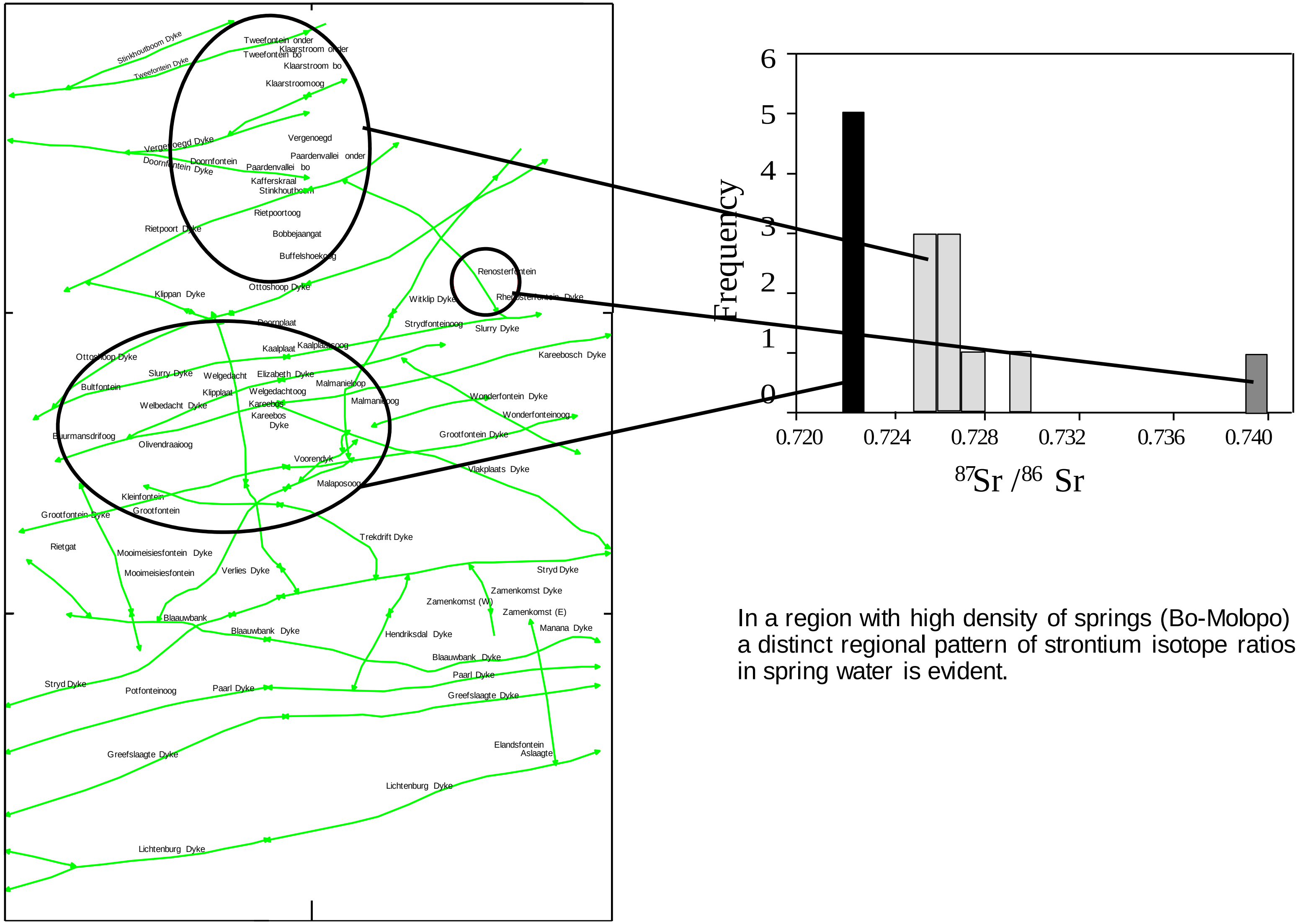


Figure 19. Plot of $^{87}Sr/^{86}Sr$ in water against longitude to seek regional effects.



In a region with high density of springs (Bo-Molopo) a distinct regional pattern of strontium isotope ratios in spring water is evident.

Figure 20. **Map of the Bo-Molopo area showing the spread of ^{87}Sr values to seek local distributions.**

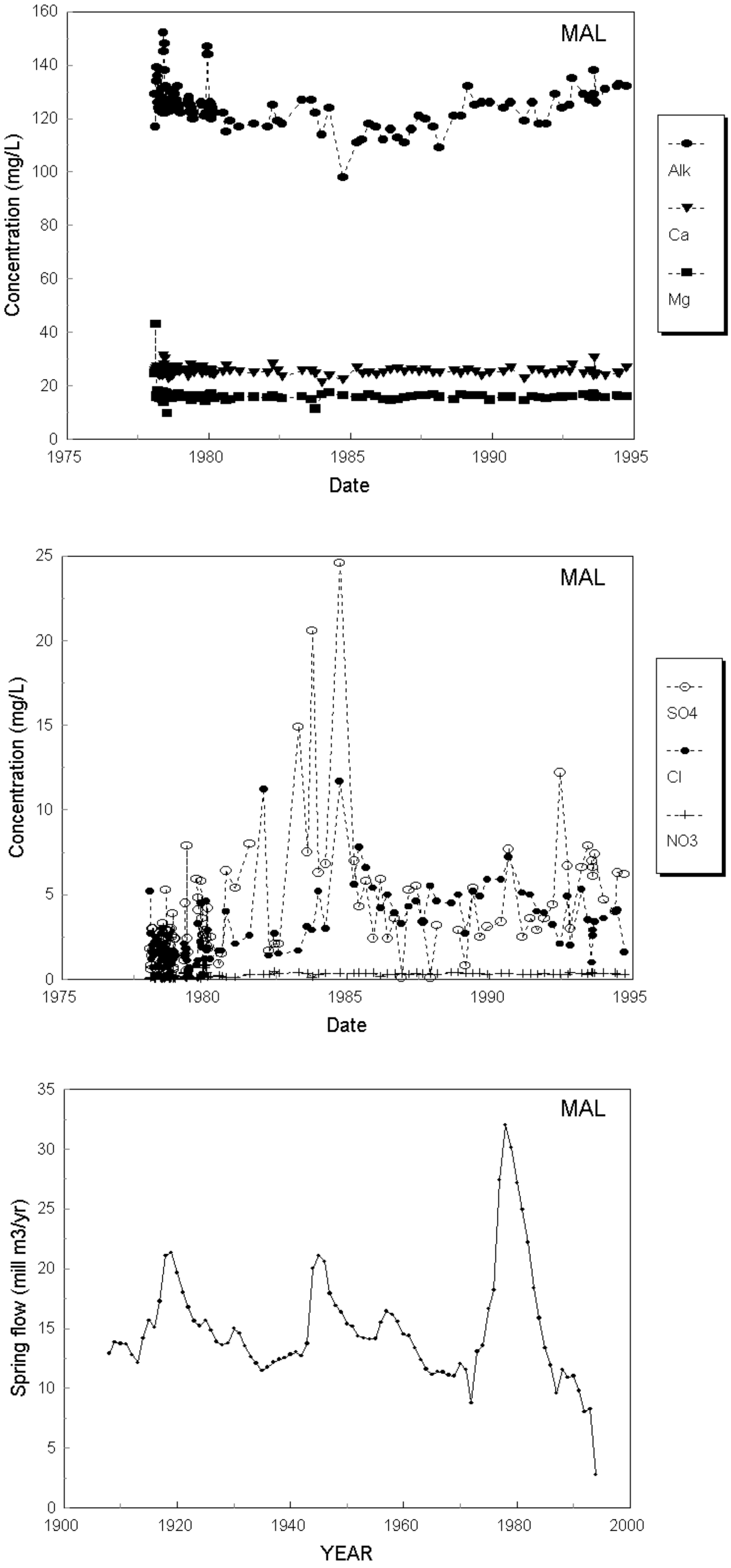
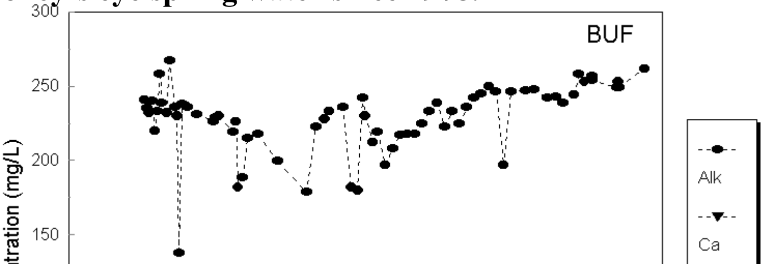


Figure 21. **Time series of (a) major and (b) minor elements and (c) spring flow in the Maloney's eye spring water since 1978.**



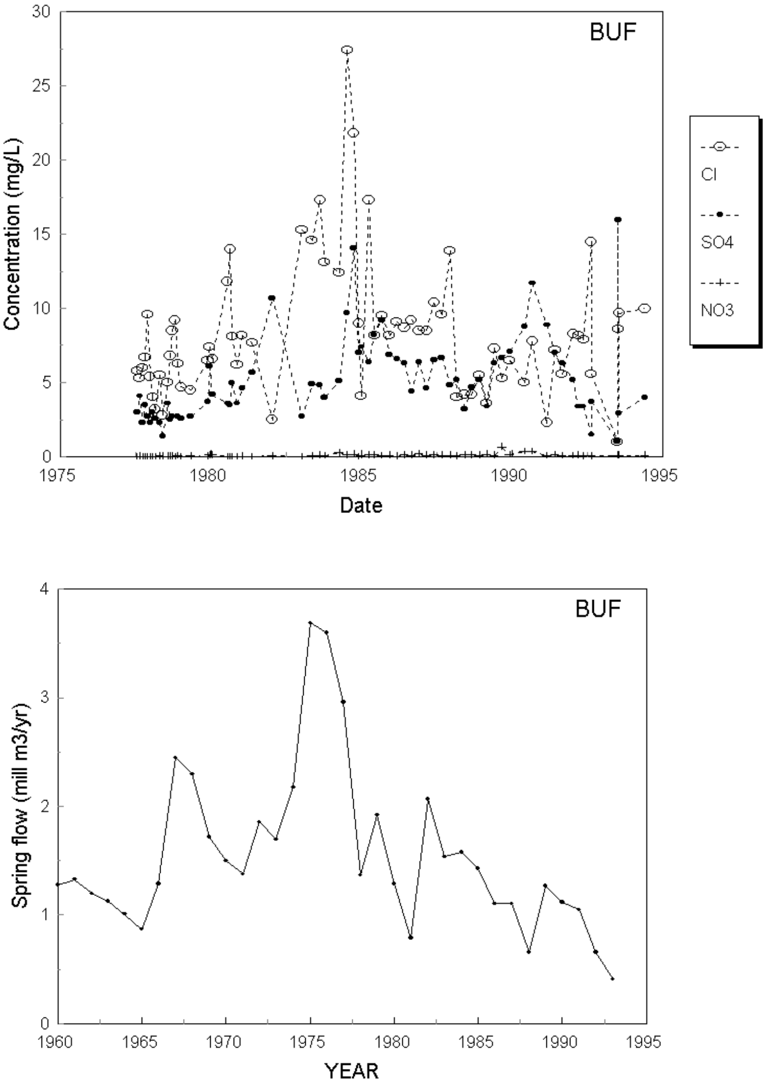


Figure 22. **Time series of (a) major and (b) minor elements and (c) spring flow in the Buffelshoek spring water since 1978.**

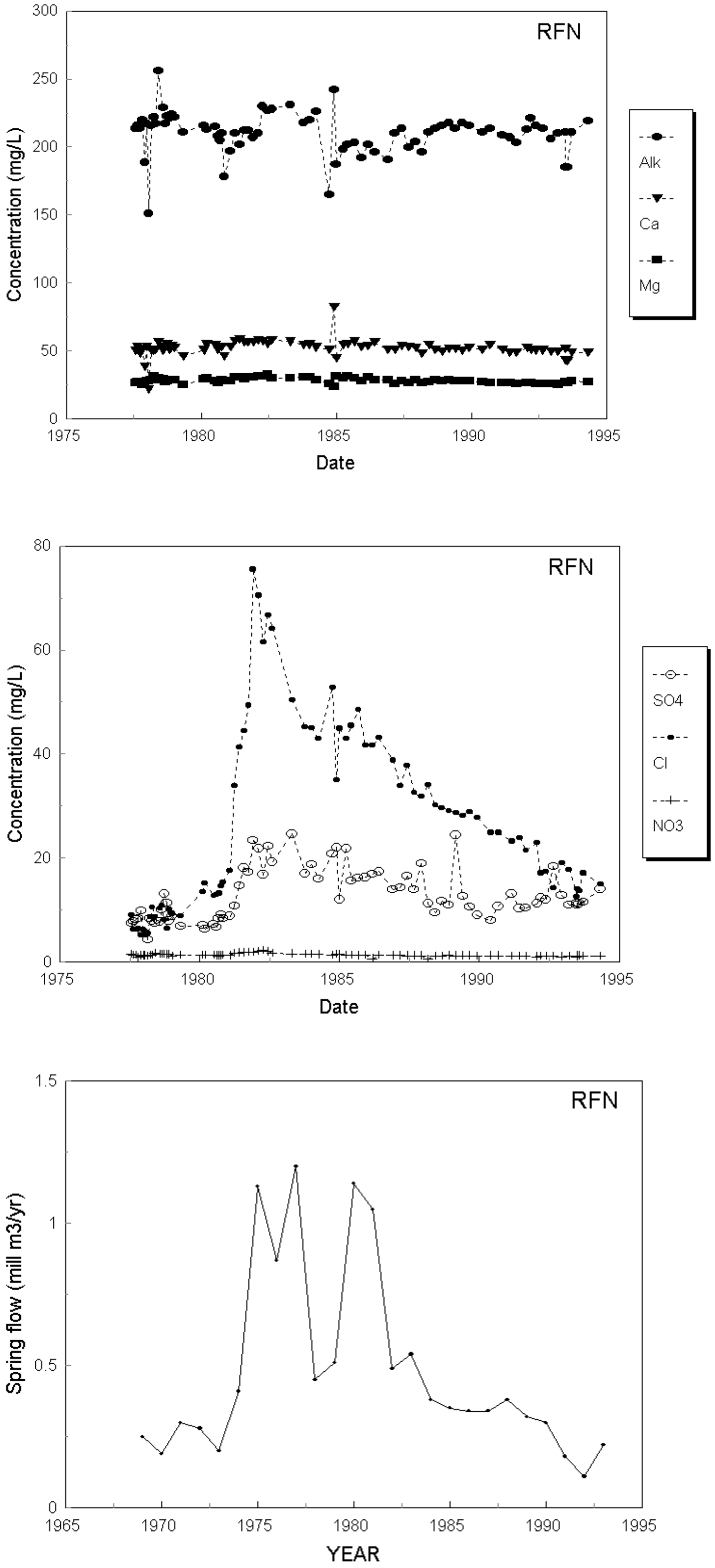


Figure 23. Time series of (a) major and (b) minor elements and (c) spring flow in the Rhenosterfontein spring water since 1978.

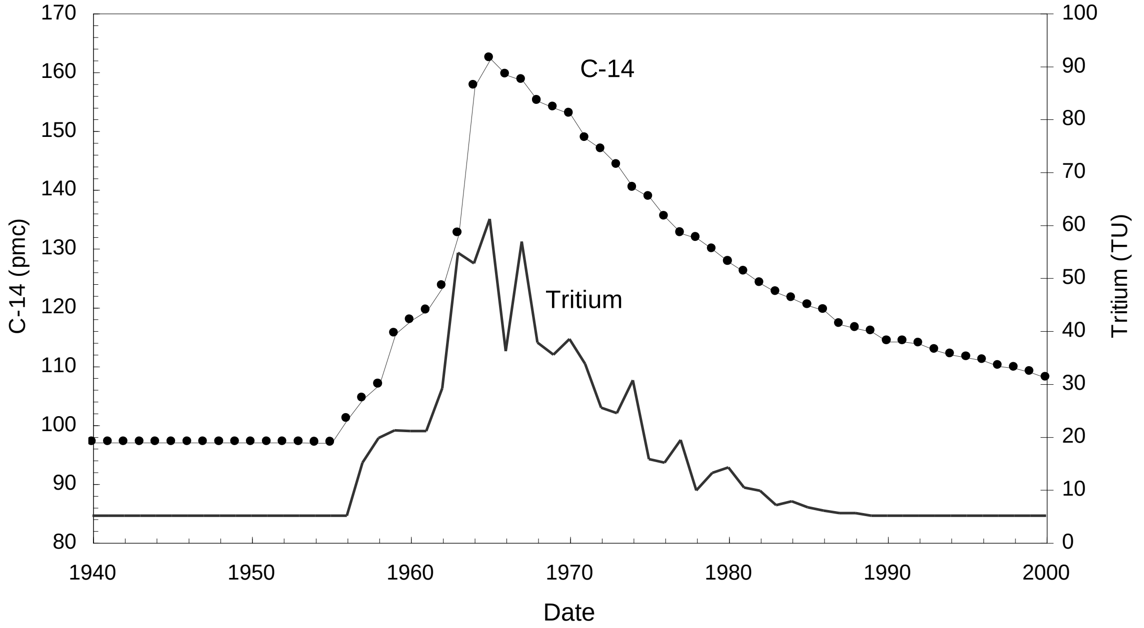


Figure 24. **Time series of atmospheric ^{14}C content (solid circles) and rainfall tritium (smooth line) values showing the increases caused by nuclear weapon tests since 1955 and the subsequent decay of these high levels.**

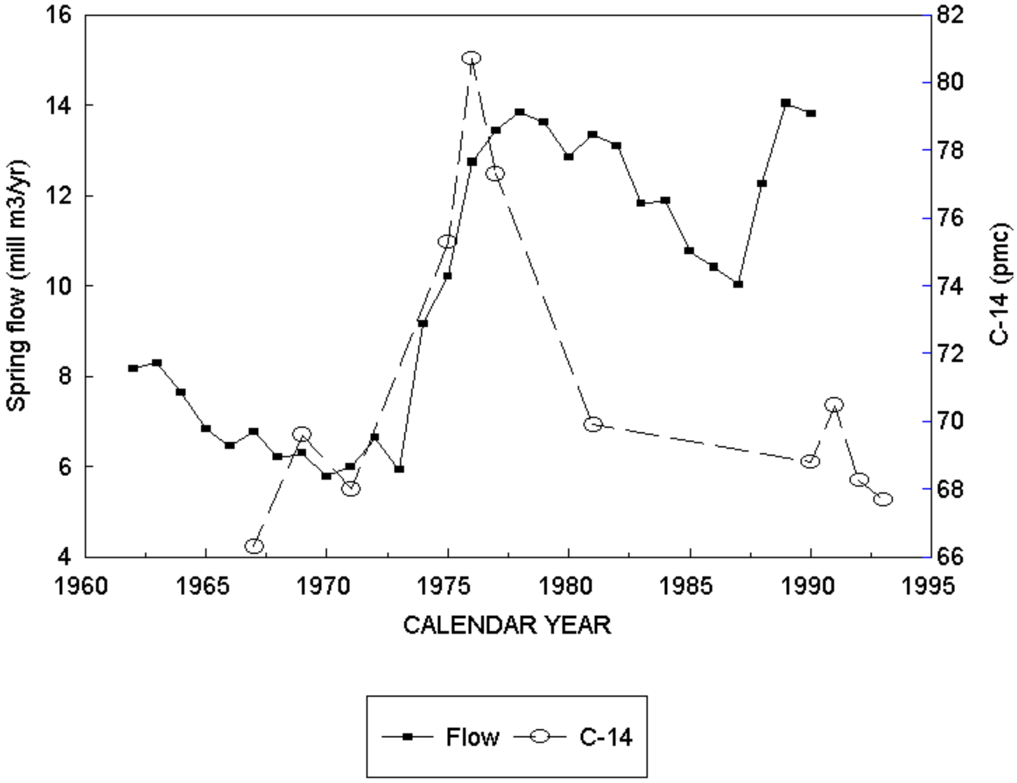
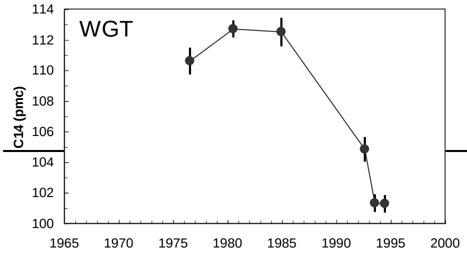
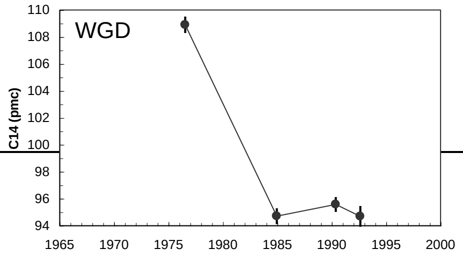
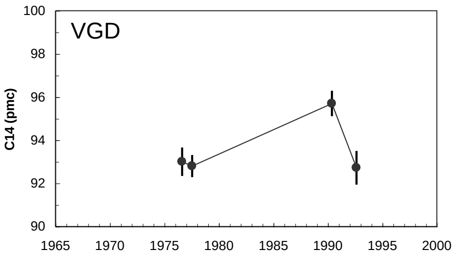
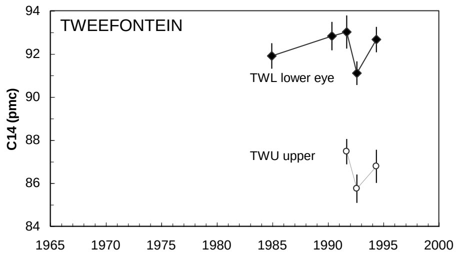


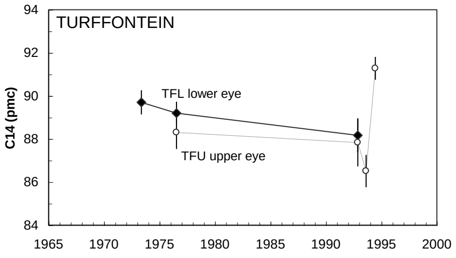
Figure 25. **Time series of ^{14}C and spring flow of the Kuruman main eye (KUA) during the last few decay (from Bredenkamp 2000).**

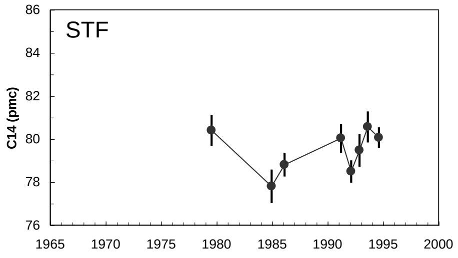


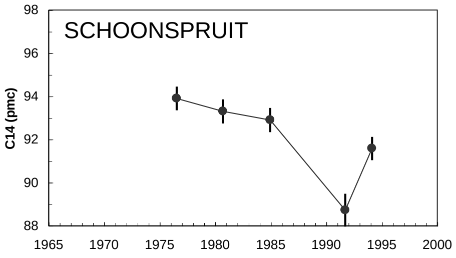


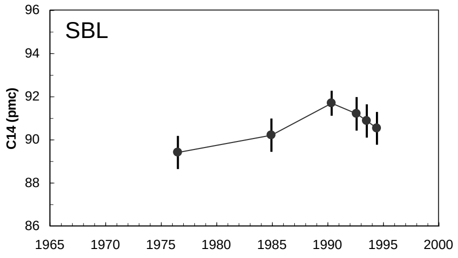

VGD
C14 (pmc)
100
98
96
94
92
90
1965 1970 1975 1980 1985 1990 1995 2000

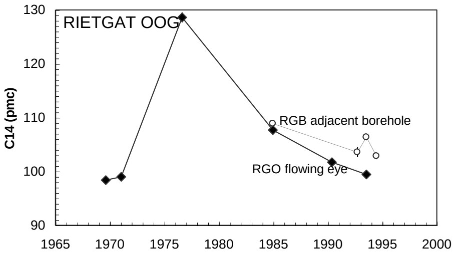

TWEEFONTEIN
TWL lower eye
TWU upper
C14 (pmc)
94
92
90
88
86
84
1965 1970 1975 1980 1985 1990 1995 2000

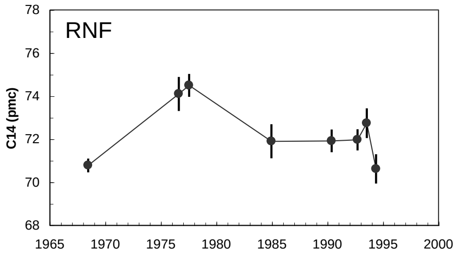

TURFFONTEIN
TFL lower eye
TFU upper eye
C14 (pmc)
94
92
90
88
86
84
1965 1970 1975 1980 1985 1990 1995 2000

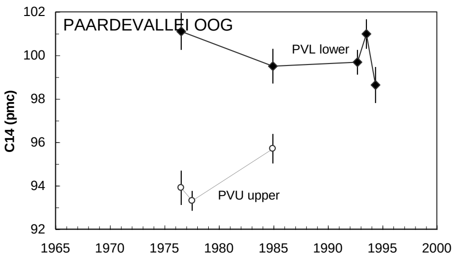

STF
C14 (pmc)
86
84
82
80
78
76
1965 1970 1975 1980 1985 1990 1995 2000

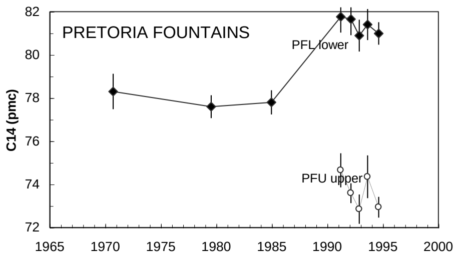

SCHOONSPRUIT
C14 (pmc)
98
96
94
92
90
88
1965 1970 1975 1980 1985 1990 1995 2000


SBL
C14 (pmc)
96
94
92
90
88
86
1965 1970 1975 1980 1985 1990 1995 2000


RIETGAT OOG
RGB adjacent borehole
RGO flowing eye
C14 (pmc)
130
120
110
100
90
1965 1970 1975 1980 1985 1990 1995 2000


RNF
C14 (pmc)
78
76
74
72
70
68
1965 1970 1975 1980 1985 1990 1995 2000


PAARDEVALLEI OOG
PVL lower
PVU upper
C14 (pmc)
102
100
98
96
94
92
1965 1970 1975 1980 1985 1990 1995 2000


PRETORIA FOUNTAINS
PFL lower
PFU upper
C14 (pmc)
82
80
78
76
74
72
1965 1970 1975 1980 1985 1990 1995 2000

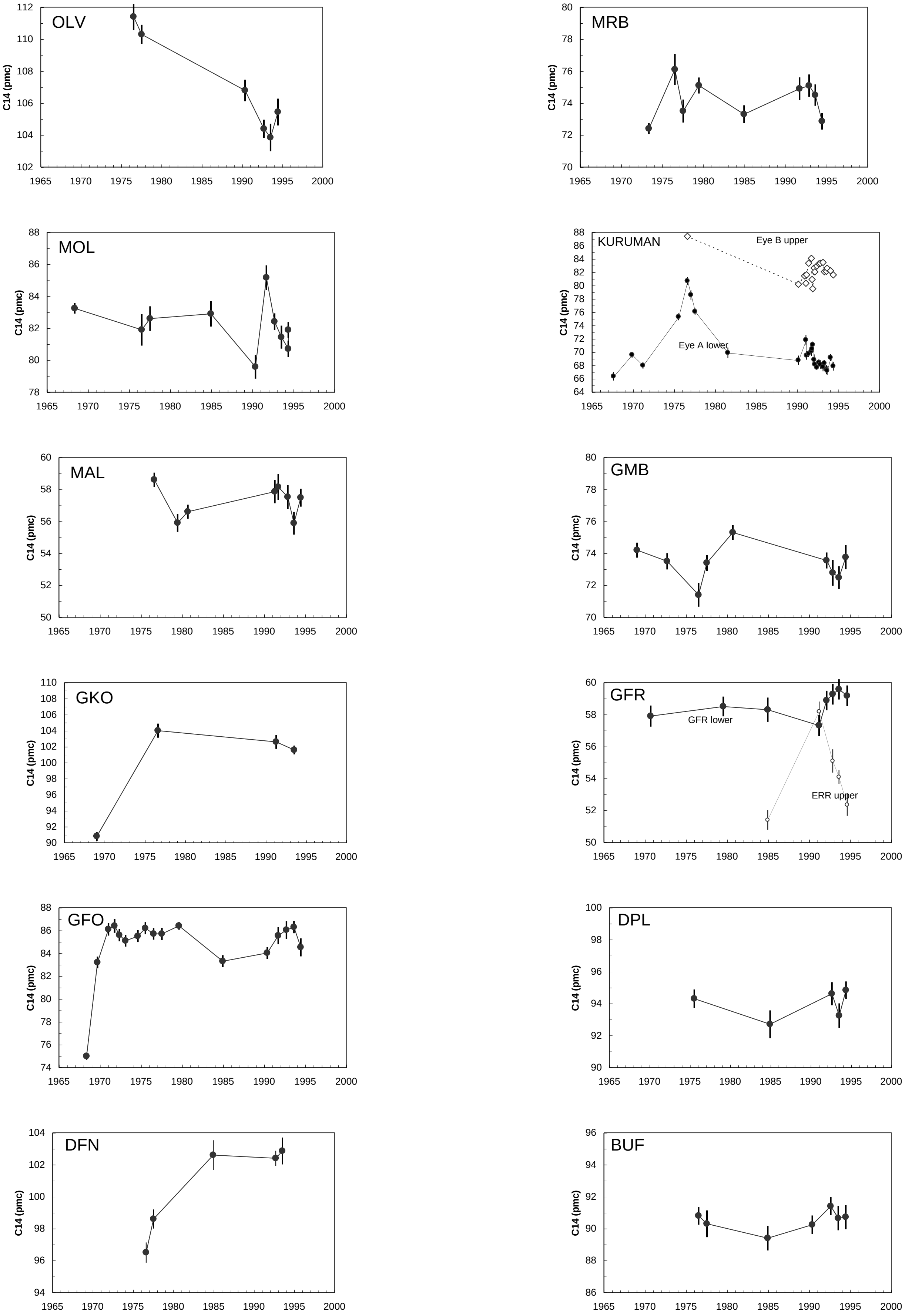


Figure 26. **Composite figure depicting the variations of ^{14}C in spring waters with time.**

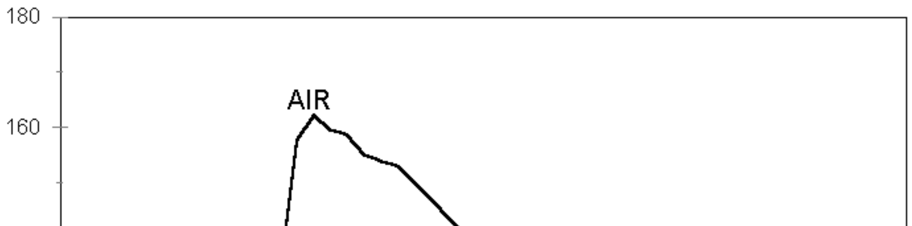


Figure 27. **Model values of ^{14}C variations expected from atmospheric ^{14}C input into an exponential mixing model (Verhagen *et al.* 1991) using an initial ^{14}C content of 85% modern. The mean residence times (MRT) of the models are indicated (5-100 years). The atmospheric ^{14}C levels are shown as "AIR".**

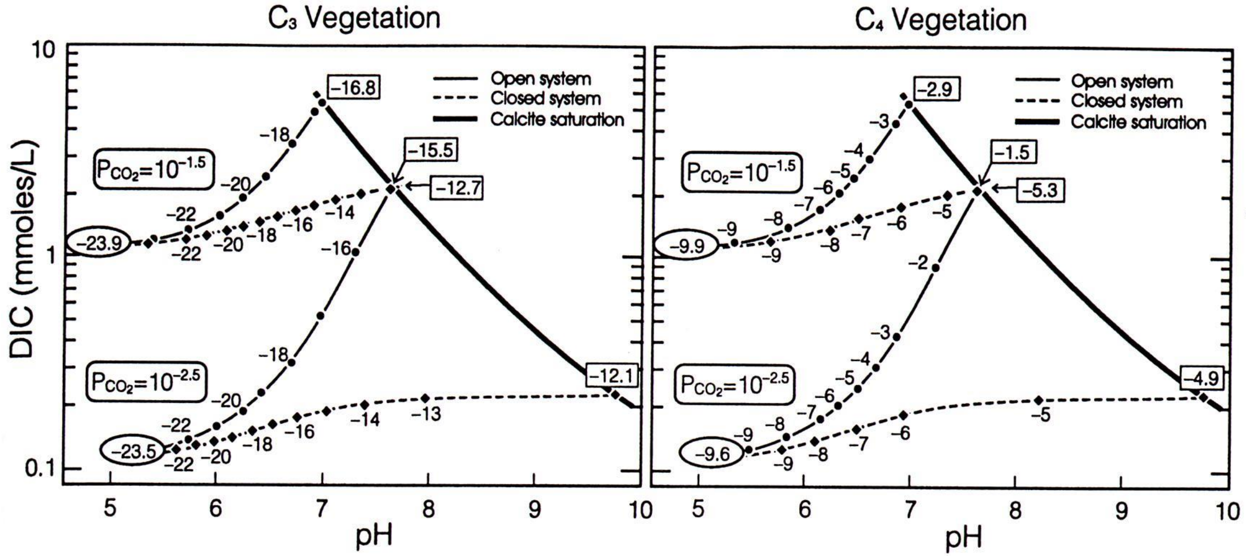


Figure 28. **Progress of pH and Total Inorganic Carbon (TIC=DIC=CO_2+HCO_3+CO_3) during solution of carbonate as an open and as closed model (Clark & Fritz 1997, Fig 5.6). The ^{13}C content of such solutions are indicated for the separate cases of C3 (trees and shrubs) and C4 plants (grasses).**

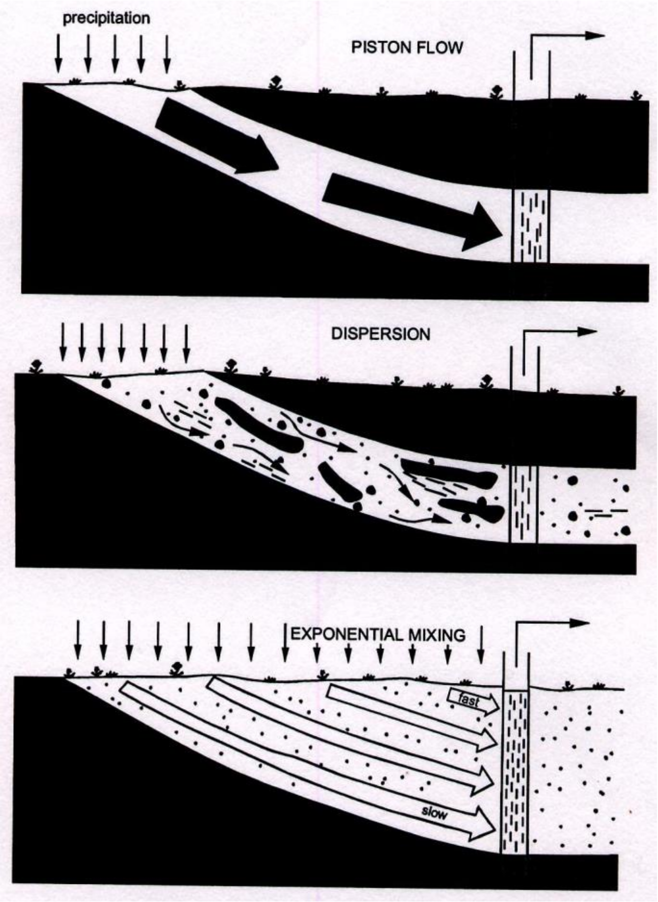


Figure 29. **Three cases of groundwater movement by piston-flow without and with dispersion in a confined aquifer and as exponential mixing in an unconfined aquifer (from Geyh 2000).**