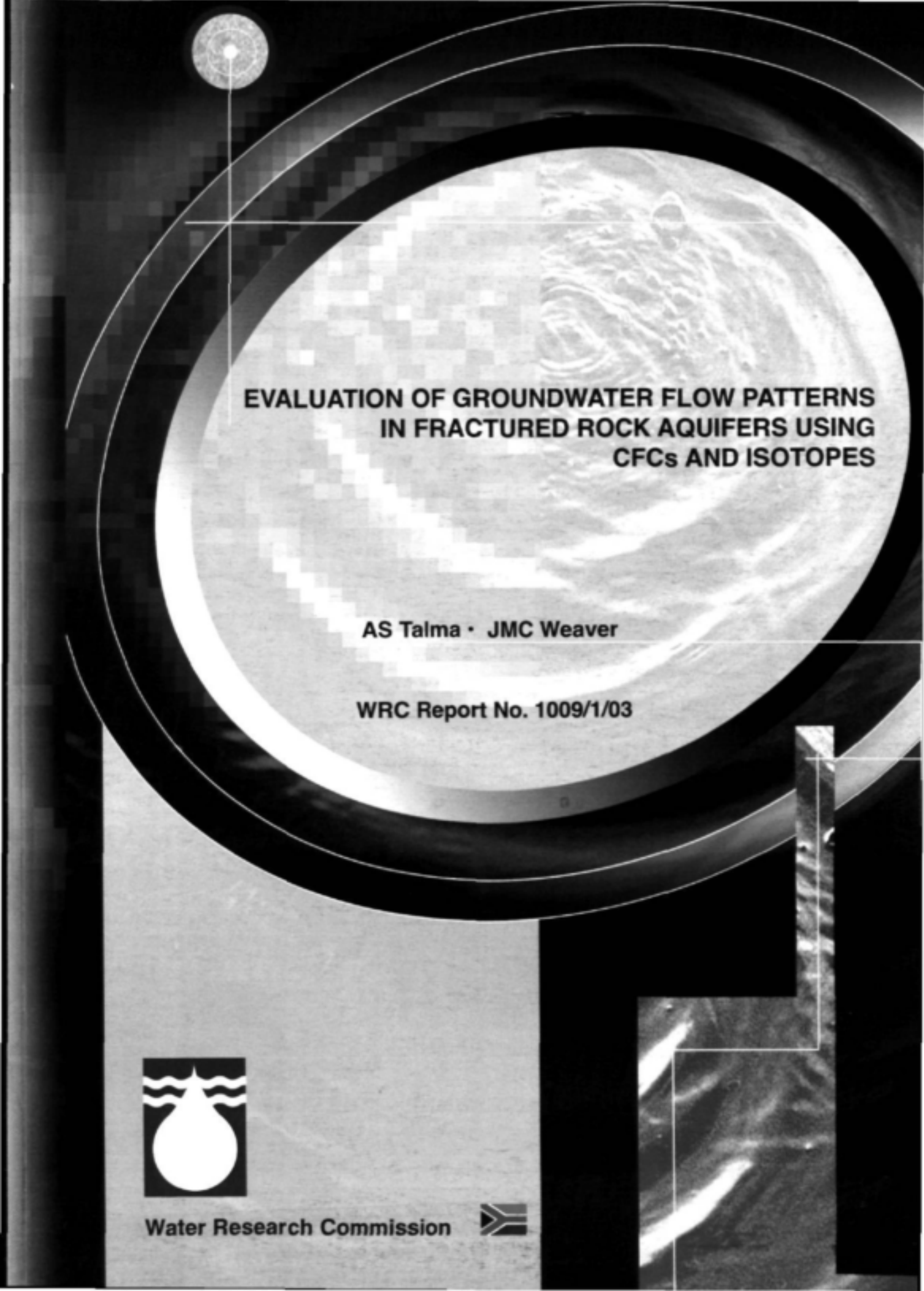

EVALUATION OF GROUNDWATER FLOW PATTERNS IN FRACTURED ROCK AQUIFERS USING CFCs AND ISOTOPES

AS Talma • JMC Weaver

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Water Research Commission

EVALUATION OF GROUNDWATER FLOW PATTERNS IN FRACTURED ROCK AQUIFERS USING CFCS AND ISOTOPES

Report to the

WATER RESEARCH COMMISSION

on the Project "Evaluation of groundwater resources
in fractured rock aquifers at a catchment scale
using evidence of mixing of groundwater
from CFC and isotope data."

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Introduction

Fractured rocks are the major source of groundwater supplies in South Africa. Over 90% of the surface area of South Africa, groundwater occurs in secondary openings in so-called hard rocks. These openings occur in very irregular fashion and make prediction of aquifer properties very difficult. Reliable tools for resource evaluation in fractured rock aquifers are nevertheless needed for efficient management of these resources. The Water Research Commission identified hard rock (or fractured rock) aquifers as a theme of groundwater research requiring a high priority in terms of funding. The present project is therefore a part of the WRC Fractured Rock Research Programme.

The chlorofluorocarbon gases, CFC-11, CFC-12 and CFC-113, were developed during the 1930s. These gases are chemically stable, safe and have convenient boiling points resulting in widespread use in society. Used CFC gas accumulates in the atmosphere where it poses a serious hazard to stratospheric ozone. This has led to successful international action to reduce global CFC emissions (Montreal Protocol). The known growth rates of CFCs in the atmosphere over the last fifty years, the rapid mixing in the world's atmosphere, their solubility in water and their good chemical stability have enabled this hazard to become a useful tool for hydrologists. This phenomenon is used to trace water movement in the oceans, in surface water and in groundwater and will likely remain useful for a few decades in the near future.

The development of a reliable sampling and analytical procedure for CFC in groundwater by the US Geological Survey has ensured wide application of this technique during the last decade. CFC applications in groundwater rest on the assumption that groundwater at the water table is in equilibrium with atmospheric air, including its CFC component, following the laws of solubility. Once water moves in the saturated zone below the water table, it will not be able to acquire or lose any additional CFC. The CFC quantity in the water will be characteristic of the atmospheric CFC level prevailing during the last contact with the atmosphere. This forms the basis of the concept of CFC dating of groundwater. The steep increase of atmospheric CFC levels with time ensures that dates can be well defined up to the mid 1990s. This is in contrast to tritium and radiocarbon where the input curve has become rather flat since 1963. The dates derived in this manner can be considered model recharge dates.

Earlier projects in the Table Mountain Group and Karoo Group sandstones (Weaver *et al* 1995, Weaver and Talma 1999) have shown that CFCs can be quite useful groundwater evaluation tools in South Africa. The existing techniques for groundwater dating, or generally, tracing water residence times underground, use radiocarbon (^{14}C) and tritium (^{3}H) which each have their advantages and disadvantages. These techniques have been in use in the southern African region since the late 1960s and have been proven immensely useful. The applications rely on specific flow models to interpret the isotope measurements and for fractured rock aquifers with their very random and irregular flow character, the applicability of such models are difficult to assess. The help of any additional data is therefore beneficial for accurate resource evaluation.

Objectives

The overall aim of the present project as formulated in the agreement between CSIR and WRC is:

- To develop a method of integrating and analysing groundwater age data provided by ^{14}C, CFC-11, CFC-12, CFC-113, tritium and other isotope analyses so that groundwater mixing ratios for fractured rock aquifers can be determined.
- To investigate the application of these mixing ratios to groundwater resource evaluation so that the reliability of these evaluations can be refined.

Project Approach

The first task was to identify and select suitable sites where case studies were likely to be successful within budget and time limits. The requirements for suitable study sites were formulated as:

- Fractured rock aquifers where it is probable that mixing of young and old water occurs
- The hydrogeology of the site should be reasonably well known.
- Some isotope and/or chemical data should be available.
- Groundwater recharge ages should be within the past 10-20 years, to make full use of the major CFC variations.
- A sufficient number of sampling points (boreholes) should be available for sampling.
- Established pumps in those boreholes would simplify the sampling procedure.

The project team contacted a number of hydrogeologists, reviewed existing reports and visited a few sites. Thirteen sites were evaluated and subsequently three sites were selected:

- ⇨ Leeukuil, a small gneiss/granitic aquifer to the west of Pietersburg/Polokwane in Limpopo Province.
- ⇨ A selection of 11 springs in the dolomitic areas of the Chuniespoort Group between Pretoria and Zeerust.
- ⇨ Leeu Gamka in the Karoo, south of Beaufort West, where there is clear evidence of mixing between irrigation and groundwater in farmers' boreholes.
- ⇨

Water from a selection of boreholes from these sites was sampled and analysed for the tracers mentioned above, for stable isotopes and for chemistry. The data obtained were assessed in terms of description of the processes occurring underground and evaluation of the time scales involved.

Groundwater flow model

The interpretation of tracer concentrations in groundwater relies strongly on the input behaviour of the specific tracer that is employed, the perceived flow path of the specific tracer and the time ranges involved. The complexity of water flow and tracer behaviour and the availability of aquifer information require appropriate approaches. For the present project the simplest types of models, the lumped parameter models, were used. In these cases one assumes linear relations between tracer concentrations in the input (recharge) and in the output (groundwater) and that the aquifer properties can be described with only a few parameters that are applicable to the entire aquifer. This simplification is necessary when only a minimum of information about the aquifers is actually available.

The input functions of the tracers are the tracer concentrations during recharge and, before AD1950, these were essentially constant over time. For that period one can then simply apply conceptual models as analytical functions between in- and output values. Since 1950 however atmospheric concentrations have changed. ^{14}C and tritium in recharge has increased due to the contamination from the atmospheric nuclear weapon tests between 1955 and 1963 and atmospheric CFC levels have steadily increased. These increases have greatly expanded the usefulness of tracers for groundwater evaluations, but necessitate a numerical rather than analytical approach to modelling.

Such a set of models was set up on a spreadsheet, "MRTMODELS", where the tracer inputs and numerical integration were calculated in annual steps. The inputs of the five tracers are required and the aquifer responses are simulated with a range of aquifer parameters that are presented graphically and numerically.

MRTMODELS presents the data for two lumped parameter models;

- ⇨ The piston flow model describes the flow of water as that of a single parcel flowing along a flowline through the aquifer. The water sample will then present the tracer levels as they were during recharge subject only to decay in the case of the radioactive tracers. This model produces a single age for a sample, which is the flow time from recharge point to sampling point. This model is applicable to confined aquifers.

- ⇨ The exponential flow model (or box model) is more generally applicable to phreatic aquifers. It assumes that the water at the sampling point is a mixture of contributions of water having a range of ages. The distribution of ages is an exponentially decreasing function with a characteristic time. The mathematics is similar to that of a mixed box model in which water with variable input functions is mixed and the mixture overflows the box. The tracer concentration in the mixture represents that of the mean residence time (MRT) of water in the box and is the characteristic time of the exponential distribution of input functions.

Each of the models produces relations between tracers as functions of age or MRT against which real-life measurements can be fitted to test the validity of the models. This was done in the case studies that were undertaken during this project.

Field study: Leeukuil

In this granite/gneiss aquifer groundwater occurs in the weathered overburden and the fracture base rock. Two parallel sub-catchments have been studied by sampling from existing pumped boreholes along the two drainage lines. Tritium and CFC both indicate significant quantities of pre-1955 recharge water in the boreholes. Halfway down both sub-catchments, nitrate levels increase due to seepage from manure heaps from the piggery that is located in the catchment. These pollutant waters are indicative of excessive local recharge and higher CFC levels.

The flow pattern resembles that of flow along a surface somewhat below the water table to which local seepages are added. The tracer data fit those of the exponential flow model and the binary flow model. The latter model appears to be more applicable for the samples that are contaminated by piggery waste.

Field study: Dolomite Springs

The springs in the Dolomites are the result of the compartmentalization of the aquifer by dolerites, thereby forcing the water to the surface. Each sample therefore represents its own catchment, or compartment. The aquifers consist of some karst erosion features at and below the water table and deeper fractures in the limestone. Selection of the springs for the present project was based on favourable sample conditions and to obtain a range of mean residence times.

While some springs deliver water to some extent contaminated (as also evident from the CFC levels), most are quite pristine. Most springs exhibit the tracer relations typical of the exponential flow model, while some show typical behaviour of mixing between two distinct younger and older water types. There may be an influence of ventilation of groundwater in the karstic features of the Dolomites. The presence of mine and other waste water pollution in some spring water is evident from both chemical anomalies and high CFC values. Mean residence times of spring water in the compartments are in the order of tens to hundreds of years.

Field study: Leeu Gamka

In this agricultural area along the Gamka river, water is extracted from the Beaufort sandstone underlying the alluvium upon which heavy irrigation takes place, mainly from sprinklers. In addition there is some water importation from the Leeu Gamka dam upstream. Groundwater is extensively recycled as can be observed from the higher water salinity and CFC downstream towards the south and the consistent high tritium values that are close to the present day rainfall levels.

The tracer patterning from the boreholes fits the exponential mixing model quite well. There appears to be slightly elevated CFC-12 levels and reduced CFC-11 levels. The water properties (chemistry and isotopes) can clearly be separated into sources of old ‘inflow’ water and mixtures with the younger recycled water.

Conclusions

The work of the present project has demonstrated that the piston-flow model is unlikely to be applicable to fractured rock aquifers. In all cases there is substantial mixing of water from various origins. Whether this mixing occurs in the fractures of the aquifers, or in the sampling boreholes is immaterial. The combined use of CFCs, isotopes and chemistry has shown that both the exponential mixing model and the binary mixing models are applicable for all three fractured rock aquifers, namely for the Dolomites, for a granite/granite gneiss aquifer and for a Karoo sandstone.

Significant CFC levels above the maximum atmospheric limit (100 pmf) indicates contamination of the groundwater. Different contamination events seem to generate characteristic CFC profiles. Combining CFCs with macro chemistry has proved very useful in detecting, or confirming, examples of low levels of pollution.

In general there seems to be a loss of CFC-11 in the groundwater compared to the other two CFCs. This can be due to the tendency of CFC-11 to be reduced in anoxic environments or be adsorbed on organic matter in the aquifer. CFC-12 and CFC-113 generally provide consistent patterns in groundwater.

A general algorithm whereby the flow regimes for all three aquifers can be evaluated from tracer data only, is not possible. Each site requires an approach that is suitable to the conceptional hydrogeology of the specific aquifer and its flow distribution pattern.

The overall aims of the project as formulated in the agreement between the WRC and the CSIR have been met.

Recommendations

1. The combined use of CFCs, isotopes and chemistry in groundwater enables one to conclude with some degree of certainty which mixing model is applicable to the study. Thus for a regional or local aquifer which has a high degree of importance and for which proper management is needed, we recommend that a program of investigation be carried out which includes the suite of sampling and data evaluation demonstrated in this project. Proper management of an aquifer implies that the flow system is understood, and this would include an understanding of mixing

processes. The estimated cost for such an exercise is in the region of R100 000 which is acceptable in relation to the alternatives available and the potential applications of the water. We recommend that the combined use of CFCs, isotopes and chemistry be more commonly applied in Southern Africa.

2. The spreadsheet flow model, MRTMODELS, needs to be improved. One aspect is to incorporate the fact that recharge in the arid zone can vary from year to year and this should be incorporated as a separate data set.

3. CFCs can be used as an early warning system for detecting anthropogenic pollution of an aquifer. The present project has highlighted a few cases where CFCs are elevated, but other pollution indicators are barely above normal concentrations. For sensitive and strategically important water-supply sources it is recommended that regular sampling for CFCs are carried out in order to provide early warning of pollution.

4. Lack of knowledge of the regional distribution of tritium in modern and past rainfall has hampered the usefulness of tritium as a tracer for mixed water. An evaluation of the past distribution of tritium in rainfall is required.

5. In addition it is becoming necessary for more data to be made available of the present day distribution of tritium in rainfall. A sampling and analysis programme throughout the country is necessary, to supplement the data presently available.

6. An evaluation of the effective tritium content of recharge is required. This should be based on the rainfall data base and accommodate the selectivity of recharge events in our arid region.

7. The tracers $^3H/^3He$ and SF_6 are less susceptible to sample contamination and have been used in some published investigations with great success. Particularly $^3H/^3He$ is useful to assist in unravelling the complexities of the tritium input during recharge. It is recommended that these techniques be introduced in further studies of this nature.

8. More detailed numerical groundwater models than the lumped parameter models employed here, should be developed to incorporate these short-lived tracers. The first attempt by the ETH Group (Switzerland) in Botswana, seems promising and should be followed up with additional and appropriate case studies.

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ABBREVIATIONS AND ACRONYMS

BFM	Binary flow model
CFCs	Chlorofluorocarbons: collective name for Cl and F containing carbon compounds
CFC-11	Trichloro-fluoro-methane ($CFCl_3$)
CFC-12	Dichloro-difluoro-methane (CF_2Cl_2)
CFC-113	Trichloro-trifluoro-ethane($C_2F_3 Cl_3$)
CSIR	Council for Scientific and Industrial Research
D	Deuterium (^2H)
DFM	Dispersion flow model
DO	Dissolved Oxygen (mg/L)
DOC	Dissolved Organic Carbon: expressed as mg C/L
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity (specific conductance) usually expressed in mS/m at 25^0C
EFM	Exponential flow model
Freons	Alternative name for CFCs
GNIP	Global Network for Isotopes in Precipitation (IAEA)
Halocarbons	Alternative name for CFCs
IAEA	International Atomic Energy Agency
L/s	Litre per second: water flow unit
Mono pump	Brand name for a borehole pump
MRT	Mean Residence Time
mS/m	Milli-siemens per metre: units of electrical conductivity (also known as millimhos per metre)
nm	Not measured
pg/kg	Picogram per kilogram: analysis unit for CFCs
pmc	Percent Modern Carbon: analysis unit for radiocarbon

pmf	Percent Modern Freon: unit for reporting freon (Talma *et al* 2000)
PFM	Piston flow model
TDS	Total Dissolved Solids
TU	Tritium Unit: analysis unit for tritium (^{3}H)
uPVC	Ultra-violet light protected PVC
USGS	United States Geological Survey
WRC	(South African) Water Research Commission
WSM	Water Systems Management
^{13}C	Non-radioactive isotope of carbon
^{14}C	Radioactive isotope of carbon
^{18}O	Non-radioactive isotope of oxygen

CHAPTER 1: INTRODUCTION

1.1 Aims

The aims of this current project (hereafter called WRC-CFC-2) as set out in the project proposal to the WRC are:

- ⇨ to develop a method of integrating and analysing groundwater age data provided by ^{14}C, CFC-11, CFC-12, CFC-113, tritium and other isotope analyses so that groundwater mixing ratios for fractured rock aquifers can be determined.
- ⇨ To investigate the application of these mixing ratios to groundwater resource evaluation so that the reliability of these evaluations can be refined.
- ⇨ WRC-CFC-2 was developed following completion of an earlier WRC project (Weaver and Talma 1999: hereafter called WRC-CFC-1).

1.2 Motivation

The motivation for WRC-CFC-2 as contained in the proposal was as follows:

The WRC project K5/731 (Weaver and Talma 1999): "Chlorofluorocarbons (CFC's) and groundwater age-dating in South Africa's Fractured Rock Aquifers" (WRC-CFC-1) successfully tested the CFC-in-groundwater method in three fractured rock environments. This methodology provides an opportunity to obtain quite accurate recharge dates, which is possible due to the steep increase of atmospheric CFC levels during the past decades. This is in contrast to tritium and radiocarbon for which the recent input curves are rather flat. The fractured rock test sites for this project were:

- ⇨ quartzites from the lower Table Mountain Group (TMG) at Oudtshoorn,
- ⇨ quartzites and shales from the upper TMG and
- ⇨ sandstones and shales from the Karoo Supergroup.

In all the three sites groundwater recharge ages for a number of the sampled boreholes were older than the lower limit for the CFC-method, i.e. older than 50 years. These older ages were confirmed by the ^{14}C results. However in many of these samples low levels of CFC's were present.

Most aquifers where the CFC method has been applied are primary aquifers that have been sampled with nested piezometers where mixing of young and old groundwater is rare. In such aquifers rainwater recharges and flows through the system along discrete flow lines between which mixing is limited to some dispersion. A sample collected in the aquifer in this way would be representative of a particular recharge event. However, South Africa's aquifers are predominantly fractured rock where it is quite feasible for a young water to mix with a 10 000 year-old water. During the first WRC project we experienced this phenomenon where CFC results produced recharge dates of 1960/70, but ^{14}C isotope analysis gave ages of 1000 years and older. Graphical manipulation (presented by Talma *et al* (2000) at IAH2000) showed that it may be possible to explain these low levels of CFCs by mixing of young and old groundwaters. More exciting is that it may be possible to determine the actual ratios of mixing. If this is so then there are great possibilities for using these mixing ratios to refine groundwater flow models in these fractured rock aquifers. In turn this will enable water resource managers to evaluate groundwater reserves with greater confidence than is currently allowed with the current tools and knowledge available.

Unfortunately the first project has only a few sample results, which could be used for the graphing and testing of groundwater mixing ratios. The primary aim of this first project was to gain experience in using the technique, to learn the methodology and to test the CFC method, which was successfully done.

It is now important to obtain a much larger sample set so as to more rigorously test the possibility of using ^{14}C, tritium and CFCs for determining mixing ratios. The mixing ratios will in turn be used when carrying out resource evaluation for the sustainable development of fractured rock aquifers.

1.3 Previous work: locally and abroad

Thompson (1976) was the first researcher to recognise dissolved CFCs as a dating tool for groundwater. Subsequent to this the use of the method was sporadic and a rather esoteric event. However, the development by Busenberg and Plummer (1992) of the US Geological

Survey of a sophisticated and reliable sampling and analysis method has enabled CFC technology to be widely used in groundwater studies.

In 1994 the CSIR (Weaver and Talma) approached Dr Neil Plummer of USGS and he agreed to collaborate and assist in developing the method in South Africa. This involved lending a sampling apparatus, providing detailed instructions, advising when problems were encountered and carrying out analyses of samples collected. The CSIR provided the initial funding for this first phase. During this phase sampling was carried out at Atlantis, Western Cape and Agter Witzenberg, Western Cape (Weaver *et al*., 1995).

Subsequent to this initial phase, an application for funding was made to the WRC. The funding was approved and the second phase started in January 1996. This project (WRC-CFC-1) was published by the Water Research Commission in 1999 as “Field Studies of Chlorofluorocarbons (CFCs) as a groundwater dating tool in fractured rock aquifers” (Weaver and Talma 1999). The study looked at three fractured rock aquifers:

- ⇨ Agter-Witzenberg: Table Mountain Group quartzites and shales;
- ⇨ De Wetsdorp: Karoo sandstones and shales (Talma *et al* 1998);
- ⇨ Klein Karoo Rural Water Supply Scheme: Table Mountain Group quartzites.

The conclusion that was made from WRC-CFC-1 was that “*the data generated by these three case studies have demonstrated the utility and potential of CFC analyses of groundwater in South Africa’s fractured rocks. The application of simple age-dating of groundwater in our aquifer rocks is certainly not as straight forward as is the case in the primary aquifers found in the CFC literature.”*

The tracer data of the Agter-Witzenberg study were re-interpreted later by using concentrations of CFC, rather than recharge dates (Talma *et al* 2000). It became evident that for fractured rock aquifers, mixing lines between the various tracers can be quite useful to identify components of different water sources. This observation resulted in the present project where the object is to deliberately source water from fractured rock to look for complex mixing situations.

CFC dating has shown to be a successful tool to study water flow in primary aquifers (Busenberg and Plummer 1992, 2000, Ekwurzel *et al* 1994). Applications in fractured rocks or more complex flow systems are limited. Katz *et al* (2001) showed a fair concordance between

CFC-11, CFC-113 and tritium and mean residence times of 20 years in nitrate contaminated springs in Northern Florida USA. In the Shenandoah Mountains, VA USA, residence times in the order of two years were derived from a spectrum of different isotope and gas analyses (Plummer *et al* 2001).

1.4 Overview of the project and site selection

The first task was to identify and select suitable sites for which case studies could be developed. Requirements for suitable fractured rock aquifer study sites were:

- A fractured rock aquifer is required where it is probable that mixing of young and old takes place.
- The hydrogeology of the site should be reasonably well known, since additional preparatory work would be too costly.
- Some isotope and/or chemical data should be available.
- Groundwater recharge ages should be within the past 10-20 years, to make full use of the major CFC variations.
- A sufficient number of sampling points (boreholes) should be available for sampling.
- Established pumps in those boreholes would simplify the sampling procedure since purging times can then be reduced.

The following 5 sites were considered possible targets prior to project initiation.

- Vryburg, deep boreholes in a quartzite aquifer,
- Kuruman, two distinct sources of water, from dolomites and banded ironstones,
- Grootfontein (Lichtenburg), many boreholes available for sampling in this dolomite aquifer,
- Rustenburg, a complex flow pattern in a number of different geological units,
- Agter Witzenberg, previously studied with detailed geochemistry and isotopic information.

The first phase of the project involved site selection. The project team contacted a number of hydrogeologists and read many reports. Thirteen sites were considered for further investigation. These were:

1. Leeukuil (Polokwane/Pietersburg)

   This site satisfied all requirements: Pierre Mouton in Polokwane/Pietersburg established preliminary water balances; there is a good record of water levels over a decade; there are ample well-equipped boreholes and good collaboration with the main water user in the area. A reconnaissance sample trip (April 1999) had established that suitable ages are likely and consistent chemical data obtained.

2. Springbok Flats, North of Pretoria

   A section of the area called Moretele 2 located in the southern boundary of the Stormberg basalt outcrop and to the west of Settlers was targeted. Some isotope data had been obtained by CSIR and also by Martinelli & Associates in this area in the 1980s. Boreholes appear to be still available (R Meyer, pers comm.), but are not equipped. The conceptual model of flow in the area suggested flow along the basalt/sandstone contact. ^{14}C (in the range 78 to 99 pmc) and tritium (zero) had been measured. Given the time scale and limited capacity of the project, it was considered not warranted to expend resources on this site, especially as none of these boreholes were being actively pumped.

3. Dolomites of the North West Province/Far West Rand

   The Dolomites represent the largest and best-known fractured rock aquifer in the country. Initially we planned to intensively sample a small catchment, but could not identify such a site. Recent isotope measurements from a DWAF project underway indicated that CFCs could elucidate mixing features. The team thus decided to sample a series of springs for which a set of historical isotope data (^{14}C and tritium) was available.

4. Tierfontein (Malmesbury)

   To the south west of Malmesbury are a number of actively pumped boreholes taking water from a granite aquifer. This aquifer appeared to be quite suitable initially. However the ^{14}C content of one of the upgradient (presumed recharge area) boreholes was 83.8 pmc. This is pre-bomb, indicating groundwater at the lower limit of CFC concentrations, and it was feared that the ‘downstream’ water might be too old for the purposes of this project.

5. Agter Witzenberg (Western Cape)

During the previous phase of this project, CFC samples were collected here (Weaver and Talma 1999). The CFC results indicated a more detailed age structure for the younger water than was obtained from either of the radioactive isotopes tritium and ^{14}C. The groundwater flow pattern developed during an earlier project (Weaver *et al* 1999) was confirmed, as was the intensive mixing that occurs. The team decided not to expand the sampling network at Agter Witzenberg, but to rather test other hydrogeological settings.

6. Leeu Gamka (Karoo)

This area has a large number of boreholes drawing water from saturated alluvium and deeper groundwater. Chemically the water can be very well distinguished. Borehole responses are sufficiently rapid to deduce that irrigation water is actively being recharged. The possibility to sample mixtures of local groundwater, canal water from the Leeu Gamka dam and irrigation recharge made this an attractive study area.

7. Dendron (Limpopo Province)

There are many boreholes in this area. The information received is that the aquifer is over-exploited and the water table is quite deep. Sampling would be too complex.

8. Coetzersdam (Vryburg)

This aquifer has very deep water levels, which show no seasonal variation and therefore is not likely to have sufficiently young recharged water. No isotope data are available.

9. Kuruman (Northern Cape)

The catchment area of the Kuruman eye is quite large. The known ^{14}C and tritium data suggest that ages might be such that CFC levels could be low. This would defeat the object of the present project where we need to test aquifers with short turnover times.

10. Hartebeesfontein (West Rand)

This small aquifer shows a rapid water level response. No isotope data is available to judge its suitability. There are many boreholes available.

11. Sishen (Northern Cape)

While the aquifer underlying the mine yields mixtures of water types, the ^{14}C and tritium levels indicate that the water mean residence time (MRT) is likely to be too great for mixing details to be unravelled by using CFCs. Sampling is also likely to be difficult due to the fixed infrastructure of the mine.

12. Rietfontein (Gordonia)

DWAF water level data from this aquifer suggest that there might be sufficient young water. There are not that many boreholes, however and at present no isotope data available on which to base any assessment of water age. The very arid environment of this location in Bushman land may imply that recharge is very low there and that the water ages may well be beyond that where CFC would be expected in the water.

13. Stilbaai springs (Western Cape)

Too little is known of these springs at this stage. No boreholes appear to be available in the recharge area of the springs.

The sites that were eventually selected for this project were Leeukuil near Pietersburg, the Dolomites and Leeu Gamka (Figure 1.1).

1.5 Project methodology

In the three sites that were selected a range of boreholes was sampled as described in the appropriate chapters. Samples were taken for ^{14}C, tritium and CFC using existing pumping systems with the proper approaches to eliminate contamination. Chemistry and stable isotope samples were taken using standard techniques (Weaver 1992). Analyses were done in the laboratories of Environmentek in Stellenbosch (chemistry), Quadru in Pretoria (stable isotopes and ^{14}C), Schonland Research Institute, Witwatersrand University (tritium) and US Geological Survey, Reston VA, USA (CFC).

It is of critical importance during sample collection for CFC to prevent contamination from external CFC sources. The detection limit of CFCs is approximately 1 pg/kg, thus the introduction of as little as 0.01 cm^3 of modern air during sampling is detectable. Contamination is a serious problem especially with samples of older water (Busenberg and Plummer, 1992). Sources of contamination are: air contact, plastic materials in the pump and pump discharge line, glues used for the borehole casings and grease and oil in the system. The sampling technique is therefore carefully geared towards minimising contamination. Samplers and sample containers should be made from either clean metal or glass.

Busenberg and Plummer (1992) have designed a CFC sampling apparatus to sample groundwater in a closed system to exclude air from the sample. The water sample is sealed (by welding) in a borosilicate ampoule for transport. This apparatus is constructed in such a way that water is only in contact with stainless steel, teflon and aluminium. The glass ampoule is flushed with ultra-pure nitrogen gas that has passed through a molecular sieve trap to remove all traces of CFCs. The ampoule is then filled with borehole water, after which it is sealed with a flame torch. During sampling and sealing the nitrogen gas is continuously flowing, preventing air contamination. After extensive borehole purging has taken place, samples can be collected at about 10-minute intervals. A set of 5 samples is needed for analysis in order to establish that contamination-free samples have been obtained. This sampler, based on the USGS design, was made in Pretoria, and was used in the previous CFC project (Weaver and Talma 1999).

Busenberg and Plummer (1992) have adapted a gas chromatograph to handle the extraction of CFC from ampoules and CFC analysis without air contamination. The analytical uncertainty is ±1 pg/kg which translates into an error of ±3% for concentrations greater than 50 pg/kg (younger water) and increases to an error of ±50% (old water) at the detection limit (Ekwurzel *et al.*, 1994). Detection limits of 1 pg/kg allows the identification of post-1940 recharge water using CFC-12 and post-1947 recharge using CFC-11.

The measured concentrations of the CFC gases are divided by the solubility of the gas in water at the assumed recharge temperature to derive a partial pressure of the CFC in air that would be in equilibrium with the water. From the atmospheric pressure at the recharge site, this can be translated into a CFC mixing ratio in the atmosphere. Using the known atmospheric CFC curves, a recharge date can be calculated under the assumption of piston flow (see next chapter for a more detailed discussion of the flow concepts). Following the practice in radiocarbon, the term ‘per cent modern freon (pmf)’ has been introduced (Talma *et al* 2000) for the ratio of the CFC content in water compared to what it would have achieved in equilibrium with atmospheric air at the maximum levels (the past 5 years). This seems a more appropriate parameter to deal with in the type of data evaluation necessary for this project. The process can be followed in Appendix 2, which is derived from the spreadsheet calculation of recharge date and pmf.

The southern hemisphere CFC atmospheric data base was compiled by E Busenberg and is based on the revised ALE-GAGE atmospheric measurements of the Cape Grim (Tasmania) monitoring station (Prinn *et al* 2000). Pre-1980 concentrations were calculated from available CFC production and release data (AFEAS 1996).

In this project no attempt was made to measure the actual recharge temperatures. The required nitrogen and argon analytical facilities are no longer operative at the CSIR. The mean annual air temperature at the location has been assumed to provide a good approximation of recharge temperature. This approach is justified by the depth (usually >5m) of the water table in all of the study sites. At this depth the soil temperature is equal to the mean annual surface air temperature. Errors in the estimation of temperature will have an effect on the calculated pmf values (Figure 1.2): a temperature error of 1 °C will affect the pmf value by 5%. Temperature effects are a serious consideration when calculating the equilibrium CFC levels in river water where a daily temperature cycle may exist (see Chapter 5: Leeu Gamka). The other parameter for this calculation is height above sea level. In the case of the three study sites selected this is not a problem since the areas are all fairly flat and even if the recharge area might not be known very well, there is not much topographic variation.

The data of the five tracers as well as the chemistry and stable isotopes given in Appendix 1 were evaluated together to achieve the aims of the project.

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CHAPTER 2: GROUNDWATER FLOW PATTERNS

2.1 Processes

Any constituent added to water can, in principle, be used to follow its flow path underground. Chemical tracers can be introduced to the water cycle by anthropogenic activities and then be labelled pollution if the consequence is considered hazardous. Other tracers are the radioactive constituents of air and water (such as tritium and ^{14}C) that enter the water cycle and by their decay indicate the groundwater residence time. All of these can be used to interpret the movement of water underground.

The tracers relevant for this project are those that are useful for following the water cycle in what is called ‘recent times’, or the last half-century. Between 1952 and 1963 atmospheric nuclear weapon tests produced large quantities of tritium (^{3}H), radiocarbon (^{14}C) and ^{36}Cl. These substances mixed in the atmosphere in various ways and found their way into the hydrological cycle. Nuclear reactors worldwide have been producing the radioactive isotope Krypton-85. In the absence of a realistic sink, the ^{85}Kr content of the atmosphere has continually increased. This has provided hydrologists with another tracer for recent recharge. It is not often used because of the analytical difficulties of measuring the low radioactive levels found in groundwater.

CFCs (chloro-fluorocarbons) were once considered to be one of the successes of the 20th century chemical industry. CFCs have stable chemical properties, liquefy readily and have therefore found uses in refrigeration equipment, manufacturing, fire extinguishers, aerosol cans, etc. Their stability and low solubility in water has led to a steady rapid increase of CFCs in the atmosphere since 1950. Their ability to destruct ozone in the stratosphere is expected to be catastrophic for the environment and has led to the Montreal protocol which has virtually halted CFC manufacture worldwide. The solubility of the three CFCs (CFC-11, CFC-12 and CFC-113) in water and their low reactivity with materials with which groundwater is in contact, makes them good tracers for groundwater flow and the number of laboratories worldwide with CFC analysis capacity is increasing. Sulfur hexafluoride (SF_6) is another very stable gas that is being used for groundwater tracing. SF_6 due to its non-conducting nature is used as an isolating gas in electrical switchgear. The atmospheric concentration is steadily rising, although the levels are still much lower than those of the CFC gases.

For general reviews of these tracer applications in groundwater, see the publications of the International Atomic Energy Agency (IAEA) and recent isotope hydrology textbooks (e.g. Mazor 1991, Clark and Fritz 1997,Kendall and McDonnell 1998, Geyh 2000, Cook and Herczeg 2000, Yurtsever 2001). For various reasons the tracers used in this project are limited to ^{14}C, tritium, CFC-11, CFC-12 and CFC-113.

Radiocarbon has been used as a water tracer since the early 1950s when it was shown that its half-life of 5730 years enables radiocarbon to be used for the determination of ages of palaeowaters back to many tens of thousands of years. For the present project the relevance of radiocarbon lies in the rise of the atmospheric ^{14}C content from 95 pmc to 160 pmc in the southern hemisphere in the 1950’s and its decrease to the present value of 110 pmc. This ‘bomb-^{14}C’ pulse is used to identify recently recharged groundwater. The transfer of ^{14}C from air to groundwater takes place through plants and involves dissolution of carbonate from soils, which usually do not contain any ^{14}C and possible additional uptake of aquifer carbonate in the saturated zone. For this reason, there can be some delay before the ^{14}C pulse actually reaches the water table and there is usually a ‘dead carbon’ correction. The first is taken care of in some models by assessing the actual delay time. The second can be estimated by general assumptions regarding the initial ^{14}C content which can sometimes be backed up by chemical or other isotope data (Clark and Fritz 1997). The third can be corrected for by more detailed chemical modelling corrections provided there is sufficient knowledge of the aquifer and its groundwater.

The natural background value of tritium is estimated to have been 3.5 TU before the maximum bomb produced pulse of 80 TU was reached in 1963 in the southern hemisphere (IAEA 1992). The half-life of tritium is 12.43 years and this implies that the tritium content of water from the maximum bomb pulse has reduced to about 10 TU in 2000. This is a characteristic of the southern hemisphere only; in the northern hemisphere tritium levels are still above the background. The effective input curve of tritium into the hydrological cycle in the southern hemisphere at the present time therefore consists of an increase in the late 1950s to 10 TU and a slow decrease to the present day value of 3.5 TU (Figure 2.1). The main advantages of using tritium is that sampling is simple and that it is a conservative tracer.

The three CFC gases have presented promise as tracers on account of the steady rise in their atmospheric concentrations which is presently flattening off and for CFC-11 and CFC-113 slowly decreasing. The input function is therefore a steadily rising curve and is particularly useful for the very recent decades (Figure 2.1). Other advantages of CFCs as tracers are their stability (low reactivity) with most materials found underground. The disadvantages are that the levels are extremely low and sampling techniques must therefore be scrupulous to avoid air contamination. Oil or plastics dissolve or adsorb CFCs and may not be used in sampling lines unless they have been very well purged. The analytical cost of CFC analysis is on par with ^{14}C and tritium. For reviews of CFCs as groundwater tracers see Plummer and Busenberg (2000) and the USGS CFC laboratory website URL: http://water.usgs.gov/lab/cfc/

2.2 Tracer Models

The interpretation of tracer behaviour in groundwater relies strongly on the input behaviour of the specific tracer that is employed, the perceived flow path of the specific tracer and the time ranges involved. The complexity of water flow and tracer behaviour and the availability of aquifer information require appropriate approaches. Three broad categories of models are usually used to evaluate tracer behaviour in groundwater aquifers in increasing order of complexity (Yurtsever 2001, IAEA 2002):

- Lumped parameter (or black box) models, in which a linear relation between tracer input and output is assumed and in which the properties of the entire aquifer are described in a single uniform manner.
- Compartmental models, in which the aquifer is assumed to consist of a number of black boxes that interact in ways that can be parameterised.
- Full blown numerical models, in which advective transport, dispersion and other parameters can be included using MODFLOW or other similar software packages.

In the present project the lumped parameter approach is followed: essentially since there is a scarcity of aquifer information available for the test sites used in this . There are three models used to evaluate the response of aquifers to the input of a time variable input (^{14}C, tritium or CFC) transferring from the atmosphere to groundwater (Maloszewski and Zuber 1982; Verhagen *et al* 1991; Zuber and Maloszewski 2001).

The simplest case is that of **piston flow (PFM)**. It is so-called since the behaviour of water flow resembles that of a piston or slug of water flowing through a pipe. This approach is usually used in confined flow systems. In this case one is visualising flow as that of a parcel of water that is recharged and flows unaltered towards the observation point (Figure 2.2A). The water in the parcel does not mix with other water parcels and, in terms of the radioactive tracers, its behaviour resembles that of an archaeological artefact that only loses its activity due to radioactive decay. The tracer input will appear in the observation location in the same shape after some delay: the age of the water. This is the classic form of dating since there is a fixed relation between the tracer content at recharge, C_0, and the concentration in water at an age of τ years:

$$C(\tau) = C_0 . e^{-\lambda\tau}$$

where λ is the decay constant of the tracer. This is the simplest conceptual model to consider and the radiocarbon contents of many water analyses are reported as ages based on a constant input function (as in the pre-bomb period). Where the ages are low enough that the input functions are irregular (e.g. with tritium, ^{14}C and CFC of the past 50 years), then the input pulse will be reproduced at the observation points, though with some dispersion added (Figure 2.2B). In such cases some wiggle matching may be required.

There are situations, particularly in artesian water where piston flow models are quite applicable (Geyh 2000). The model is also applicable in primary aquifers with very regular flow properties when samples are taken at very specific depths. This flow system can be categorised as a combination of flow lines each of which resemble piston flow behaviour.

The **binary model (BM)** is used to describe the mixing occurring between two types of water with different properties (Katz *et al* 2001, Burton *et al* 2002). Its typical application is the situation where water from overlying and underlying aquifers are mixed either through leakages between the separating layers, during pumping in the sampling borehole or during spring discharge. The tracer concentrations are determined by linear mixing lines and are usually related to each other along straight lines between the properties of the two end-members.

The binary model is useful to describe pollution addition to water (Eglington *et al* 2001) but requires sufficient definition of distinct end-members. This model has also been successfully used to describe the mixing of dolomite spring water from the Kuruman springs (Bredenkamp 2000) and mixing of recent recharge and deep-seated old water from a group of six boreholes in the Table Mountain Group. In the latter case a number of properties of the two end-members were very different and the mixing process could be clearly demonstrated (Talma *et al* 2000, Cavé *et al* 2002).

The **dispersion model (DM)** is an adaptation of the piston flow model to reality (Figure 2.2C). The exchange of water from the water parcel with its surrounding water is modelled using a dispersion parameter, P_D. It is a useful approach when dealing with time series of isotopes when dealing with isotope variations in the input.

In the **exponential flow model (EFM**), the water input is presumed to enter the water table over the entire area (Figure 2.2C) and flow lines then converge towards one particular direction. This model is applicable for the modelling of age related tracers (e.g. ^{14}C, tritium and CFCs). It resembles the box model used by chemical engineers to describe processes in reaction vessel with different inflows and outflows and mixing in the box in between. This model is the extreme dispersion model since one assumes that the water is dispersed throughout the aquifer. Because of its mathematical simplicity, the EFM is generally used for a phreatic aquifer and has a sound geohydrological basis on the assumptions that the aquifer properties are homogenous and that sampling is equal at all depths. In this case, the spring, or the borehole tapping the entire borehole depth, will deliver a mixture of water that has recharged at different times in the past. This implies that the water collected in the sampling vessel (borehole or spring) is a mixture of water with 'ages' ranging from zero to infinity and the average tracer concentration is determined by a distribution function g(t). Each component of this mixture can then be considered a separate piston flow system. The concept of 'mean residence time' (τ) is used to describe the distribution of water ages (Verhagen *et al* 1991).

The distribution of water with delay times, t, is exponential:

$$g(t) = \frac{e^{-t/\tau}}{\tau}$$

with the critical distribution parameter, τ, the mean residence time of water in the aquifer.

When the input function of a particular tracer is constant over time (as was the case for ^{14}C and tritium before 1950 AD) then the relation between input and output concentration, C_0 and $C(\tau)$, is described in a simple manner by

$$C(\tau) = \frac{C_0}{1 + \lambda\tau}$$

Since 1950 the input concentrations of the tracers used in this project increased and some later decreased somewhat. The transfer functions must therefore be handled numerically for this period as described in the next section. It also means that the input function will reappear in the observation pont in a smoother shape of which the amplitude and shape will depend on the mean residence time of water in the aquifer (Figure 2.3).

In its simplest form, the recharge (R: as metre/year) and the water content of the aquifer (S: as metre depth of water) then determine the mean residence time (MRT or τ)

$$MRT=S/R$$

and is an alternative means of quantifying recharge (Bredenkamp *et al* 1995).

The use of tracers to describe flow in a phreatic aquifer was initially conceptualised by Vogel (1967) to describe the water flow through a sandy aquifer on a Dutch island and was later formalized by Maloszewski and Zuber (1982), Verhagen *et al* (1991) and Gieske (1995). This 'Vogel' model has been extensively used in primary phreatic aquifers utilising various tracers (Geyh 2000).

This model has also been applied to fractured aquifers, for example by Bredenkamp and Vogel (1970) in the dolomite aquifers, by determining the depth gradient of ^{14}C and tritium. The same concept (mixing of a range of recharge ages) has been used to interpret the relation between ^{14}C and tritium (both pre-and post-bomb) in terms of the behaviour along a relation of these parameters with different MRT (e.g. Verhagen *et al* 2000). The location on this line is determined by the MRT of water in the aquifer. At the same time, one can make an estimate of the other unknown quantity, the initial ^{14}C content of groundwater, which is determined by the amount of dead carbonate dissolved during hydrochemical development of groundwater. In the present project the concept has been carried forward by using the three CFC gases in an attempt to better characterise the contributions of the different components in phreatic flow models.

2.3 Spreadsheet model calculations

The input functions of the tracers used in this project (^{14}C, tritium and CFCs) were constant before 1950 and this enabled simple analytical computation to be done to evaluate tracer levels through the various models when run at that time. Since 1950 the tracer input functions have each changed in its own irregular manner and their processing through the flow models now requires numerical computation with suitable time intervals.

Various software models have been written in different forms: BOXMODEL: (Zoelmann and Aeschbach-Hertig 2000), TRACER (Bayari 2002), PCFLOW by Maloszewski and Zuber (IAEA 2002). These can be used to produce time series of model responses from given inputs or produce age or MRT from a single parameter for specific models. No software could generate the response of all five tracers together at a single point in time.

A workbook 'MRTMODELS' was therefore set up to achieve this. It uses the known values of the input functions of five tracers (^{14}C, tritium, CFC-11, CFC-12 and CFC-113) each as input on a separate worksheet. One worksheet is used to control the others by means of entering the observation year (t), the delay times of each tracer to the water table (t_u) and the dilution of ^{14}C by dead carbon (q) (Figure 2.4). The Excel© spreadsheet format has been used for its ease of programming, simple graphic capability and data compatibility. It does have disadvantages of lack of adaptability in some respects (e.g. time step intervals, lack of robustness in terms of ranges, etc).

The output of the model consists of the values of the five tracers through the piston-flow and the exponential mixing models as function of a range of mean residence times. This output is stored on another worksheet and shown graphically on the control worksheet (Figure 2.4). Figures of the relations between different tracers for the PFM and EFM are also produced (see for example figures 3.14, 4.11 and 5.12 for examples on the present project).

An unique feature of MRTMODELS is the ability to build in a delay of any tracer, t_u, to reach the water table. This possibility of employing an under-saturated zone (UZ) lag is intended to model the behaviour of any of the tracer that may be held up in the soil zone and therefore be delayed in reaching the water table relative to the other tracers. This is a feature that may be applicable in our arid areas with deeper groundwater tables and low recharge rates where significant time delays may be evident in the unsaturated zone. Applications of this feature are to be found in some of the present study areas where it appears that tritium is delayed relative to CFCs (Figure 3.15).

For the piston flow model the output concentration is calculated from

$$C(t,\tau,t_u) = C_0(t - t_u).q.e^{-\lambda\tau}$$

where $C_0(t)$ is the concentration of tracer in year t

t_u is the delay time for the tracer to reach the water table

λ is the decay constant of the tracer (0 for CFC)

τ is the mean residence time described above

For the exponential flow model the output concentration is calculated from the equation (Verhagen *et al* 1991)

$$C(t,\tau,t_u) = \frac{e^{-\lambda t_u}}{\tau}\int_0^{\infty} C_0(t - t_u - t').q.e^{-\lambda t'}.e^{\frac{-t'}{\tau}}.dt'$$

For purposes of the spreadsheet calculation, the integral is replaced by summation over an adequate number of years (depending on the tracer involved) to ensure sufficient precision.

The relations between the five tracers according to various flow and input scenarios can then be plotted and one can attempt a match between the model results and the real-life sample data. In the absence of 5-dimensional visualisation capabilities, we here use the approach of Talma *et al* (2000) to plot various pairs of tracers (Figures 3.14, 4.11 and 5.12) in such combinations that they may be meaningful in relation to the sample data.

MRTMODELS is available from the lead author, Siep Talma, at stalma@csir.co.za

2.4 Model application

The model described above has been run with locally suitable data inputs. ^{14}C input data have been taken from atmospheric ^{14}C measurements done at CSIR Pretoria since 1967 and interpolated tree ring samples prior to that (Vogel pers comm.). Rainfall tritium data have been derived from the tritium data published in the GNIP data base for Pretoria (IAEA 2001) supplemented by rainfall data from the CSIR rainfall collection of Pretoria rainfall from 1968 to 1981. Suitable approximations have been made to smooth the time series to reach the present day levels of 3.5 TU (Verhagen pers comm.) and also apply these to the pre-1960 period. These tritium levels are assumed to be applicable to all three of the study areas. The CFC input data have been provided by Dr Ed Busenberg (USGS CFC laboratory) and are based on Australian atmospheric CFC measurements with suitable interpolation at data gaps and comparison with northern hemisphere measurements. There is ample evidence that the CFC level of unpolluted air is fairly constant in the southern hemisphere and about 10% lower than in the northern hemisphere. The main uncertainty on the side of CFC input into groundwater is the possibility of local releases of CFC from wastes or CFC usage or spillage that may enter the ground.

The model results were used as reference curves against which the measured tracer values from the three test sites have been compared for interpretation. These are discussed for the three test sites in detail in Chapters 3, 4 and 5.

2.5 Fractured rock aquifers – two perceptions

A consideration that the reader and practitioner must bear in mind when considering the phrase “fractured rock aquifer” is the difference between the Southern African and the North American and European conceptual models of groundwater flow in fractured rock aquifers.

In both North America and Northern Europe a number of projects have investigated groundwater flow in fractured rock, which have resulted in significant advances in the hydrogeological science. Project sites that immediately come to mind are the Mirror Lakes site in New Hampshire, USA, which is in schists intruded by granite, and the Aspo Hard Rock Laboratory in Sweden, also in crystalline rocks. In these terrains the soil cover is a few metres thick, followed by a weathered and fractured zone a few metres thick and then the fresh crystalline rock with discrete fracturing. These fractures are separated by blocks of fresh or unweathered rock, with very low to nil hydraulic conductivity.

In Southern Africa the contrast to the above conceptual model, is that between the soil layer and the fractured granite is a thick layer of highly weathered to weathered in situ regolith. In areas where the pre-Africa erosion surface is present, this zone can be about 70 metres and up to 140 metres thick. In areas where African erosion surfaces are present some of this weathered rock has been eroded and the remnant regolith can range from 10 or 20 metres, and up to 50 or more metres. This is well documented in a number of publications, especially Wright and Burgess (1992).

The causative agent that has resulted in the difference between these two terrains is that the Northern Hemisphere has experienced a relatively recent period of glaciation and this thick weathered zone has been removed.

Thus a North Hemisphere hydrogeologist, when reading the phrase “fractured rock aquifer”, is usually considering groundwater flow in discrete fractures, which are connected at scales of single decimals of a metre to metres. The Southern Hemisphere hydrogeologist would envisage groundwater flow in the saprock and the regolith zone in which connectivity is of the order 0.1 to 0.001 metres and can be considered intergranular. Flow in the deeper discrete fractures is often not taken into consideration. This is particularly evident in water supply boreholes where drilling is usually stopped after 10 or 20 meters of fresher rock below the saprock is encountered. The experience is that these deeper discrete fractures are widely spaced and the chance of intersecting one does not justify the added drilling expense.

The consequence of these two differing geological models of weathering is differing conceptual flow models. Thus different mixing models should be considered. The Northern Hemisphere model is one of flow in discrete fractures and the mixing model that should be considered most likely is one of mixing of two end-members. The Southern Hemisphere experience indicates the exponential flow model could be more applicable.

The above discussion is a general view and is not an exclusive either-or situation. In both areas there will be a number of exceptions. The discussion does apply most often to crystalline rock terrains, such as Mirror Lake and Aspo. This contrast was strongly brought home to the one author (John Weaver) at the IAH 1993 conference in Olso, Norway, and particularly during the post-conference excursion. A number of the papers presented at this conference dealt with the discrete fracture model and it was only during the post-conference tour that the ideas and experimental results being conveyed by these Northern Hemisphere researchers became clearer when the actual field exposures were viewed.

Southern African aquifers, which more closely resemble the Northern Hemisphere model, would be the quartzites of the Table Mountain Group and the deeper zones of the sedimentary rocks of the Karoo Group. Both of these, however, have elements of both models.

Groundwater chemistry from similar geologies sometimes reflects these two differing models. For example geochemical weathering of granites in the Northern Hemisphere is active and the groundwater has a high pH (7–8) and bicarbonate-type water. In contrast, groundwater from Southern Africa granites, which have filtered through many metres of highly weathered and leached regolith usually have pH of about 6 and are relatively low in bicarbonate.

The purpose of this discussion is to sensitise the reader that the term “fractured rock aquifer” can evoke differing conceptual models depending on the reader’s experience in the field.

2.6 Sampling of fractured rock aquifers

All the boreholes that have been sampled during this project have been equipped with pumps and are production boreholes. As they are fitted with pumps it is assumed these are high yielding boreholes in relation to other boreholes, which have not been equipped. The assumption that has been made is that this high yield is derived from either one fracture zone (water strike) or a few closely spaced fracture zones (water strikes). Furthermore it is assumed that when sampled, the water sample collected will be entirely, or dominated by, water from that fracture zone, and that any minor fractures above (or below) this fracture zone will have a negligible effect and can be disregarded.

2.7 The Issue of Scale

Miller and Gray (2002) discussed the question of the scale at which one should view aquifers and water flow in their article: “Hydrogeological research: Just getting started”, which looked at trends of research in groundwater. They stated: “One of the most difficult problems in all of science is the so-called problem of scale. This is of central importance in porous medium systems in which we seek to describe transport phenomena over scales that range from the molecular to hundreds of kilometres, and over time scales that range from the picoseconds associated with some reactions to the centuries associated with issues such as waste disposal. Resolving critical phenomena across this wide range of spatial and temporal scales and developing models that reflect this range of scale in a consistent and coherent fashion is an open problem of awesome complexity.” The same statement applies to fractured rock aquifers.

If one plans to examine groundwater isotope or groundwater chemistry evolution in a geological horizon then one must be careful to measure like with like. Thus to collect a set of samples from three catchments and then compare the data one has to very careful and first look at each catchment individually and conceptualise the flow regime in each catchment. Once this has been done, only then can data be compared on a catchment-to-catchment basis. For example sampling nitrate on a grid pattern of 10 km per sample will give a picture of nitrate distribution at a regional scale, but will not provide insights into the evolution of nitrate concentration along a flow path if the catchments are only a few hundred square kilometres in size.

As stated in the title, this project looked at catchment scale phenomena, The process was to carefully conceptualise the flow model for the area under question and to ensure that the samples collected came from a defined catchment so we were able to compare like to like. Thus, for Leeu Gamka a single catchment was examined. For Leeukuil the catchment comprises two defined sub-catchments that were compared. For the Dolomites each spring sample represented a single catchment: thereby comparing catchments with each other.

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CHAPTER 3: CASE STUDY - LEEUKUIL, CAPRICORN DISTRICT

3.1 Geographical setting

The selected site is about 10km due west of Polokwane (Pietersburg), and is at about 29^0 20' E and 23^0 55' S. The study area comprises a small catchment of about 8km^2 with an elevation difference of about 100 m from high ground to the lowermost drainage point. Kruger (1983) describes the area as moderately undulating plains with moderate relief, low to medium drainage density and more than 80% of area has a slope of <5%.

The climate is hot and dry. Rainfall occurs in summer between October and March and usually consists of convective thunderstorms. The mean annual rainfall is about 500 mm.

In the south-east portion of the catchment a group of smallholdings called Leeukuil Landbouhoewes are located (Figure 3.1). In the remainder (>80%) of the catchment mixed farming (cattle grazing on grassland and some cultivation) is practised. The central area is occupied by a piggery, which has a considerable effect on the groundwater, both quality (disposal of piggery waste water) and quantity (pumping of groundwater for use in the piggery).

One of the smallholding owners is Mr Pierre Mouton, a hydrogeologist with WSM Consulting. He was able to provide detailed knowledge of the aquifer. The majority of the boreholes have been drilled for exploration and water-supply for the piggery. These boreholes are shown on the site map (Figure 3.1).

3.2 Geology and hydrogeology

The area is underlain by the Hout River Gneiss, which forms part of the Basement Complex (Brandl 1986). Within the Hout River Gneiss a wide variety of granitoid rocks have been included. They include leucocratic migmatite and gneiss, grey and pink hornblende-biotite gneiss, grey biotite gneiss and pegmatite rocks. They largely underlie flat country and are poorly exposed. The rocks are of Randian Erathem age and are 2700 to 2800 million years old.

In the study area the rocks are coarse-grained leucocratic migmatites and gneisses. These consist of dominant quartso-felspathic layers with thin parallel streaks, mainly of biotite. There are a number of NE-SW trending diabase dykes which, in the area of intrusion, change the gneiss to a pink colour.

Groundwater occurs in crystalline basement aquifers. These basement aquifers are developed within the weathered overburden and the fractured bedrock. The weathered residual overburden is termed the regolith, and includes the soil, the stone line and the saprolite. The main water strikes occur in the transition zone from the regolith to the fresh bedrock. This study area conforms to the description of a classic southern hemisphere aquifer (see section 2.5). The weathered/fractured zone is termed the saprock (Wright 1992). The regolith is relatively thin and boreholes are seldom more than 50m deep. The yield prospect (Haupt 1995) is high and borehole yields are generally more than 10 L/s. Boreholes drilled in the vicinity of the diabase dykes tend to be higher yielding (pers. com. P Mouton, 1999).

3.3 Site selection and sampling

Three site visits were made. The initial visit was during April 1999 in order to assess the suitability as a test-site. Five boreholes and the dam were sampled. The samples were analysed for chemistry and ^{18}O, and two samples for ^{14}C and ^{13}C. The results indicated the groundwater was both young and had varying chemistry, thus the full sampling run was carried out in October and December 1999. The results are shown in Table 1 of Appendix 1. Maps showing the distribution of selected parameters are shown in Figures 3.2 to 3.10.

As can be seen on these maps the boreholes tend to be drilled close to the drainage lines. The catchment comprises two drainage lines. The eastern drainage line starts at the edge of Leeukuil Smallholdings and boreholes LK1 and LK2 are smallholding supply boreholes. Lower down the catchment are three piggery boreholes UV1B, UV2 and UV5. These three boreholes were heavily pumped, but due to excessive draw-downs affecting the boreholes on the Leeukuil Smallholdings, the rate of pumping has decreased. The water supply has been replaced by increased pumping from boreholes along the western drainage line. Three small storage dams are located along this eastern drainage line (Figure 3.1). There are also a number of piggery waste disposal sites.

The western drainage line starts at a farm cultivating dry-land crops and cattle grazing where borehole DS1 is used for household and garden watering. Boreholes UVD1, UVN1, N4, UVN3, UV8 are used for piggery water supply. Borehole RF1, at the confluence of the two drainage lines, is used for household water supply on a smallholding.

3.4 Discussion of results

The isotope and chemistry results (Figure 3.2 to 3.10) support the water level data that the two catchments are hydraulically independent. The pattern of chemical and isotope changes as one moves downgradient is similar. The youngest water is to be found in the upper reaches of the catchment and downgradient CFC and ^{14}C levels decrease indicating older water. Then further downgradient, polluting activities and artificial recharge (in the form of storage dams on the surface, Figure 3.1) alter this pattern. Table 3.1 summarizes this pattern and indicates the nitrate-polluted samples (UVN3 and UV8) in the western catchment (Figure 3.11 to 3.13).

Table 3.1: Leeukuil. CFC, isotope and chemistry changes along the flow path of the western sub-catchment, showing the influence of surface activities.

Western Sub-catchment							
Upgradient → Downgradient						Contamination	
Bh No	DS1	DS2	UVD1	UVN1	RF1	UVN3	UV8
CFC-11 (pmf)	19	14	2	4	-	13	32
CFC-12 (pmf)	33	36	8	8	-	29	52
CFC-113 (pmf)	20	22	4	4	-	85	38
^{14}C (pmc)	101	101	95	96	-	106	100
Tritium (TU)	0.9	0.8	0.3	0.8	-	0.5	0.8
$\delta^{18}O$ (‰ SMOW)	-4.5	-4.4	-4.5	-4.7	-4.1	-3.9	-4.5
Ca (mg/L)	18	28	29	26	16	53	47
Cl (mg/L)	23	26	26	28	15	79	123
NO_3–N (mg/L)	12	2.5	0.9	3.8	1.3	20-31	8.7
DOC (mg/L)	1	<1	<1	<1	<1	1.7	<1

A similar trend is observed for the eastern sub-catchment, but the pattern is not as clearly defined. The flow is indicated along the line LK1, LK2, UV1B and UV2. UV5 is down gradient and shows signs of being contaminated by nitrate and chloride and also shows elevated CFC levels. Table 3.2 shows these changes along the flow path (Figure 3.11 to 3.13).

Table 3.2: Leeukuil. CFC, isotope and chemistry changes along the flowpath of the eastern sub-catchment, showing the influence of surface activities.

Eastern Subcatchment					
Upgradient → Downgradient					**Contamination**
Bh No	LK2	LK1	UV1B	UV2	UV5
CFC-11 (pmf)	18	-	41	20	29
CFC-12 (pmf)	32	-	75	36	59
CFC-113 (pmf)	23	-	35	17	35
^{14}C (pmc)	98	95	108	110	115
Tritium (TU)	0.1	-	1.8	1.9	1.6
$\delta^{18}O$ (‰ SMOW)	-4.5	-4.6	-4.1	-1.6	-3.8
Ca (mg/L)	34	35	29	45	125
Cl (mg/L)	62	66	50	67	215
NO_3 – N (mg/L)	5	4	4	7	55

$\delta^{13}C$ values are between –10 and –12 ‰ PDB (Figure 3.4a), which is a reflection of the grassland vegetation in the area. The exception is –5.8 ‰ for borehole UV5, which is polluted by piggery waste, which is likely to have influenced the ^{13}C value.

$\delta^{18}O$ is uniform along the flow lines throughout between –4.1 and –4.7 ‰ SMOW (Figure 3.5a). Some of the polluted samples show small increases reflecting the addition of evaporated water to the groundwater flow (Tables 3.1 & 3.2). The exceptions are UV2 and N4 at –0.7 and –1.5 ‰, both being fed by nearby surface storage upgradient. In other respects, UV2 does not show any anomaly, while the chemistry of N4 differs completely.

The polluted samples (UV5, UVN3, UV8) are characterised by high nitrate (Figure3.9b) and chloride (Figure 3.8b) levels and associated calcium (Figure 3.7a), magnesium (Figure 3.7b) and sodium (Figure 3.6b). These samples also have significant N_2O levels (semi-quantitatively measured at USGS, Appendix 1, Table 1). The polluted sites are located to the north and downgradient of the piggery on the Leeukuil farm. The piggery disposes of its manure in large dumps. The high nitrate levels in the groundwater can then be deemed the products of seepage from the manure heaps. The high $\delta^{15}N$ level (+28 ‰AIR) and the presence of N_2O in these samples, indicate that denitrification takes place, either in the manure dumps or along the seepage flow path towards the water table. Regretfully there are no dissolved oxygen analyses available to confirm denitrification. The high nitrate level in DS1 is probably a local natural feature since there are no obvious pollution features at present and the ^{15}N content is in the range of natural nitrate (Appendix 1 Table 1).

The transient tracers show some measure of concordance (Figures 3.14 A-F). Radiocarbon does not vary significantly (Figure 3.3B), nor is it expected to since the other tracers all indicate that the water ages are in a region where ^{14}C is hardly likely to change (Figures 3.14C & D). The ^{14}C content is consistent with that of very recent water that has only been slightly diluted with dissolved carbonate (initial ^{14}C content 85-100%). CFC-11 is consistently lower than CFC-12 (Figure 3.14A): a feature found in the other study sites as well. CFC-113 is concordant with CFC-12, except for UVN3 where CFC-113 is contaminated (Figure 3.14B). The comparison of the tracer concentrations with each other (Figures 3.14 A-F) indicates that the piston flow model *per se* is not valid in this area since there are no data points above the exponential model line. For some of the data points the exponential flow model can be valid here. Tritium is in general too low to account for the CFC levels found or conversely, the three CFCs (Figures 3.2A, 3.2B, 3.3A) are too high for the tritium levels found (Figure 3.4B). This feature could be explained by using the piston flow model and assuming that the bomb tritium pulse has been delayed by some 15 years (Figure 3.15).

3.5 Conclusions from this site

The assembled data indicate that the flow system of the two separate sub catchments is essentially as originally envisaged: flow along the gradient in two sub-catchments. The boreholes that were sampled are essentially along the two drainage lines and each can therefore be considered a separate sampling point for the part of the catchment located upstream (Table 3.3). The western sub-catchment shows this feature quite clearly, the eastern one less so, probably because of the low number of samples taken. It can be seen that the entry of pollution rapidly lowers MRT of the water as far as CFC is concerned, but not for tritium. There is clearly some additional water input and much higher pollution input from the manure dumps, but the water from the boreholes is still pre-dominantly flowing in from the south, i.e. from the upgradient recharge zone.

Table 3.3: Calculations of mean residence times (in years) of the water sampled at each borehole in Leeukuil based on the exponential flow model.

	Mean residence time (in years) based on		
Borehole	CFC-12	CFC-113	Tritium
Western sub-catchment			
DS1	50	65	180
DS2	45	60	200
UVD1	250	350	700
UVN1	250	350	200
*UVN3**	*60*	*6*	*350*
*UV8**	*27*	*29*	*200*
Eastern sub-catchment			
LK2	55	55	>500
UV1B	13	32	80
UV2	48	80	70
*UV5**	*22*	*32*	*90*
* nitrate polluted boreholes			

The inconsistency between CFC-11 and the other two CFCs indicates that there is a removal process operative in this aquifer. This inconsistency is also noted at the other two test sites. This has also been found in sites elsewhere in the world and can be related to some removal process in the soils (N Plummer pers comm). Radiocarbon is not sensitive enough as a tracer in Leeukuil since the turnover times are evidently quite short.

The relation between the two short-term tracers, tritium and the CFCs are useful to indicate recent mixing processes. While a few samples, UVD1, UVN1 and UV2 can be described as following the path of EFM which has become very generally used in southern African aquifers a binary mixing model between young and old water is more likely for most of the others (see the dotted lines in Figures 3.14E & F). This binary mixing model is common in pollution situations. The discrepancy of zero tritium and non-zero CFC is also found in the dolomite study sites (see chapter 4.5). Low tritium in the presence of high ^{14}C (>95 pmc) is also observed elsewhere (Verhagen *et al* 2000) and it can be explained as tritium delay relative to CFC by invoking the tritium delay option on MRTMODELS (Figure 3.15). In the case of thick soils and deep water tables, such as in the Kalahari, this seems likely, but in the present study area the influence of the overburden is not expected to be significant. In severely pumped aquifers such as Leeukuil (and also Leeu Gamka), a likely mechanism for CFC enrichment could be the capture of air (and fresh CFC) in the cone of depression during rapid water table fluctuations caused by pumping. The scope of the present project did not allow the investigation of such phenomena in each aquifer.

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CHAPTER 4: CASE STUDY - DOLOMITE SPRINGS

4.1 Geographical setting

Dolomite outcrops are common features in the northern part of South Africa. They have been separated into a number of geological horizons and named accordingly. Colloquially and collectively these rocks are referred to as “the Dolomites”, and this term will be used in this report. The Dolomite springs that were selected are those that occur around Pretoria and westwards to the Upper-Molopo group of springs (between Zeerust and Lichtenburg). The outcrop of Dolomite and the springs that were sampled are shown in Figure 4.1.

The elevation of this area ranges from 1450 mamsl to 1550 mamsl. The climate is moist temperate highveld. Summers are hot and wet, while winters are cold and dry. The average rainfall ranges from 430mm around Zeerust and increases towards Pretoria to around 720mm (Schulze 1997).

Agriculture on the Dolomites is limited to the valley floors where the soil is sufficiently thick for ploughing. Large-scale agriculture (ploughing) takes place on the soils developed on the lavas of the underlying Ventersdorp Group, or on the weathered shales of the over-lying Pretoria Group.

4.2 Geology and hydrogeology

Dolomite outcrops are all part of the Chuniespoort Group, Transvaal Supergroup. Outcrops of the Chuniespoort Group are located all over North-West Province, Northern Province, Mpumalanga and Gauteng and dolomite occurrences occur in different formations (Table 4.1).

The basal formation underlying the Dolomites is quartzites of the Black Reef Formation (Eriksson and Altermann 1998). This forms a reasonably prominent ridge, with surface drainage towards the dolomites. Chert bands are variably common in the dolomite. Various cycles of karst development have resulted in a highly developed network of solution cavities, both above and below the current water-table. Abundant residual chert rubble can be found on the surface. Soils tend to be thin, with many areas having dolomite rock exposed at surface. This rock is angular and has a rough appearance, like elephant-skin.

Table 4.1: 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
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.

Groundwater occurs in fractures as well as in pseudo-karst features of the original dolomite surfaces of which most are presently covered by soils. Parts of the Dolomites are criss-crossed with dykes, which form (generally believed to be impermeable) barriers to water flow. These barriers produce, more or less, isolated compartments, which in the first instance, can be considered as separate water bodies. Flowing springs form at the lowest points of the water levels in these compartments and release considerable quantities of water. These springs feed surface water streams and are utilised for water supplies.

The springs in the Dolomites have been the subject of intensive investigation because of their importance as water sources for the area (Bredenkamp and Vogel 1970, Fleisher 1981, Hobbs 1988, Kronfeld *et al* 1994, Bredenkamp *et al* 1995). The potential for contamination seems great. Isotopes studies so far have suggested that large amounts of water are available, but modelling of the isotope data in terms of the existing conceptual flow models has not been adequate.

4.3 Site selection and sampling

Sampling of a selection of the springs in the context of the present project was undertaken. This sampling followed on an earlier sampling run of a larger selection of springs done during 1997/8 for DWAF where tritium and ^{14}C was analysed. A selection from the known springs was made in order to only utilise those springs that

- ⇨ would have defined flow conditions,
- ⇨ could readily be sampled,

- ⇨ have a minimum potential for contamination during sampling, and
- ⇨ represent a range of ^{14}C and tritium values.

Samples were collected from springs near Pretoria, along the West Rand and from the Upper Molopo area between Zeerust, Lichtenburg and Mafikeng (Table 4.2 and Figure 4.1). Spring waters were sampled using a small battery-driven bilge pump to which copper tubes were attached to feed water to the CFC sampler. Care was taken to place the pump inlet in the water at a point as close as possible to where the water emerges from the rock, thereby excluding the possibility that air (with high CFC content) could enter the sampling system. At times, this necessitated some skin-diving activities.

Table 4.2: Summary of Dolomite spring details.

Spring	DWAF code	Acronym	Geology	Flow rate M m^3/year	^{14}C range 1968-1999 pmc
Olievendraai Oog	D4H017	OLV	Monte Christo	0.2 (est)	103-112
Welgedacht Oog	D4H016	WGD	Eccles	<0.1(est)	94-109
Doornplaat Oog	A3H026	DPL	Eccles	0.7	92-95
Molopo Oog	D4M014	MOL	Eccles	14	79-86
Pretoria Fountains lower		PFL	Eccles	50 (est)	78-82
Grootfontein Oog		GFO	Monte Christo	4 (1959-69)	75-87
Mooirivier Boonste Oog		MRB	Monte Christo	14	72-76
Gerrit Minnebron	C2H011	GMB		9	71-75
Rhenosterfontein	A3H017	RNF	Frisco	0.5	70-75
Elandsfontein	A2H008	ELF	Eccles	1.2	54-89
Maloneys Eye	A2H010	MAL		15	55-57

The analytical data obtained (Appendix 1, Table 2) are based on samples taken during the present sampling run of October 1999. Some (^{14}C and tritium) data from the previous sample runs are also used in the interest of the economical utilisation of analytical resources. This is based on earlier observations that ^{14}C and tritium levels of the spring water varies very little with time (Bredenkamp 2000, Talma and Vogel 2001) and is justified by the consistent results obtained on three of the spring samples (Appendix 1 Table 2). Maps showing the distribution of selected parameters are presented in Figures 4.2 to 4.8.

A potential problem pertaining to CFCs that is unique to the dolomites is the concept of karst and caverns when dealing with groundwater flowing in these structures. In other groundwater environments air is in contact with groundwater at the water table, and CFCs equilibrate with this air. With succeeding recharge events this “parcel” of water is covered with younger water and thus removed from air contact. In a karst cavern which has both air and flowing groundwater there is the possibility that there will be some re-calibration of CFC concentrations with the air. The rate and degree of exchange will be dependant on the time that the air is in contact with the groundwater. If this air is open to the atmosphere it is probable that there will be addition of modern atmospheric CFC. If the cavern is sealed from the atmosphere, then the composition of that air will be in equilibrium with the groundwater. If the cavern is below the water table, then there is no such effect. There are no independent data to assess the likely influence of this effect and the possibility has to be borne in mind.

4.4 Discussion of results

The distribution of chemical and isotopic variations across the dolomites is in the first instance determined by the known (Talma and Vogel 2001) general trend of low ^{14}C (Figure 4.3b) and low ionic content, such as sodium (Figure 4.5a), chloride (Figure 4.5b), sulphate (Figure 4.7a) and alkalinity (Figure 4.8a) in the east, which increases westwards towards the Upper Molopo area. This general feature now seems to be confirmed with tritium (Figure 4.4b) and to some extent with CFC (Figure 4.2a, 4.2b & 4.3a) as well. Pretoria Fountains and Gerrit Minnebron stand out from this distribution with higher concentrations due to pollution from all three CFCs. The presence of pollution in these springs is evident from other parameters as well (Figure 4.5a, 4.5b, 4.7a & 4.7b).

The water quality of the dolomite springs in this area is generally good. The general chemistry is that of pure dissolved dolomite. The main constituents are therefore Ca, Mg and bicarbonate from dissolved dolomite (Figure 4.6a, 4.6b & 4.8a) and small amounts of Na, Cl, and SO_4 from rain or pollution (Figures 4.5a, 4.5b & 4.7a). The exceptions are obvious and can be seen and are noted in Figures 4.9 and 4.10.

^{14}C and tritium relations (Figures 4.3b & 4.4b) are within the bounds expected for an exponential mixing model. There are no signs of piston flow model behaviour since no ^{14}C or tritium values seem to appear in the region above the exponential mixing line in the set of figures of transient tracer relations (Figure 4.11). The ^{14}C vs T and ^{14}C vs CFC-12 relations indicate that the initial ^{14}C contents may vary between 60 and 100% modern.

CFC relations are internally consistent: CFC-11 is lower than expected, a feature also found elsewhere and likely due to some degradation or absorption onto organic matter in the soils or aquifer (Figure 4.11A). CFC-113 and CFC-12 seem very consistent (Figure 4.11B). Some of the springs clearly indicate EFM mixing patterns (Figure 4.11D & 4.11F). The trend of lower CFC-11 (Figure 4.11A) and the consistency of CFC-12 vs CFC-113 (Figure 4.11B) suggest that the tritium vs CFC inconsistency requires a re-examination of the assumptions underlying this relation for some of these spring samples. The dotted lines in figures 4.11 E and F suggest that the binary mixing between a young and an old (with either zero or up to 20 pmf CFC) can also explain this relation. An alternative model could be the PFM with some (10-20 year) delay of tritium built in as suggested in Leeukuil (Figure 3.15).

A comparison between the above results and the time series of ^{14}C obtained during the past 30 years is helpful. This set of measurements was undertaken (Talma and Vogel 2001) to follow the passage of bomb-^{14}C through the aquifers and to test the exponential flow (or other) models as shown in Figure 2.3. The eleven time series of individual springs (Figure 4.12) show considerable variation and do not fit the simple exponential model very well. In some cases a reasonable fit can be made by adjusting the curves of Figure 2.3 with varying initial ^{14}C content and some built-in delays. In other cases there are rapid changes, even within a year or two (e.g. ELF, GFO), which do not fit with a simple flow model. Bredenkamp (2000) has made attempts to apply a variation of a binary mixing model to some of the data using flow rates. This may have potential but needs to accommodate other tracers and chemistry to be more comprehensive.

Pollution of spring water is indicated in different ways. For **Gerrit Minnebron** it has been known that SO_4, Cℓ and Na have increased over the last few decades and this is supported by excessively high CFCs. Yet over the same time the ^{14}C content of the spring water has hardly changed (Figure 4.12B) and the tritium content (0.9 TU) is similar to the other springs. This is likely to be due to waste water or cooling system effluent from nearby gold mines of which only a small amount will cause the high CFC level when added to spring water. In **Pretoria Fountains** the ^{14}C level has shown a distinct increase during the past decade and the tritium content (mean is 3.2 TU) is close to that of modern rainfall and the chloride level has increased steadily over the last few decades (Bredenkamp 2000). This spring therefore has a large component of post-bomb water and the exceptionally high CFC can well be a pollutant in the aquifer (waste water or a gaseous CFC source). **Rhenosterfontein** has shown a major contamination event during 1981 to 1983 when the chloride content of the spring water increased to 75 mg/l and sulphate to 28 mg/l (Bredenkamp 2000). Since then the levels are down virtually to the values of 1980. The cause of this event could be the delayed response of the major recharge events of 1976, or there could have been an agricultural cause (ploughing followed by recharge). During all of this time however the ^{14}C level of the water remained constant at 70 to 75 pmc (Figure 4.12B). The tritium level is presently quite low (0.6 TU) but CFC levels are close to air saturation (64, 68 and 80 pmf). **Grootfonteinoog** is a major water supply source and has shown a recent tendency of increasing nitrate content (Talma and Vogel 2001) which does not fit into the general chemical pattern (Figure 4.9). In this spring, there have not been any significant ^{14}C variations during the past 30 years (Figure 4.12B) while tritium is halfway towards the present-day rainfall amount. The CFC patterns are however not significantly different from other springs that do not show these effects (e.g. ELF, OLV and DPL).

4.5 Conclusions from this site

The data from the different combinations of tracers present somewhat different pictures of the processes determining water flow in each of the springs. The CFCs give an internally consistent picture that follows the prediction of both the exponential and the piston flow model (Figure 4.11A & B). The relations between ^{14}C and both CFC-12 and tritium fit the exponential model and suggest a range of initial ^{14}C contents between 50 and 90% (Figure 4.11C & D). There are no sample points in any of the fields where the exponential and piston flow models yield different results and the piston flow model is therefore not relevant in these aquifers. Mean residence time calculations based on the EFM model show a range of values across the entire region (Table 4.3).

Comparison of the short-term tracers tritium and CFCs show that only two of the springs (MOL and WGD) follow the exponential flow model used here. Some of the others can be explained as either binary mixing between young and old water, or delay of tritium (or advance of CFC). Given that the EFM model is the classic explanation for spring flow (Vogel and Bredenkamp 1970) this observation raises the following questions regarding the flow pattern and isotopic behaviour in the dolomite spring aquifers:

- ⇨ Is there slower transport of tritium and ^{14}C through the vadose zone towards the water table compared to the more rapid gaseous transport of CFC?
- ⇨ Is there a possibility that groundwater has contact with air at some time after leaving the water table. In a classical karst situation one can foresee water flowing through open spaces that can be ventilated by recent atmospheric air. This would cause raising the CFC levels without increasing the tritium level of the water: Reducing the CFC content of DPL, ELF, OLV, GFO and RNF by 20 to 30 pmf would bring the tracer plots exactly on the exponential model curves of Figure 4.11E and F.
- ⇨ Can one perceive the flow to consist of a deep flow through fractures in the solid part of the dolomites and a shallow flow through classic karst environment? This would explain a binary flow pattern of isotope behaviour.

Table 4.3: Mean Residence Time (MRT) results for the Dolomite springs.

Spring	Acronym	MRT CFC	MRT tritium	Flow rate M m^3/year	^{14}C range pmc
Olievendraai Oog	OLV	20	70	0.2	103-112
Welgedacht Oog	WGD	40	60	<0.1	94-109
Doornplaat Oog	DPL	30	120	0.7	92-95
Molopo Oog	MOL	140	170	14	79-86
Pretoria Fountains	PFL	Contaminated	15	50	78-82
Grootfontein Oog	GFO	15	70	4	75-87
Mooirivier Boonste Oog	MRB	55	>500	14	72-76
Gerrit Minnebron	GMB	Contaminated	150	9	71-75
Rhenosterfontein	RNF	12	300	0.5	70-75
Elandsfontein	ELF	20	95	1.2	54-89
Maloneys Eye	MAL	90	>500	15	55-57

The increases of major ions (Cl, SO_4, NO_3, Na) plus ^{14}C and which is correlated with excessively high CFC in Pretoria Lower Fountains and Gerrit Minnebron, are indicative of industrial sources. Whereas the major ion increases in springs in the rural areas (Rhenosterfontein and Grootfonteinoog) is more likely to be due to agricultural activities where there is no contamination source of CFC available.

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CHAPTER 5: CASE STUDY - LEEU GAMKA, KAROO

5.1 Geographical setting

Leeu Gamka is about 74 kilometres south west of Beaufort West. It is situated on the N1 highway and at the confluence of the Leeu River, Koekemoers River and Gamka River. The co-ordinates are about $23^{0}46'$ S and 29^{0} 58' E. The study area comprises a strip of irrigation land about 16 km long and 1 km wide between the N1 highway and the Gamka River (Figure 5.1).

The topography is typically that of the Karoo i.e. flat with gently undulating ground. The main drainage is from north towards the south. The minor drainage is east-west and this direction is controlled by gentle geotechtonic buckling of the strata which has resulted in a series of anticlines and synclines.

The climate in summer is hot and dry, and in winter is cold and generally dry, and can be called semi-desert. Rainfall is low with the annual average being 120 mm/year. Temperatures range from –5 to 40 ^{0}C. Some 50 kilometres to the west are the Nuweveld Mountains, which have a higher rainfall, thus providing river runoff, which is utilised for irrigation. The vegetation type is classified as Nama –Karoo.

Leeu Gamka is not a village in the true sense, but rather a farming community. There are three rail sidings, each of which has attracted a general dealer. There is a hotel, a police station and a 24-hour petrol station. The greater concentration of houses is at Bitterwater where many of the farm-workers have built RDP houses. Bitterwater also has a boarding school. Bitterwater is 3 km off the highway on the Fraserburg road. The population at Bitterwater in 1999 was 1702 (Saayman and Weaver 1999).

Irrigation is confined to the strip of alluvium between the N1 and the river. Water for irrigation is primarily obtained from groundwater with additional water from Leeu Gamka dam (via a canal) and directly from the river. During 1985 (Seward 1987) it was estimated that 638 ha of lucerne (used mainly as fodder for ostriches) and 67 ha of wheat were irrigated and the water usage was as follows:

Surface Water (Leeu Gamka Dam)	0.85 x 10^{6} m^{3}
Groundwater	12.50 x 10^{6} m^{3}

5.2 Geology and hydrogeology

The area is underlain by sandstones and mudstones of the Abrahamskraal Formation, which is the lowest formation within the Beaufort Group of the Karoo Sequence. These rocks have a series of gentle folds trending east-west. The axes of the fold synclines and anticlines are quite closely spaced, with about 30 axes mapped and recorded on the 1:250 000 geological map over the 15km of the study area. The dip of the strata is mostly less than 10º.

A strip of sandy alluvium occurs along the length of the Gamka River. This is on average 7m thick. All irrigation occurs on this alluvium where a large number of boreholes have been drilled. The DWAF hydrocensus of 1986 (Seward 1987) located about 700 boreholes of which 77 were classed as being used for irrigation. Intensive irrigation leads to over-pumping and competition for the groundwater resource. This has in turn lead to attrition of a number of pumping boreholes. At the present time, pumping seems to have settled to sustainable levels with a delicate balance between maximum aquifer yield and cost of pumping and irrigating, and financial returns from farming.

At the present time groundwater flows from the west, from the north and from the east towards the depression caused by heavy pumping of the boreholes along the river (Woodford and Chevallier 2002). It is assumed that under the natural conditions that would have existed prior to wellfield establishment, groundwater would have discharged into the river under a gradient of 1:300. Pumping along the river has now accentuated the gradient to 1:100, increasing the flow, both naturally and currently towards the river. Irrigation with this water has the effect of causing recharge, and thus recycling of the water and with consequent concentration of salts by evaporation. Boreholes BW3, GKF1 and KF1 lie to the west of the strip of irrigated land, and thus upgradient. The main pumpage is from boreholes below the irrigated land, thus these three boreholes are intercepting natural and non-recycled incoming water.

The boreholes used for irrigation are both high-yielding and close to or within the area of alluvium. This does not, however, imply that the alluvium has a controlling influence on the yield. Rather, it is the logistical requirement that boreholes should be close to electricity and the irrigation fields, that resulted in a large number of drilled boreholes, with the higher yielding boreholes selected for use. The boreholes are mostly over 40m deep and many are around 100m or more.

Water quality is quite variable, depending on location, the degree of pumping and the state of annual recharge. Table 5.1 shows how salinity (as EC) varied over a two-year period. Some of these waters would not normally be considered suitable for irrigation, especially in the Karoo. However, the sandy alluvium, plus the tolerance of lucerne towards higher salinity water, enables these waters to be used successfully for irrigation.

Table 5.1: Leeu Gamka. Variations of water and EC over a two-year period (From Woodford and Chevallier 2002, adapted from Seward 1987).

Borehole No.	Sep-Nov 1985		Jan 1986		1987	
	EC (mS/m)	Waterlevel (mbgl)	EC (mS/m)	Waterlevel (mbgl)	EC (mS/m)	Waterlevel (mbgl)
AL31	157	14.84	198	5.17	102	11.94
AL37	214	9.18	227	7.49	202	11.72
BY10	110	19.92	99	9.91	133	11.78
GN42	73	16.75	58	5.36	73	10.00
SN7	311	8.43	200	8.61	286	13.83
SN16	67	20.13	67	19.89	69	20.69
VR6	137	35.85	214	13.50	101	29.72
VR20	100	22.70	112	18.08	112	20.47
WD9	156	33.46	314	13.69	154	18.50
WD37	118	35.77	106	14.95	73	24.00

5.3 Site selection and sampling

Three site visits were made. The first visit in 1999 was to evaluate the existing water supply of Bitterwater Village (Saayman and Weaver 1999). The local council planned to build an additional 50 RDP houses, and wished to know if the water resource could support this expansion. Our conclusion was that there is sufficient groundwater available. Two boreholes were sampled for water quality during this investigation.

The second visit was made in March 1999 to assess the suitability of Leeu Gamka as a research site for the present project. Three boreholes were sampled for chemistry, ^{18}O, deuterium and tritium. A number of boreholes were assessed for the suitability to collect samples for CFC analysis. The presence of tritium in all three of these samples, plus the description of Seward (1987) indicated that Leeu Gamka would be a suitable research site. A few days after the second site visit, a major rainstorm occurred. The rivers were in full flood and the N1 highway was temporarily closed. A sample of this peak-flow was collected and is listed as LGR1 (Table 3 in appendix 1: sampling date 10 March 2000).

The full CFC and isotope sampling run was undertaken in July 2000. The sampled boreholes and river sampling sites are shown on Figure 5.1. The analytical results are shown in Table 3 of Appendix 1. Some CFC ampoules were lost during transport of these samples to the US. There are therefore only single ampoule CFC results for KF2 and LG3 (see Appendix 2). Maps showing the distribution of selected parameters are presented in figures 5.2 to 5.11.

5.4 Discussion of results

Figure 5.2a, 5.2b and 5.3a. These three CFC results generally support the conceptual flow model of older water (low CFC) flowing towards the wellfield zone. Thus boreholes BW3, GKF1 and KF1 which are west of the irrigated lands have low CFC concentrations. Boreholes within the irrigation area (hereafter referred to as mixed waters) have higher CFC values. GH2 is obviously contaminated with only CFC-12 (at 551 pmf) much too high. Boreholes GH1, GKF2, KF2 and KF3 have CFC-12 at or above 100 pmf and higher than the other two CFCs. These appear to be the results of some form of contaminated groundwater. It implies that the excess CFC-12 above CFC-11 and CFC-113 is some measure of the recycling of water in this area. The river water entering the area (LGR3) shows the same excess, while that leaving the area (LGR2) has lost the excess and has equilibrated with present-day atmospheric CFC levels.

Figure 5.3b. Radiocarbon shows a similar pattern to CFC. The incoming groundwater is older (^{14}C: 75, 83 and 72 pmc). The mixed water with ^{14}C ranging from 102 to 112 pmc indicates that either younger water has been added or that modern carbon has been added while infiltrating. RF1 can also be called incoming and “natural” water, but the ^{14}C signature at 104 pmc, indicates it is not as old as the other incoming waters.

Figure 5.4a. The ^{13}C signature for the two river samples (LG2 and LG3) is distinct from the groundwater. The boreholes with older groundwater have δ^{13}C of –16 to –18‰, while the mixed waters range from –15 to –13 ‰PDB.

Figure 5.4b. The tritium distribution confirms the CFC and ^{14}C distribution. Note that the river water at 2.7 and 2.5 TU appears to be “older” than some of the mixed groundwater samples.

This is likely due to a local tritium low due to the heavy rainfalls of March 2000 that preceded the sampling trip of June 2000.

Figure 5.5a. The $\delta^{18}O$ signature for three older water boreholes is slightly lower (-4.3, -3.5 and -3.6 ‰) than the mixed water which range from -3.4 to -2.5 ‰. The two river samples of June 2000 (LGR2 and LGR3) also show slight evaporative patterns. Note the LGR1 at –6.4 ‰ is the sample taken when the river was in full flood in March 2000.

Figure 5.5b. The DOC of the older groundwater, including RF1 are all low to zero, whereas the mixed water all show appreciable DOC. Not unexpectedly the 3 river samples all have high DOC.

Figure 5.6a. The older and uncontaminated water shows potassium at 2.1 to 3.7 mg/L, while that of the mixed groundwater ranges from 4.2 to 9.0 mg/L. It can be argued this is due to the generally elevated salinities of the mixed groundwater. These higher salinities are presumably due to recycling of the water with evaporation and concentration of the salts. Comparing the ratio K:TDS x 1000, these vary between 2.1 to 6.1 with no trend apparent, i.e. one cannot distinguish older from mixed groundwater. Comparing the ratio K:Ca x 1000, there is a trend of depleted K for the mixed groundwaters, probably due to removal of K by the crops.

Figures 5.6b, 5.7a, b, 5.8a, b, 5.9a. These figures of Na, Ca, Mg, SO_4, Cl and alkalinity show similar distributions of higher values related to higher salinities. The pattern is complex with ratios being quite variable.

Figure 5.9b. Silica for all boreholes except KF2 is 11 to 13 mg/L. Of note is that for river low-flow conditions silica is quite low at 2.4 and 4.7 mg/L. It is assumed that this is partially due to micro-organisms depleting silica. In comparison the flood-flow water sample shows 9 mg/L of silica, indicating a high component of groundwater. Another possible explanation is that during low-flow conditions the silica is in the colloidal state and is “bouncing” along the river-bed river-water interface, and our sampling only sampled the mid-water, missing this silica (pers comm. P. Ashton). During flood-flow the turbulent conditions caused thorough mixing, and the 9 mg/L is a reflection of the groundwater and surface overland flow mixture, ie 3 parts groundwater at 12 mg/l plus 1 part overland flow water at 0 mg/L.

Figures 5.10a, b. Boreholes having groundwater with reducing conditions (the presence of both H_2S and ammonia) are found both in the older water group and the mixed water group. Boreholes with oxidising conditions, i.e. nitrate present, are also found in both groups.

Figures 5.11a, b. No apparent pattern is noted.

Figures 5.12 A to F. There does not appear to be a relation between CFC-11 and CFC-12 as noticed in the other test sites. Evidently there is another source of CFC-12. CFC-11 is very roughly proportional to CFC-113, so the absorption mechanism for CFC-11 found in the other two test sites is also present here. The combination of tracers also suggests a separation of the 'old' and 'mixed' water types. These suggest the young waters are close to atmospheric ^{14}C content, i.e. little dilution by soil carbonate, while the old waters show initial ^{14}C contents of 70-80%. The tritium, ^{14}C and CFC-113 levels are concordant with an exponential mixing model. Exceptions are KF1 and GKF1 and KR1. There are a few significant tritium values against quite low CFC-113 and CFC-11 levels: quite the opposite of some of the samples from Leeukuil and the Dolomite springs.

Figure 5.13. ^{13}C distributions support a clear grouping between the old waters, the river water and the mixed water samples.

Figures 5.14 and 5.15. Mixing lines between DOC, sulphate and chloride support the concept of gradual salinisation of the borehole water. River waters do not fit this trend.

Figure 5.16. Chloride indicates the same clear separation between the old and mixed water. Again RF1 and KF1 do not appear to be part of this pattern.

5.5 Conclusions from this site

The data obtained in this project at Leeu Gamka clearly support the model of salinisation on the alluvial lands along the Leeu Gamka River due to agricultural activity. The 'old' waters are coming from the west (BW3, GKF1, KF1) and are typified with reducing conditions, low levels of the recent tracers and low salinity. In the Leeu Gamka river agricultural lands enrichment of the salt levels occurs due to recycling of agricultural water. The activity of farmers pumping groundwater and irrigating fields, (with the addition of some surface water from the Leeu Gamka dam) results in concentrations of salts, aeration of the water and an increase of salinity. The ^{14}C

"clock" is reset and CFC-12 increases to above 100 pmf during (sprinkler) irrigation and when the water percolates through the soil horizon.

Supporting this conceptual model is ^{13}C, which for the "natural groundwater" is about –16 to –18, while for the mixed water is about –15 to –13‰. However CFC-11 and CFC-113 appear not to be affected by this irrigation/percolation cycle. Some of this mixed water is reduced as is evident from the low dissolved oxygen level and the presence of NH_4 and H_2S (Table 5.2 and Appendix 1 Table 3). The heterogeneity of chemical parameters in close proximity to each other is likely to be the result of different depths of the boreholes and nature of the fracture system below the alluvium.

Table 5.2: Leeu Gamka. Summary of tracer results.

SOURCE	CFC-11 pmf	CFC-12 pmf	CFC-113 pmf	Tritium TU	^{14}C pmc	Cl mg/l	SO_4 mg/l	DO mg/l
Old water								
BW3	5	23	7	1	75	43	74	2.1
KF1	0	4	0	1.1	72	63	158	0.5
GKF1	1	20	3	2	83	163	533	0.4
Mixed water								
KF3	51	90	67	2.8	112	285	291	1.3
GKF2	42	125	78	2.4	108	413	540	0.6
GH2	52	551	55	3	109	469	620	1.0
KF4	62	98	66	3.2	111	594	890	1.9
GH1	42	125	48	2.5	102	609	708	2.0
KF2	22	122	70	2.2	105	780	537	0.5
River water								
LGR3 entering	9	111	31	2.5	106	543	480	5.8
LGR2 leaving	85	99	94	2.7	110	638	667	6.4

In general one can see that there are a number of samples with CFC values in excess of 100 pmf (Table 5.2). By our definition of pmf (percent modern freon) this could indicate either a wrong temperature used for the calculation, which can account for discrepancies of 10-20% (Figure 1.2). The relational data of figure 5.12 suggest that there is a measure of CFC-12 added to these samples. The excessively high 551 pmf for CFC-12 in GH2 is due to contamination in the water from either air-conditioning equipment, aerosol cans, or something similar. GH2 is closest to an irrigation dam, it also has the highest ^{18}O content and show the greatest variation between the two sampling runs (Appendix 1 table 3): factors which increase the possibility that the water in this borehole is shallow and subject to contamination. The consistent appearance of CFC-12 at 120 pmf is also likely to be a temperature effect during winter recharge for instance, since a consistent contamination effect of exactly 20% above the modern value for all three boreholes is unlikely. Whatever the reason for the CFC-12 anomaly, it destroys any concordance between CFC-12 and the other tracers (Figure 5.12). The other tracers indicate a general concordance and support the application of the exponential mixing model in this area.

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CHAPTER 6: CONCLUSIONS

6.1 Using CFCs, isotopes and chemistry to identify and quantify mixing

Three groundwater mixing models have been considered, namely a zero mixing (piston flow) model, a binary mixing model (two end members) and the multi-input (exponential flow) mixing models.

A zero mixing model is a model where the parcel of water that originally enters the aquifer is essentially the same as the one that is sampled. The only changes are chemical evolution and radioactive decay. This model is called the piston flow model (Figure 2.2). The dispersion model has not been used here due to a lack of suitable data to describe the dispersion process.

The binary mixing model is one for which two waters of differing ages or chemical composition are mixed and two end members can be used to define the degree of mixing. This model requires that the two end-members can be defined (by sampling and analysis, or by theory). It is often used for pollution studies where the chemistry of the natural incoming water and that of the polluted groundwater are defined and different, but the ages are not necessarily different. Previously the project team successfully used this model to distinguish older deep-flowing groundwater from shallow seated younger groundwater in the quartzites of the Table Mountain Group at Agter- Witzenberg (Talma *et al* 2000, Cavé *et al* 2002). There are some data from Leeukuil and form the Dolomites that suggest a measure of binary mixing to be applicable.

The more complex model is the exponential flow model for which water enters the water-table over the entire flow path (Figure 2.2). This model is commonly applied to phreatic or unconfined aquifers, which are usually porous rock aquifers. Fractured rock aquifers in Southern Africa have mostly been perceived to be semi-confined to confined aquifers. For igneous and higher-grade metamorphic geologies the conceptual groundwater flow model is that geochemical evolution has resulted in a highly weathered upper zone (regolith) overlying a weathered and fractured zone which grades into virtually solid fresh bedrock. The hydraulic conductivity of the weathered /fractured zone is one or two orders of magnitude greater than the regolith which usually has a high clay content. Even the lower grade metamorphism geologies, such as the argillaceous formations of the Karoo, exhibit these features, with higher yielding water-strikes generally being deeper rather than shallow. For these fractured rock aquifers it has generally been considered that the exponential flow model is more applicable.

This programme of CFC research has indeed demonstrated that the piston-flow model is unlikely to be applicable for fractured rock aquifers (Southern African version thereof). The combined use of CFCs, isotopes and chemistry has shown that the exponential mixing model can be used in many applications, namely for the Dolomites, for a granite/gneiss aquifer and for a Karoo sandstone. A binary (two-component) mixing model was found appropriate in one earlier study in the TMG quartzites (Talma *et al* 2000) and could also be applicable to Leeukuil and some of the Dolomite spring compartments. Without the inclusion of CFCs this increased complexity would not have been known.

6.2 Using CFCs, isotopes and chemistry to identify contamination of groundwater

Excessive levels of CFCs (above 100 pmf) indicates contamination. This contamination can be either during the sampling procedures, or it can be anthropogenic contamination of groundwater.

The sampling and analysis protocol is designed to indicate whether contamination has occurred during sampling or from the equipment. The sampling procedure involves extensive flushing of the sampling equipment before the glass ampoules containing water are sealed. Laboratory analysis is done on a series of ampoules in sequence. Contamination during sampling would be indicated by a steady decrease of all the CFC levels during the analysis (from ampoule 1 to 6). Only in Leeukuil borehole UVN3 (see Appendix 2 Table 1 and Figure 3.14B) can this be seen for CFC-113. This value is therefore suspect, but, incidentally, is derived from a borehole contaminated by high nitrate. The other CFC samples collected appear to represent the CFC level of the water in the borehole or spring. Finality would be obtained if questionable boreholes could have been sampled repeatedly, but that was beyond the capabilities of the present project.

In so far as the present limited data set could be considered as representative, it appears that different pollution events generate varying CFC profiles, as expressed in the ratios of the three CFCs. Viewing the 'fingerprints' of all CFC samples one can see specific patterns (Figure 6.1). The Leeu Gamka site yields a peak pyramid pattern indicative of added CFC-12 as is also evident from other plots from the area (Figure 5.12). This sharp pyramid is also evident in Leeukuil, an agricultural situation as well. The flatter pyramid is evident in the Dolomite springs and a few Leeu Gamka boreholes. Very likely these represent unpolluted samples. Two of thee Dolomite springs, known to be influenced from the city and from mine waste show the upside down pyramid typical of CFC-12 depletion.

Combining CFCs with macro chemistry has proved very useful in detecting or confirming, examples of low levels of pollution, either high or low CFC-12 contributions. In the Dolomite springs, Pretoria Lower Fountains and Gerrit Minnebron, the contaminant has relatively low CFC-12 content compared to CFC-11 and CFC-113, while in Leeu Gamka and two other dolomite springs (Rhenosterfontein and Grootfontein Oog) CFC-12 dominates (Figure 6.1). The reason could be found in the fact that CFC-12 was, and frequently still is, the more generally used halocarbon for aerosol cans and air-conditioners, while CFC-11 and CFC-113 have generally been used in more specialised refrigeration plants, industrial cleaning and fire extinguishers. Different CFC patterning in various polluted environments have been noted elsewhere (Plummer and Busenberg 2000). This is attributed to either atmospheric releases that end up in water, direct leakage of CFC from storage tanks or transport of CFCs adsorbed on organics from waste waters.

6.3 Loss of CFC-11

In general there seems to be a loss of CFC-11 in the groundwater compared to the other two gases. Loss of CFC-11 can be caused by the tendency of CFC-11 to be reduced in anoxic environments or be adsorbed on organic matter in the aquifer (Plummer and Busenberg 2000). This is considered not applicable in our study areas since we deal with well-aerated waters and the organic content of our soils and aquifer materials is low. In situations of deep water table where there is a long diffusion path for atmospheric CFC to reach the water table, there is a tendency for CFC-11 to be retarded (Weeks *et al* 1982, Cook and Solomon 1995). This is also unlikely since recharge in both Leeukuil and the Dolomites should be quite rapid given the shallow sub-outcrops. A possibility is that there are local anoxic pockets in the aquifer where CFC-11 is reduced. However this phenomenon of lower than expected CFC-11 has also been reported from the USGS investigations (Plummer pers comm), and is thus accepted as being usual.

6.4 Achievement of the aims of the project.

The aims of this current project as proposed to the WRC in 1998 were:

- ⇨ to develop a method of integrating and analysing groundwater age data provided by ^{14}C, CFC-11, CFC-12, CFC-113, tritium and other isotope analyses so that groundwater mixing ratios for fractured rock aquifers can be determined.
- ⇨ to investigate the application of these mixing ratios to groundwater resource evaluation so that the reliability of these evaluations can be refined.

The mixing ratios referred to are the relative contributions of different recharge years to the water balance of an aquifer. An Excel© workbook was set up to handle the input of the five tracers (^{14}C, tritium, CFC-11, CFC-12 and CFC-113) into a piston flow and an exponential flow model to model the behaviour of these tracers. Various graphic representations were employed to display model and sample data in different ways that can provide information of the processes occurring underground. The graphs that have been developed give an indication of the various tracer relations applicability for some simple (exponential or piston) flow models. These activities satisfy the first aim.

A number of groundwater, spring and river water samples have been collected from three study sites, (Leeukuil near Pietersburg, Leeu Gamka in the Karoo and from the Dolomite springs in Gauteng and Northwest Province) which have fractured rock aquifers with different geology. The samples have been analysed for a variety of CFCs, isotopes and chemical parameters. These have indicated various processes occurring in the groundwater systems. In a number of situations the different data sets provide consistent interpretations. In other situations, the simple models envisaged here, are clearly not sufficient. These activities address the second aim of the project.

The team has not been able to establish a general algorithm whereby all three aquifers can be evaluated. Each situation requires an approach that is suitable to the conceptional hydrogeology of the aquifer and its specific flow distribution pattern.

The overall aims of the project as formulated in the agreement between the WRC and the CSIR have been met.

6.5 Costing of multi-tracer investigations

To undertake collection of the full suite of determinants, analysis and data evaluation is a reasonably expensive exercise. Aside from the cost of analysis, the need to collect CFCs samples using specialised equipment does increase the cost. CFC analyses have been done at no charge for the present project, due to the kind offices of the USGS. Semi-commercial laboratories will undertake CFC analyses, for which the cost is about the same as for tritium analyses.

An example costing using 2002 costs is estimated below. These are based on the assumptions that, the site is reasonably accessible from Gauteng (where the sampling equipment is housed), the boreholes are production boreholes equipped with accessible sampling points and there are more than 10 boreholes to be sampled. If any of these do not apply then the estimated cost per borehole will be higher. The costing per borehole is:

⇨ Sample collection	R1 500 to R2 000
⇨ Chemistry analysis	R600
⇨ ^{14}C and ^{13}C	R1 200
⇨ tritium	R1 500
⇨ CFC	R1 500
⇨ ^{18}O and D	R400
⇨ Total cost per sample is about	R6 500 to R7 000
⇨ Data analysis and reporting	about R20 000

Thus an exercise involving 10 to 12 boreholes will be the order of R85 000 to R104 000. While this is a significant addition to the borehole establishment; it improves the value derived from borehole exploration considerably.

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CHAPTER 7: RECOMMENDATIONS

1. The use of CFCs, isotopes and chemistry is recommended to be more commonly applied in Southern Africa. The combined use of CFCs, isotopes and chemistry enables one to conclude with some degree of certainty which one of the three mixing models is applicable to a study. Thus for a regional or local aquifer which has a high degree of importance and for which proper management is needed, we recommend that a program of investigation be included. This would include the suite of sampling, analysis and data evaluation processes as demonstrated in the present project. Proper management of an aquifer implies that the flow system is understood, and this would include an understanding of mixing processes. The estimated cost (2002 prices) for such an exercise is about R85 000 to R104 000. If one considers such a price in relation to the cost say for drilling extra boreholes, or the cost of incorrect management decisions, this is acceptable

2. The spreadsheet flow model MRTMODELS described in Chapter 2 needs to be improved. One aspect is to incorporate the fact that recharge in the arid zone can vary from year to year and this should be incorporated as a separate data set.

3. CFCs can be used as an early warning system for detecting anthropogenic pollution of an aquifer. This project has highlighted a few cases where CFCs are elevated, but other pollution indicators are barely above normal concentrations. For sensitive and strategically important water-supply sources it is recommended that regular sampling for CFCs are carried out in order to provide early warning of pollution.

4. Lack of knowledge of the regional distribution of tritium in modern and past rainfall has hampered the usefulness of tritium as a tracer for mixed water. An evaluation of the past distribution of tritium in rainfall is required.

5. More data of the present day distribution of tritium in rainfall is required. A sampling and analysis programme throughout the country is necessary, to supplement the data obtained from the IAEA GNIP programme (IAEA 2001).

6. An evaluation of the effective tritium content of recharge is required. This should be based on the rainfall data base and accommodate the selectivity of recharge events in our arid region.

7. Good reports are received of the use of the tracers $^3H/^3He$ and SF_6. These are less susceptible to sample contamination and have been used in some published investigations with success. Particularly $^3H/^3He$ will be able to assist in unravelling the complexities of the tritium input during recharge. $^3H/^3He$ was not affordable to us for the present project and the analytical technology for SF_6 was not well enough developed when the project commenced. We recommend that these techniques be applied in any further studies of this nature.

8 Numerical groundwater models should be developed or adapted to incorporate these short-lived tracers. The first attempt by the ETH Group (Switzerland) in Palapye, Botswana, (Schaffner *et al* 2000) seems promising and should be followed up with additional and appropriate case studies.

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Appendix 1

CFC’s, isotopes and chemistry data list

- ⇨ **Leeukuil**
- ⇨ **Dolomite springs**
- ⇨ **Leeu Gamka**

Appendix 1 Table 1 Leeukuil: Table showing CFC, isotope, chemistry and field data

Borehole No	DS1	DS1	DS1	DS2	UVD1	UVD1	UVN1	UVN3	UVN3	UV8	RF1	LK1	LK2	UV1B	UV2	UV5	N4 BH	N4 Dam
Date of Sampling	20/04/99	06/10/99	01/12/99	02/12/99	21/04/99	07/10/99	08/10/99	08/10/99	01/12/99	01/12/99	21/04/99	20/04/99	08/10/99	01/12/99	07/10/99	30/11/99	21/04/99	21/04/99
CFC and Isotope Data																		
CFC-11 pmf	-	19	-	14	-	2	4	13	-	32	-	-	18	41	20	29	-	-
CFC-12 pmf	-	33	-	36	-	8	8	29	-	52	-	-	32	75	36	59	-	-
CFC-113 pmf	-	20	-	22	-	4	4	85	-	38	-	-	23	35	17	35	-	-
Tritium in TU	-	0.9	-	0.8	-	0.3	0.8	0.5	-	0.8	-	-	0.1	1.8	1.9	1.6	-	-
^{14}C pmc	-	101.4	-	100.7	94.9	95.8	95.5	106.3	101.4	100.0	-	94.7	97.6	107.8	110.5	115.1	-	-
δ^{13}C ‰PDB	-	-11.9	-	-10.8	-9.9	-9.0	-11.4	-10.6	-11.9	-10.5	-	-10.6	-9.3	-8.4	-9.8	-5.8	-	-
δ^{18}O ‰SMOW	-4.54	-4.55	-4.56	-4.35	-4.5	-4.48	-4.72	-4.13	-3.7	-4.47	-4.08	-4.6	-4.48	-4.14	-1.65	-3.77	-1.52	-1.87
δD ‰SMOW	-22.4	-24.2	-22.4	-22.0	-22.4	-24.0	-24.5	-18.8	-19.0	-23.5	-18.8	-23.6	-23.5	-20.3	-10.3	-20.0	-8.0	
^{15}N ‰AIR	-	-	8.8	-	-	-	-	-	27.2	-	-	-	-	-	-	28.3	-	-
Chemistry Data																		
Potassium as K mg/L	4.8	4.9	4.6	2.1	4.7	4.9	1.5	2.8	3.0	2.5	1.5	3.7	3.8	2.7	2.3	3.5	2.7	3.8
Sodium as Na mg/L	35	34	36	82	88	87	66	101	117	97	67	53	50	112	112	130	92	24
Calcium as Ca mg/L	17	18	17	28	29	29	26	52	78	47	16	35	34	29	45	125	40	7.6
Magnesium as Mg mg/L	15	15	15	16	20	20	16	34	49	31	10	27	25	20	28	74	26	3.7
Ammonia as N mg/L	<0.1	-	-	-	<0.1	-	-	-	-	-	<0.1	<0.1	-	-	-	-	<0.1	0.39
Sulphate as SO_4 mg/L	12	11	12	7	4.5	3.7	3.8	16	29	20	13	9.6	7.5	13	22	44	5.4	3.3
Chloride as Cl mg/L	23	23	25	26	26	28	28	79	136	123	15	66	62	50	67	215	18	5.9
Alkalinity as $CaCO_3$ mg/L	96	97	97	261	307	306	220	304	324	234	187	198	187	296	336	363	371	71
Nitrate plus nitrite as N mg/L	12	12.2	10.2	2.5	0.97	0.91	3.9	19.6	31	8.7	1.3	4.4	5.1	4.2	6.6	55	0.36	0.57
N_2O (USGS)	-	med	-	med	-	0	trace	large	-	Vlarge	-	-	small	small	small	large	-	-
Fluoride as F mg/L	0.14	0.18	0.16	0.44	0.39	0.41	0.39	0.33	0.31	0.31	0.54	0.20	0.23	0.42	0.39	0.27	0.33	0.21
Lithium as Li mg/L	0.10	0.10	0.1	0.05	0.04	0.47	0.57	0.58	0.06	0.05	0.04	0.05	0.53	0.06	0.64	0.07	0.05	<0.01
Silica as Si mg/L	24	28	29	28	23	28	29	31	30	32	26	24	30	31	29	32	26	6.1
Strontium as Sr mg/L	0.15	0.16	0.13	0.18	0.25	0.27	0.18	0.42	0.59	0.37	0.2	0.24	0.25	0.29	0.39	0.86	0.29	0.1
Dissolved Organic Carbon mg/L	1.0	<1	<1	<1	<1	<1	<1	<1	1.7	<1	<1	<1	<1	<1	1.0	1.9	2.4	30
Conductivity mS/m (25°C)	40	40	39	60	66	66	54	97	126	94	43	64	60	76	90	172	73	18
pH (Lab)	7.0	6.8	6.7	7.2	7.9	7.9	7.3	7.5	7.4	7.2	8.1	7.5	7.4	7.2	7.4	7.2	7.9	8.1
Saturation pH (pHs) (20°C)	8.4	8.3	8.4	7.7	7.6	7.6	7.8	7.4	7.2	7.6	8.1	7.8	7.8	7.7	7.4	7.0	7.4	8.8
Field Parameters																		
Field temp	-	21.4	-	-	-	-	22.4	21.4	-	21.4	-	-	21.6	22.5	23.2	-	-	-
Field pH	-	6.5	-	6.9	-	7.1	6.9	7.0	-	7.0	-	-	6.9	6.7	-	6.8	-	-
Field alk (meq/l)	-	-	-	4.9	-	-	4.3	-	-	4.5	-	-	-	6.6	6.1	-	-	-
Field DO (mg/l)	-	3.4	-	-	-	3	1.2	2	-	4.4?	-	-	4.3	-	2.3	-	-	-

- Denotes not measured

Analytical precision (1-sigma) of a tritium analysis is 0.2 TU
Analytical precision (1-sigma) of 14C analyses range between 0.4 and 0.6 pmc

Appendix 1 Table 2 Dolomite springs: Table showing CFC, isotope, chemistry and field data .

Borehole No	DPL	ELF	GFO	GMB	MAL	MOL	MRB	OLV	PFL	RNF	WGD
Date of Sampling	19/10/99	29/10/99	18/10/99	28/10/99	28/10/99	19/10/99	28/10/99	18/10/99	29/10/99	19/10/99	20/10/99
CFC and Isotope Data											
CFC-11 pmf	34	53	48	254	18	12	27	56	3763	64	22
CFC-12 pmf	55	64	80	135	22	15	33	77	1006	80	35
CFC-113 pmf	35	48	54	142	14	9	23	49	8391	68	25
Tritium in TU*	1	1.6	1.9	1	0.3	0.9	0.1	1.9	3.3	0.6	2.1
Tritium in TU	1.4	1.4	-	-	-	-	-	-	3.1	-	-
^{14}C pmc *	95.3	66.3	85.4	74.2	57.5	82.2	76	106.3	81.2	71.7	99.3
δ^{13}C ‰PDB*	-8.6	-11.2	-7.6	-7.8	-7.7	-7.1	-6.6	-9.3	-9.2	-8.2	-9.2
δ^{18}O ‰SMOW	-4.41	-4.12	-4.7	-3.4	-4.74	-5.3	-4.49	-3.79	-3.58	-5.2	-4.48
δ^{18}O ‰SMOW*	-4.44	-4.32	-4.84	-3.49	-4.56	-5.02	-4.7	-4.07	-3.92	-5.25	-4.94
δD ‰SMOW	-23.6	-20	-24.8	-16.1	-26.4	-26.4	-26.7	-20.9	-18.6	-28.5	-25.1
Chemistry Data											
Sodium as Na mg/L	2.0	3.0	5.4	19	2.4	1.3	3.5	5.3	11	12	2.4
Calcium as Ca mg/L	55	25	67	68	26	42	46	71	46	51	61
Magnesium as Mg mg/L	31	15	34	41	16	26	27	42	28	27	35
Sulphate as SO$_4$ mg/L	6.0	2.5	3.2	128	2.9	0.8	2.4	9.2	13	11	4.8
Chloride as Cl mg/L	3.7	2.3	5.0	22	3.0	2.3	2.4	7.4	23	16	4.3
Alkalinity as CaCO$_3$ mg/L	256	122	280	206	130	211	227	332	193	218	293
Nitrate plus nitrite as N mg/L	0.7	1.3	5.8	2.8	0.4	0.6	1.0	0.9	3.0	1.1	0.4
Fluoride as F mg/L	0.15	<0.1	0.14	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	1.3	0.15
Lithium as Li mg/L	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Silica as Si mg/L	6.8	8.6	10.6	8.3	6.7	6.1	7.5	8.2	9.0	6.3	6.0
Strontium as Sr mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Dissolved Organic Carbon mg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Conductivity mS/m (25°C)	49	25	57	70	26	41	42	65	47	49	55
pH (Lab)	7.7	7.3	8.0	7.4	7.8	8.1	7.6	7.5	7.9	7.8	7.6
Saturation pH (pHs) (20°C)	7.7	8.3	7.6	7.7	8.2	7.8	7.8	7.5	7.9	7.8	7.6
Field Parameters											
Field temp*	20.1	18.9	20	19.7	19.8	21.7	19.8	19.8	20.8	21.8	19.7
Field pH*	7.0	7.2	7.1	7.3	7.5	7.5	7.3	7.0	7.3	7.2	7.0
Field alk (meq/l)*	5.9	2.6	5.85	4.1	2.7	4.8	4.8	7.7	3.8	4.5	5.9
Field DO*	3.6	6.3	5.7	5.8	5.3	7.2	5.5	2.5	5.1	4.6	1.8

Items marked with * were collected and analysed during sampling runs in 1997 and-1998

\- Denotes not measured

Analytical precision (1-sigma) of a tritium analysis is 0.2 TU
Analytical precision (1-sigma) of 14C analyses range between 0.4 and 0.6 pmc

Appendix 1 Table 3 Leeu Gamka: Table showing CFC, isotope, chemistry and field data .

Borehole No	BW1	BW3	BW3	BW3	GH1	GH2	GH2	GKF1	GKF1	GKF2	KF1	KF2	KF3	KF4	KR1	RF1	LGR1*	LGR2*	LGR3*
Date of Sampling	06/04/99	06/04/99	01/03/00	05/07/00	06/07/00	01/03/00	11/07/00	01/03/00	06/07/00	10/07/00	07/07/00	07/07/00	10/07/00	10/07/00	07/07/00	10/07/00	10/3/00	11/07/00	11/07/00
CFC and Isotope Data																			
CFC-11 pmf	-	-	-	5	42	-	52	-	1	42	0	22	51	62	6	56	-	85	9
CFC-12 pmf	-	-	-	23	125	-	551	-	20	125	4	122	90	98	35	93	-	99	111
CFC-113 pmf	-	-	-	7	48	-	55	-	3	48	0	70	64	66	3	78	-	94	31
Tritium in TU	-	-	1.3	0.7	2.5	4.4	3.0	2.5	1.6	2.4	1.1	2.2	2.8	3.2	2.6	2.9	3.0	2.7	2.5
^{14}C pmc	-	-	-	74.7	102.4	-	109.3	-	82.7	107.9	71.6	105.1	112.1	111.3	108.3	103.7	-	110.2	105.8
δ^{13}C ‰PDB	-	-	-	-16.8	-18.4	-	-15.4	-	-17.8	-13.8	-15.9	-12.9	-13.5	-13.3	-15	-13.3	-	-8	-6.2
δ^{18}O ‰SMOW	-	-	-3.92	-3.59	-3.33	-1.42	-2.63	-3.35	-3.48	-3.38	-4.33	-3.35	-4.75	-2.87	-2.54	-4.99	-6.37	-2.94	-3.22
δD ‰SMOW	-	-	-22	-21	-24	-5	-17	-16	-21	-21	-26	-22	-32	-20	-17	-34	-43	-20	-23
Chemistry Data																			
Potassium as K mg/L	2.1	2.1	2.1	2.2	5.2	5.4	4.8	3.8	4.2	4.9	3.7	7.6	7.3	6.8	9.0	2.4	8.3	9.5	8.2
Sodium as Na mg/L	117	65	64	63	476	516	450	368	388	336	154	404	280	638	1213	71	111	538	369
Calcium as Ca mg/L	65	73	70	69	255	249	205	71	84	214	45	164	132	215	261	89	79	162	143
Magnesium as Mg mg/L	5.0	10	10	10	59	69	55	3.0	3.3	43	2.9	43	25	64	78	15	25	66	63
Ammonia as N mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.35	0.55	<0.1	0.59	0.35	0.10	<0.1	0.66	<0.1	0.4	<0.1	<0.1
Sulphate as SO_4 mg/L	130	74	78	74	708	785	620	408	533	540	158	537	291	890	1475	95	150	667	480
Chloride as Cl mg/L	73	45	44	43	609	551	469	210	163	413	63	481	285	594	1200	90	146	638	543
Alkalinity as $CaCO_3$ mg/L	198	213	211	212	338	433	403	289	275	310	220	234	333	390	412	208	194	236	186
Nitrate plus nitrite as N mg/L	0.5	2.5	2.5	2.7	5.8	6	7.5	<0.1	<0.1	1.1	<0.1	<0.1	7.4	5.5	0.23	4.0	<0.1	0.43	<0.1
Fluoride as F mg/L	1.3	0.54	0.48	0.58	0.65	0.68	0.73	1.5	1.5	1.1	1.2	0.79	0.86	1.1	1.0	0.50	0.38	0.61	0.52
Silica as Si mg/L	-	-	10	12	12	11	13	11	12	13	13	5.7	12	11	12	11	9.0	2.4	4.7
Strontium as Sr mg/L	-	-	2.4	2.0	6.4	6.4	5.2	6.7	7.0	7.7	3.2	6.5	3.9	6.4	14	2.3	1.2	4.3	3.1
Dissolved Organic Carbon mg/L	<0.2	<0.2	<0.2	<1	2.1	3.0	2.6	2.1	0.7	2.9	0.4	4.3	2.2	4.5	4.1	0.3	5.9	5.1	15
Conductivity mS/m (25°C)	89	71	72	70	366	369	319	201	210	276	94	282	205	395	662	89	110	356	281
pH (Lab)	8.0	7.6	7.7	7.8	7.5	7.7	7.6	7.7	7.8	7.7	8.1	7.9	7.7	7.8	7.7	7.3	7.6	8.3	8.2
Saturation pH (pHs) (20°C)	7.5	7.4	7.4	7.4	6.7	6.6	6.7	7.3	7.3	6.8	7.6	7.1	7.0	6.7	6.6	7.3	7.4	7.1	7.2
Ortho phosphate as P mg/L			<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
TDS (calc)	570	454	461	448	2342	2362	2042	1286	1344	1766	602	1805	1312	2528	4237	570	704	2278	1798
Field Parameters																			
Field temp	-	-	-	-	20.2	-	22.5	-	24.5	21.3	27.2	16.7	21.8	20.4	23.4	24.8	-	11.3	17
Field pH	-	-	-	6.4	6.75	-	6.7	-	7.1	7.4	7.5	7.3	7.3	6.9	7.2	6.9	-	8.4	8.5
Field alk meq/l	-	-	-	4.2		-	7.8	-	5	6.4	4.2	4.6	6.2	8	8.4	3.8	-	4.2	3.6
Field DO mg/l	-	-	-	2.1	2	-	1	-	0.4	0.65	0.5	0.5	1.3	1.9	0.4	2.4	-	6.4	5.8
H_2S	-	-	-	-	n	-	-	-	y	n	y	y	-	n	-	n	-	n	n

* River Water

Analytical precision (1-sigma) of a tritium analysis is 0.2 TU
Analytical precision (1-sigma) of 14C analyses range between 0.4 and 0.6 pmc

Appendix 2

CFC data listing

CFC data listing

Sample	Ampule	Temp	elev	Concentration in Solution			Calculated Atmospheric Partial Pressure in pptv			Model CFC Recharge Dates			Percent Modern Freon calculated			Percent modern freon averaged		
				pg/kg	pg/kg	pg/kg												
Name	No.	(ºC)	(m)	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	PMF-11	PMF-12	PMF-113	PMF-11	PMF-12	PMF-113
BW3	2	20	580	22	45	5	14	117	8	1962.5	1970	1973	5.3	21.8	9.1	5	23	7
BW3	4	20	580	21	51	3	13	131	4	1962	1971	1969	5.0	24.6	5.3			
BW3	6	20	580	23	44	4	14	113	6	1962.5	1970	1971.5	5.5	21.2	7.4			
GFK1	2	20	580	3	42	5	2	108	8	1953.5	1969.5	1973.5	0.8	20.3	10.0	1	20	3
GFK1	4	20	580	2	45	0	1	116	0	1952.5	1970	1954.5	0.5	21.7	0.0			
GFK1	5	20	580	2	39	0	1	101	0	1951.5	1969	1954.5	0.4	18.8	0.0			
GH1	2	20	580	184	262	27	115	676	42	1976.5	Contam.	1986.5	43.8	126.4	50.7	42	125	48
GH1	4	20	580	175	266	26	108	685	40	1975.5	Contam.	1986	41.4	128.1	48.3			
GH1	5	20	580	170	250	24	106	644	37	1975.5	Contam.	1985.5	40.4	120.5	45.2			
GH2	2	20	580	214	1173	29	133	3024	44	1978	Contam.	1987	50.8	565.8	53.8	52	551	55
GH2	4	20	580	211	1128	25	131	2910	39	1977.5	Contam.	1986	50.0	544.4	47.6			
GH2	5	20	580	226	1127	34	141	2906	52	1978.5	Contam.	1988.5	53.7	543.7	63.2			
GKF2	2	20	580	173	208	32	108	535	49	1975.5	2000	1988	41.1	100.1	59.5	40	94	55
GKF2	4	20	580	166	187	28	103	483	43	1975	1991	1987	39.4	90.4	52.1			
GKF2	5	20	580	172	187	29	107	482	44	1975.5	1991	1987	40.7	90.2	53.7			
KF1	1	20	580	1	9	0	1	24	0	1951	1958	1954.5	0.3	4.5	0.0	0	4	0
KF1	3	20	580	2	6	0	1	14	0	1952	1954.5	1954.5	0.4	2.7	0.0			
KF1	4	20	580	2	9	0	1	23	0	1952	1957.5	1954.5	0.5	4.2	0.0			
KF2	4	20	580	92	252	37	57	651	58	1970.5	Contam.	1989	21.7	121.8	70.2	22	122	70
KF3	2	20	580	227	197	36	141	507	56	1978.5	1993.5	1989	53.9	94.8	68.3	51	90	64
KF3	4	20	580	215	188	30	134	484	47	1978	1991	1987.5	51.1	90.5	57.0			
KF3	5	20	580	205	176	35	127	454	54	1977.5	1989.5	1988.5	48.6	84.9	65.4			
KF4	2	20	580	259	208	39	161	535	60	1980.5	2000	1989.5	61.5	100.1	73.2	62	98	66
KF4	4	20	580	261	202	32	162	521	50	1980.5	1996	1988	62.0	97.6	60.4			
KF4	5	20	580	260	201	34	161	519	52	1980.5	1995.5	1988.5	61.6	97.0	63.1			
KR1	2	20	580	27	74	2	17	192	3	1963	1974.5	1966.5	6.4	35.9	3.6	6	35	3
KR1	4	20	580	27	73	1	17	188	2	1963.5	1974.5	1964	6.4	35.1	2.6			
KR1	5	20	580	27	73	2	17	189	3	1963.5	1974.5	1967	6.4	35.3	3.9			
LGR2	2	11	580	636	325	83	252	559	78	1991	Modern	1992.5	96.1	104.5	94.3	95	99	94
LGR2	4	11	580	624	292	85	247	502	80	1990	1992.5	1993.5	94.2	93.9	96.8			

CFC data listing

Sample Name	Ampule No.	Temp (°C)	elev (m)	Concentration in Solution pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	Calculated Atmospheric Partial Pressure in pptv CFC-11	CFC-12	CFC-113	Model CFC Recharge Dates CFC-11	CFC-12	CFC-113	Percent Modern Freon calculated PMF-11	PMF-12	PMF-113	Percent modern freon averaged PMF-11	PMF-12	PMF-113
LGR2	5	11	580	631	304	80	249	523	75	1990.5	1996	1992	95.3	97.8	90.9			
LGR3	2	17	580	29	260	19	16	591	26	1963	Contam.	1982.5	6.0	110.6	31.2	6	111	31
RF1	2	20	580	235	192	40	146	495	62	1979	1992	1990	55.8	92.6	74.6	56	93	78
RF1	4	20	580	234	184	39	145	476	61	1979	1990.5	1989.5	55.5	89.0	73.9			
RF1	5	20	580	237	203	46	147	523	71	1979	1996	1991.5	56.1	97.8	86.5			
DPL	4	18	1450	140	113	20	88	297	31	1974	1980.5	1984.5	33.6	55.9	37.5	34	55	35
DPL	5	18	1450	138	108	20	87	284	31	1974	1980	1984	33.1	53.5	37.2			
DPL	6	18	1450	144	112	16	90	297	25	1974	1980.5	1982	34.6	55.9	29.9			
ELF	0	18	1600	213	128	25	137	345	39	1978	1983.5	1986	52.2	64.9	47.5	53	64	48
ELF	4	18	1600	211	126	24	135	339	38	1978	1983	1986	51.6	63.9	46.3			
ELF	6	18	1600	220	124	27	141	334	43	1978.5	1983	1987	53.9	63.0	51.4			
GFO	2	18	1450	204	162	32	128	427	49	1977.5	1988	1988	49.0	80.5	59.8	48	80	54
GFO	4	18	1450	201	159	27	127	420	42	1977.5	1987.5	1986.5	48.4	79.0	51.1			
GFO	5	18	1450	197	163	27	124	430	42	1977	1988	1986.5	47.5	80.9	51.1			
GMB	2	18	1500	1056	280	75	670	743	118	Contam.	Contam.	Contam.	255.7	140.0	142.5	254	135	142
GMB	4	18	1500	1058	279	78	671	741	123	Contam.	Contam.	Contam.	256.2	139.6	148.8			
GMB	6	18	1500	1033	252	71	655	669	111	Contam.	Contam.	Contam.	250.0	126.0	134.9			
MAL	2	18	1600	73	45	9	47	122	15	1969.5	1970.5	1978	17.9	23.0	18.0	18	22	14
MAL	4	18	1600	72	44	6	46	119	10	1969.5	1970.5	1975	17.7	22.5	12.2			
MAL	6	18	1600	73	42	7	47	114	10	1969.5	1970	1975.5	17.8	21.5	12.6			
MOL	2	18	1450	51	31	4	32	83	6	1967	1967.5	1971.5	12.3	15.5	7.6	12	15	9
MOL	4	18	1450	50	28	4	31	74	7	1967	1966.5	1972.5	12.0	13.9	8.4			
MOL	6	18	1450	49	31	6	31	83	9	1966.5	1967.5	1974	11.9	15.6	10.4			
MRB	2	18	1500	113	64	12	72	171	20	1972.5	1973.5	1980	27.4	32.2	23.6	27	33	23
MRB	4	18	1500	113	65	12	72	173	19	1972.5	1973.5	1980	27.4	32.6	23.1			
MRB	6	18	1500	113	65	11	72	174	18	1972.5	1973.5	1979	27.4	32.7	21.3			
OLV	2	18	1450	232	147	29	146	389	45	1979	1986	1987	55.8	73.3	54.2	56	77	49
OLV	4	18	1450	231	166	23	145	438	36	1979	1988.5	1985.5	55.5	82.4	43.7			
OLV	6	18	1450	234	151	26	147	398	40	1979	1986.5	1986.5	56.2	75.0	48.4			
PFL	2	18	1450	15615	2049	4485	9836	5408	6992	Contam.	Contam.	Contam.	3755.9	1018.3	8462.3	3763	1006	8391
PFL	4	18	1450	15613	1969	4344	9835	5198	6772	Contam.	Contam.	Contam.	3755.3	978.8	8196.2			

CFC data listing

Sample Name	Ampule No.	Temp (ºC)	elev (m)	Concentration in Solution			Calculated Atmospheric Partial Pressure in pptv			Model CFC Recharge Dates			Percent Modern Freon calculated			Percent modern freon averaged		
				pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	CFC-11	CFC-12	CFC-113	CFC-11	CFC-12	CFC-113	PMF-11	PMF-12	PMF-113	PMF-11	PMF-12	PMF-113
PFL	5	18	1450	15706	2051	4513	9894	5415	7036	Contam.	Contam.	Contam.	3777.7	1019.6	8515.4			
RFN	2	18	1500	265	160	33	168	425	51	1981.5	1988	1988	64.2	80.0	62.1	64	80	68
RFN	4	18	1500	265	156	37	168	415	58	1981.5	1987.5	1989	64.1	78.2	70.1			
RFN	6	18	1500	267	161	37	170	428	58	1981.5	1988	1989	64.7	80.5	70.3			
WGD	2	18	1450	95	75	14	60	198	22	1971	1975	1981	22.8	37.3	26.2	22	35	25
WGD	4	18	1450	92	68	13	58	178	20	1971	1974	1980.5	22.2	33.6	24.7			
WGD	6	18	1450	90	68	13	57	179	21	1970.5	1974	1980.5	21.6	33.6	24.9			
DS1	2	20	1350	74	63	10	50	179	16	1970	1974	1978.5	19.2	33.7	20.0	19	33	20
DS1	4	20	1350	75	64	10	51	180	17	1970	1974	1979	19.6	34.0	20.4			
DS1	6	20	1350	72	57	9	49	162	16	1969.5	1973	1978.5	18.9	30.4	18.8			
DS2	2	20	1350	56	69	12	38	196	20	1968	1975	1980	14.6	36.8	24.1	14	36	22
DS2	4	20	1350	49	62	10	34	175	17	1967.5	1973.5	1979	12.9	32.9	20.3			
DS2	5	20	1350	47	59	9	32	168	16	1967	1973.5	1978.5	12.3	31.6	19.3			
DS2	6	20	1350	55	77	11	38	217	19	1968	1976	1980	14.4	40.9	23.0			
LK2	2	20	1350	67	55	9	46	156	16	1969	1972.5	1978.5	17.4	29.5	18.8	18	32	23
LK2	4	20	1350	71	64	13	48	181	22	1969.5	1974	1981	18.4	34.1	26.6			
LK2	6	20	1350	66	59	12	45	168	21	1969	1973.5	1980.5	17.2	31.7	25.0			
UV1B	2	20	1350	161	144	18	110	408	31	1976	1987	1984.5	42.1	76.8	38.0	41	75	35
UV1B	4	20	1350	159	139	16	108	394	28	1975.5	1986	1983	41.4	74.2	33.3			
UV1B	5	20	1350	156	136	17	107	385	29	1975.5	1985.5	1983.5	40.7	72.6	35.0			
UV2	2	20	1350	78	68	9	53	192	15	1970.5	1974.5	1978	20.4	36.2	18.2	20	36	17
UV2	4	20	1350	77	65	8	53	183	14	1970	1974	1977.5	20.1	34.5	16.4			
UV2	6	20	1350	80	67	8	54	190	13	1970.5	1974.5	1977	20.8	35.8	16.0			
UV5	2	20	1350	110	112	16	75	317	27	1972.5	1982	1983	28.7	59.6	33.0	29	59	35
UV5	4	20	1350	112	112	19	77	319	32	1973	1982	1984.5	29.3	60.0	38.6			
UV5	6	20	1350	108	106	16	74	300	28	1972.5	1980.5	1983.5	28.2	56.5	33.6			
UV8	2	20	1350	123	67	19	84	189	32	1973.5	1974.5	1984.5	32.2	35.5	39.0	32	52	38
UV8	4	20	1350	123	117	19	84	331	32	1973.5	1982.5	1984.5	32.0	62.3	38.6			
UV8	5	20	1350	117	107	18	80	304	30	1973	1981	1984	30.5	57.3	36.6			
UV8	6	20	1350	116	108	17	80	306	30	1973	1981	1984	30.4	57.6	36.1			
UVD1	2	20	1350	8	17	1	5	47	2	1957	1963	1964.5	2.1	8.9	2.8	2	8	4

CFC data listing

Sample Name	Ampule No.	Temp (°C)	elev (m)	Concentration in Solution pg/kg CFC-11	pg/kg CFC-12	pg/kg CFC-113	Calculated Atmospheric Partial Pressure in pptv CFC-11	CFC-12	CFC-113	Model CFC Recharge Dates CFC-11	CFC-12	CFC-113	Percent Modern Freon calculated PMF-11	PMF-12	PMF-113	Percent modern freon averaged PMF-11	PMF-12	PMF-113
UVD1	3	20	1350	7	13	3	5	37	5	1956.5	1961.5	1969.5	1.8	6.9	5.5			
UVD1	6	20	1350	8	15	1	5	42	2	1956.5	1962	1964	2.0	7.8	2.6			
UVN1	2	20	1350	14	15	2	10	42	4	1960.5	1962.5	1969	3.8	7.9	5.1	4	8	4
UVN1	4	20	1350	15	16	2	10	45	3	1960.5	1963	1967	3.9	8.5	4.0			
UVN1	5	20	1350	14	14	2	9	40	3	1960.5	1962	1967	3.6	7.5	3.8			
UVN3	2	20	1350	51	54	63	35	153	107	1967.5	1972.5	Contam.	13.2	28.8	Contam.	13	29	85
UVN3	4	20	1350	49	53	51	34	150	88	1967.5	1972.5	Modern	12.9	28.2	Modern			
UVN3	6	20	1350	48	54	41	33	152	71	1967	1972.5	1991	12.5	28.6	85.4			

Figures

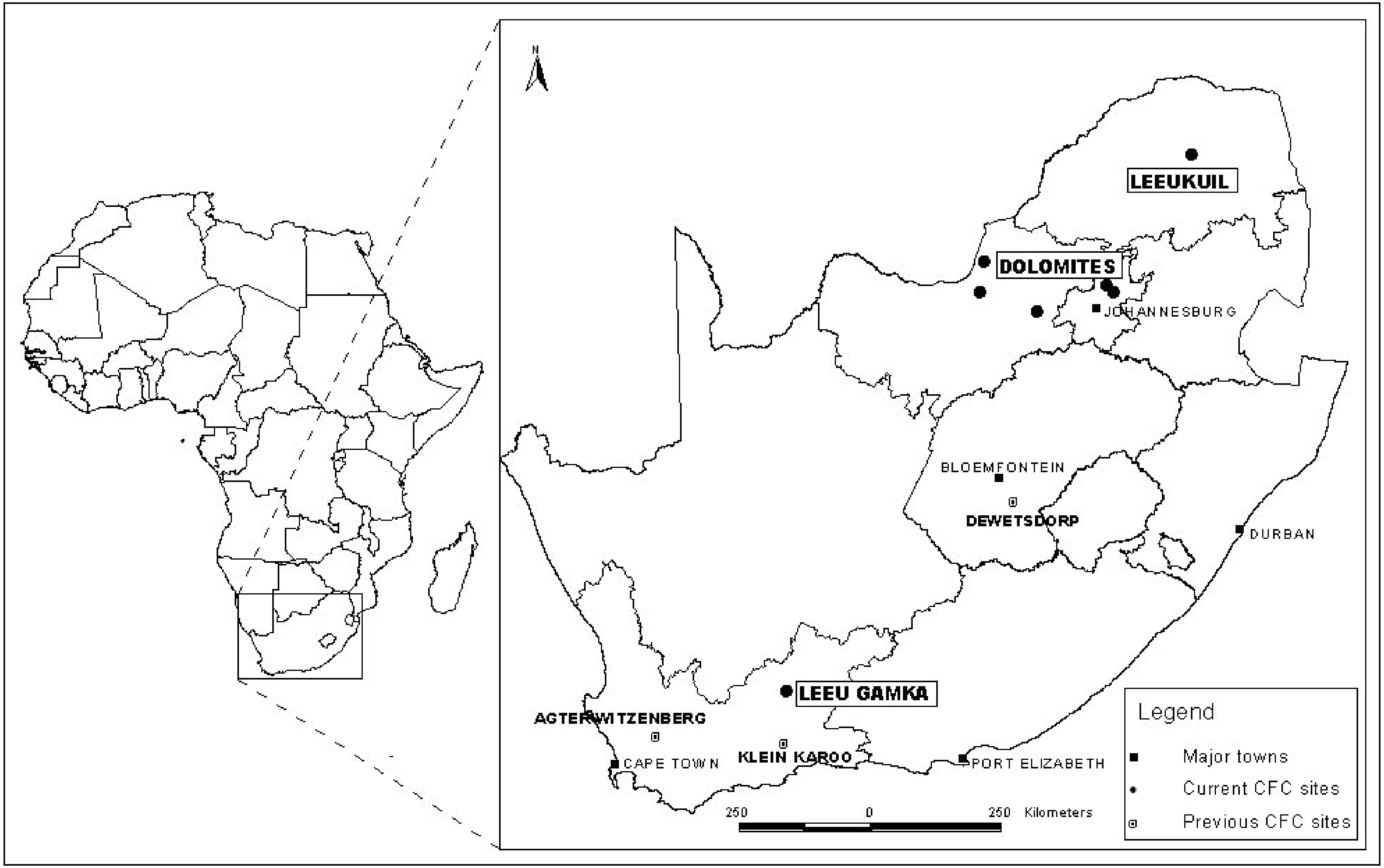


Figure 1.1 Site locality map. Leeukuil, the Dolomites and Leeu Gamka

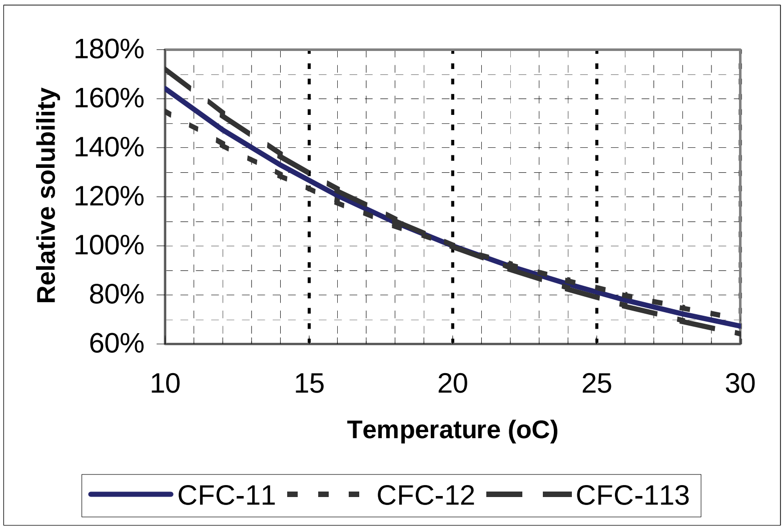


Figure 1.2 Graph of relative solubility variation of the three CFC gases with temperature (derived from equations in Plummer 2001).

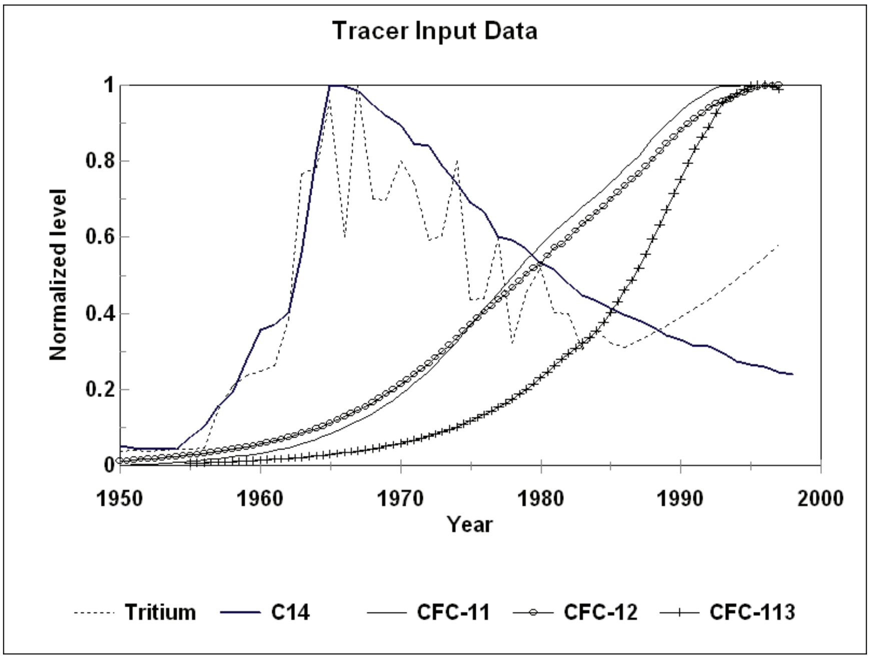


Figure 2.1 Atmospheric variations of radiocarbon, tritium, CFC-11, CFC-12 and CFC-113 during the past 50 years. The values have been normalised to their maximum and minimum values in order to indicate the effective time range of each. The tritium values are corrected for decay to 2000AD.

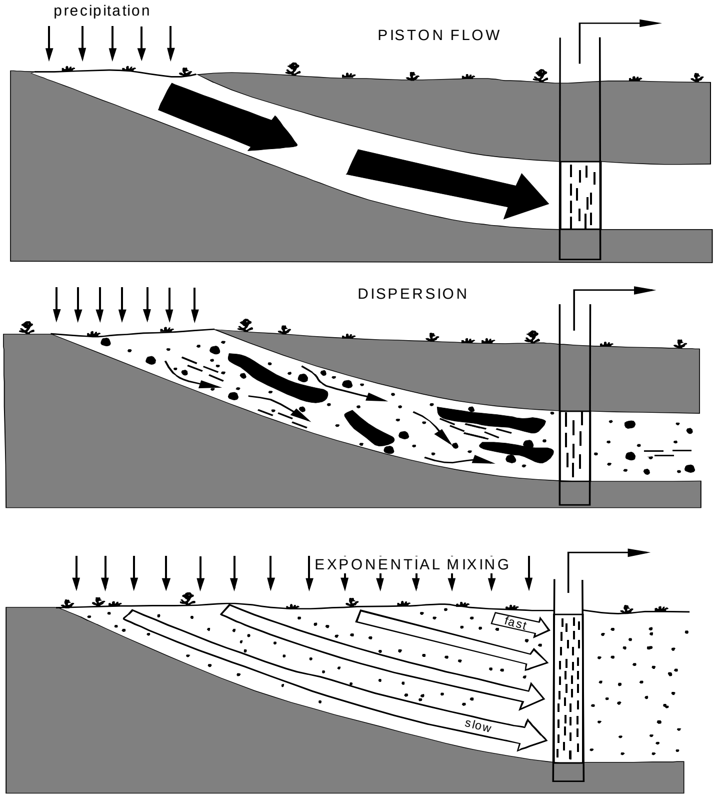


Figure 2.2 Three cases of groundwater movement by piston-flow without and with dispersion in a confined aquifer and of flow in a phreatic aquifer where water of different ages is mixed in the well or spring (from Geyh 2000)

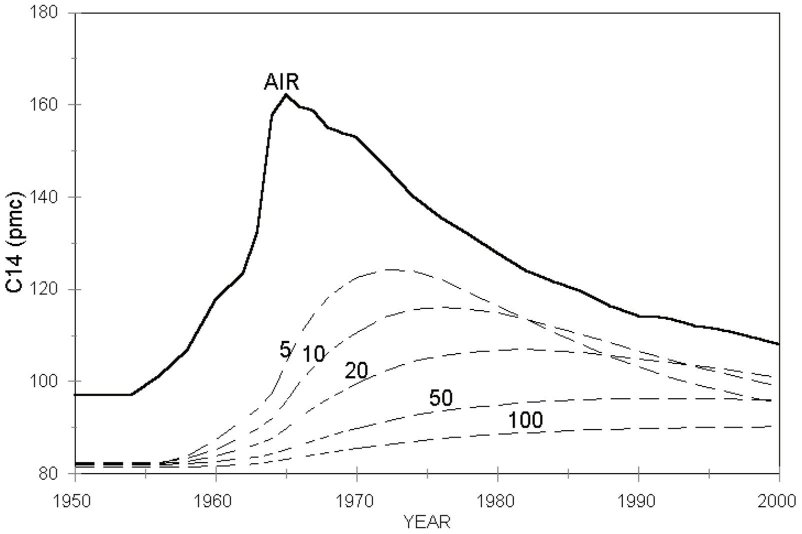
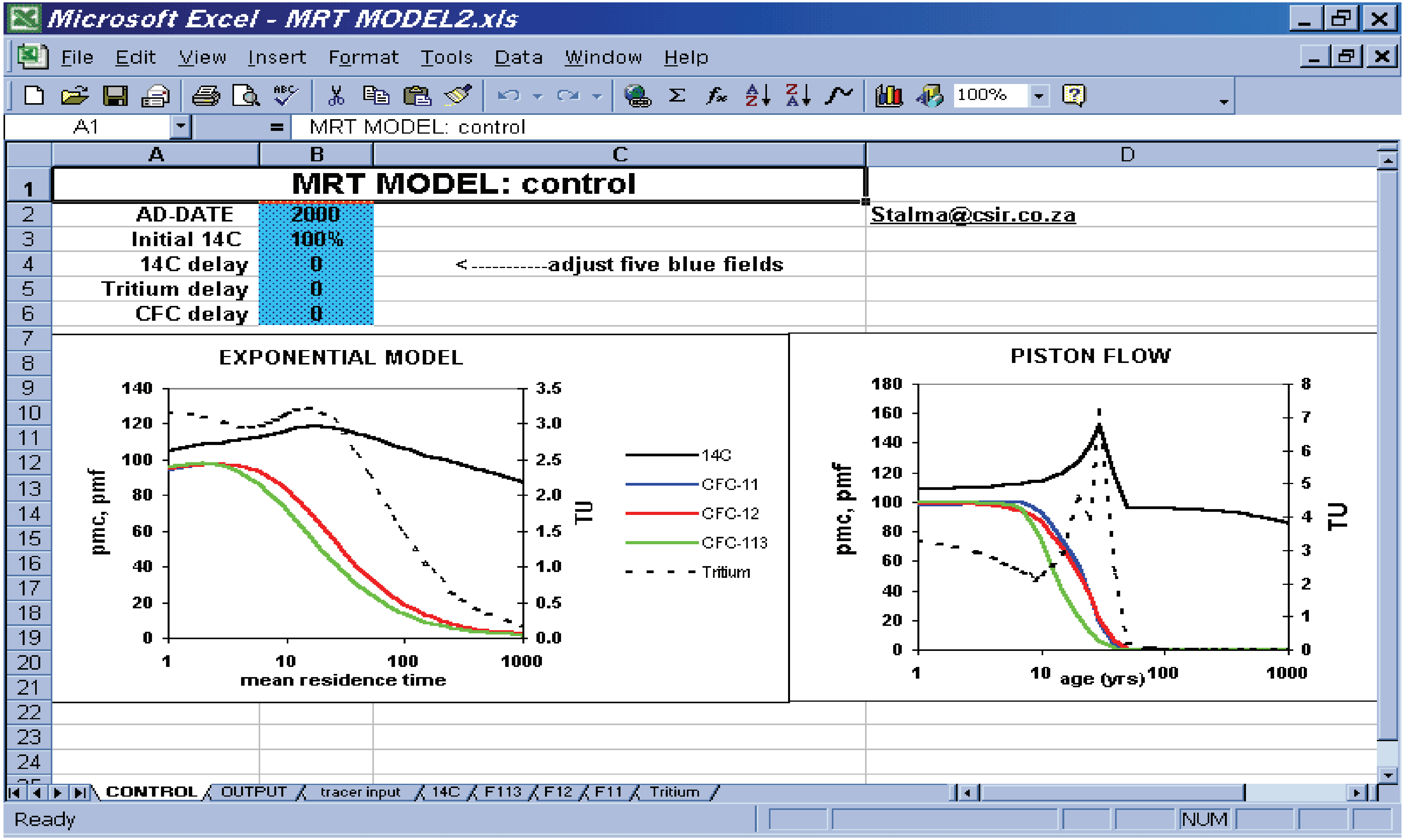


Figure 2.3 Model values of ^{14}C variations expected from atmospheric ^{14}C input into an exponential mixing model (dashed lines) using an initial ^{14}C content of 85% modern (from Talma and Vogel 2001). The mean residence times (MRT) of the models are indicated (5-100 years). The atmospheric levels are shown as “AIR” (solid line).



MRT MODEL: control

AD-DATE	2000		Stalma@csir.co.za
Initial 14C	100%		
14C delay	0	<-----------adjust five blue fields	
Tritium delay	0		
CFC delay	0		

Figure 2.4 MRTMODELS spreadsheet. Model representation whereby the responses of ^{14}C tritium, CFC-11, CFC-12 and CFC-113 in groundwater are calculated as a function of observation date, delay in the unsaturated zone and initial ^{14}C content. Scenarios are for piston flow at different ages and exponential flow with different mean residence times The figure depicts the control that the operator can exert of the software and the graphical output.

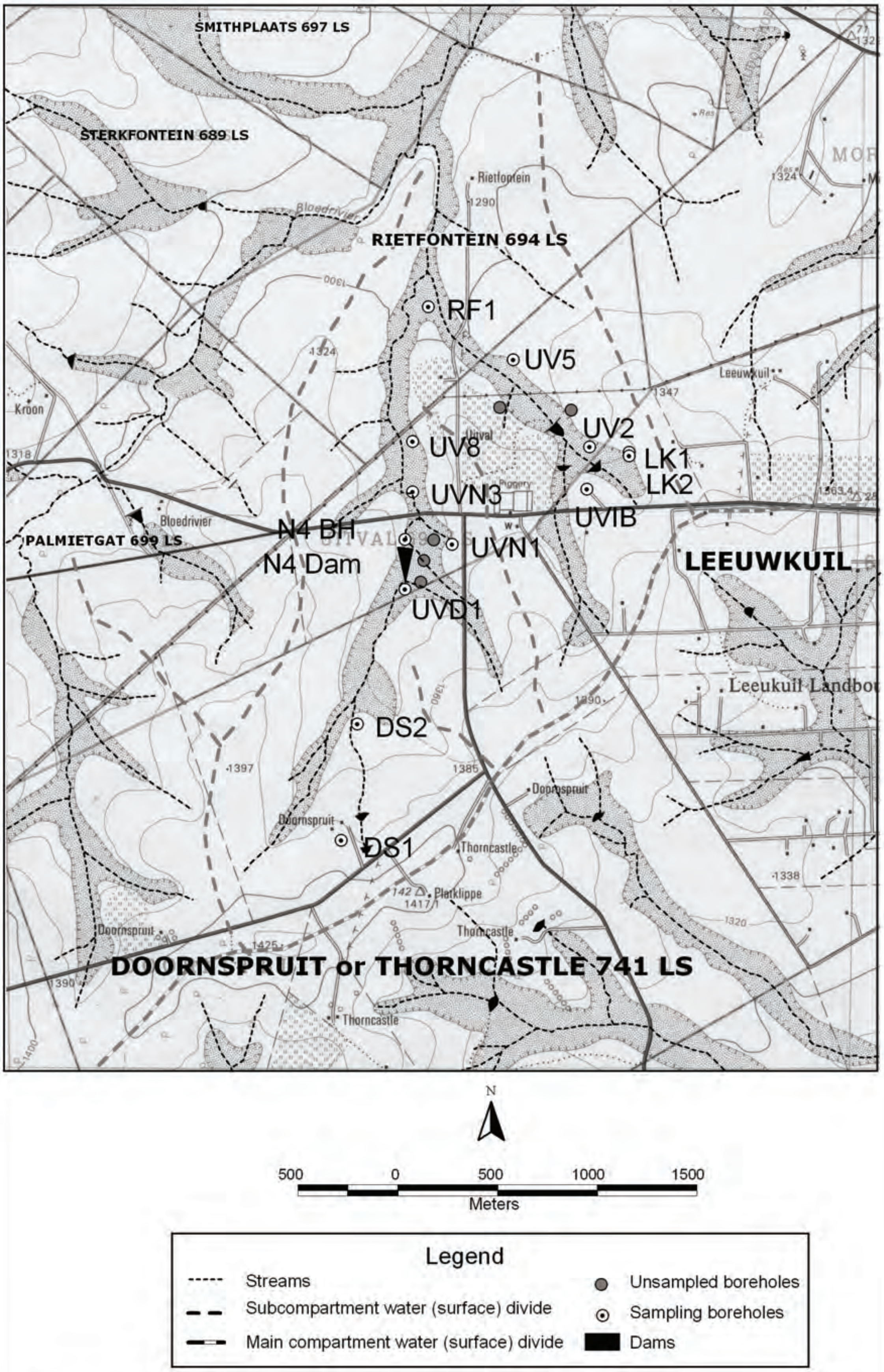


Figure 3.1: Leeukuil. Site map showing sampling points.

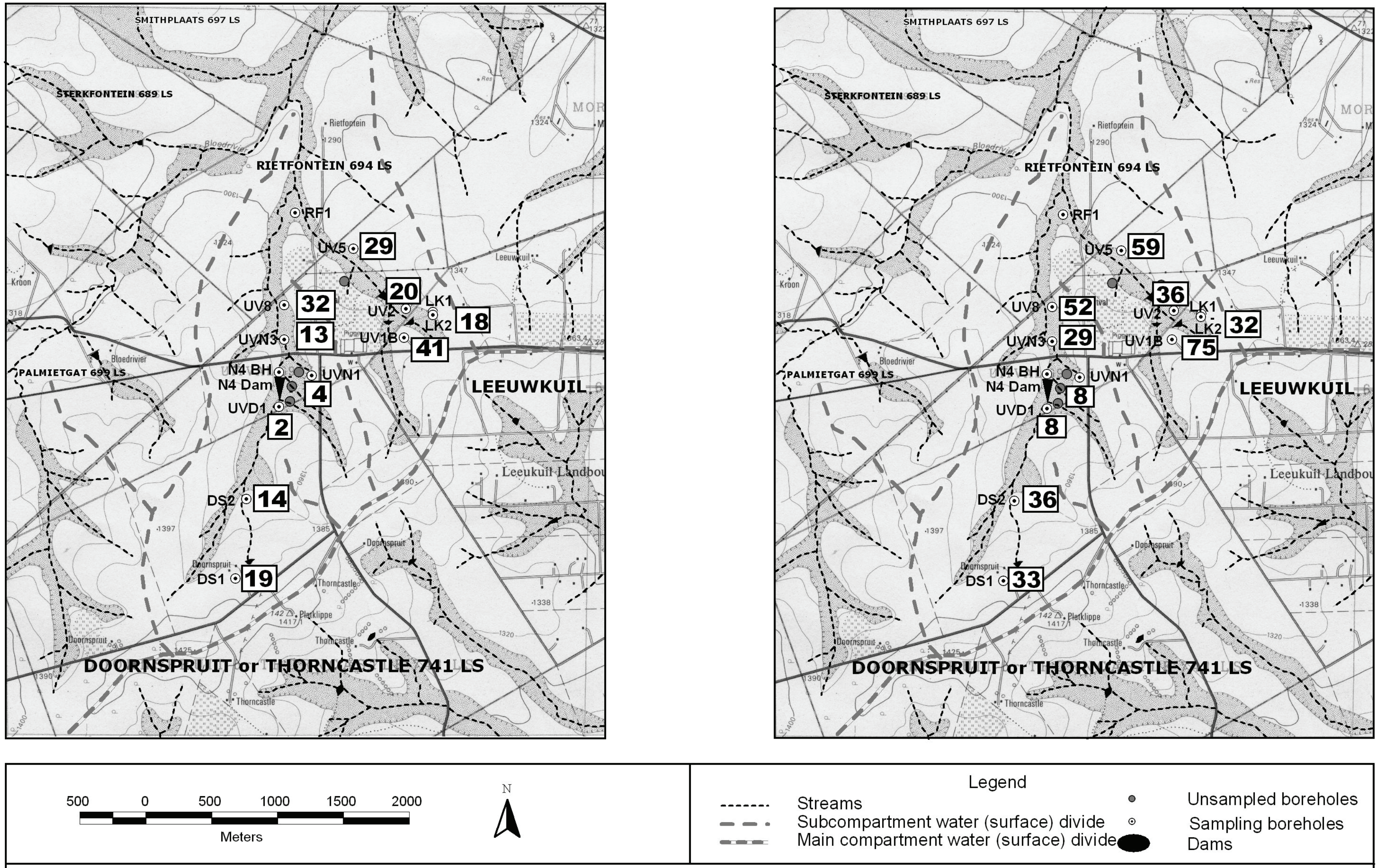


Figure 3.2 Leeukuil. Isotope and geochemistry distribution. (a) CFC-11 pmf (b) CFC-12 pmf

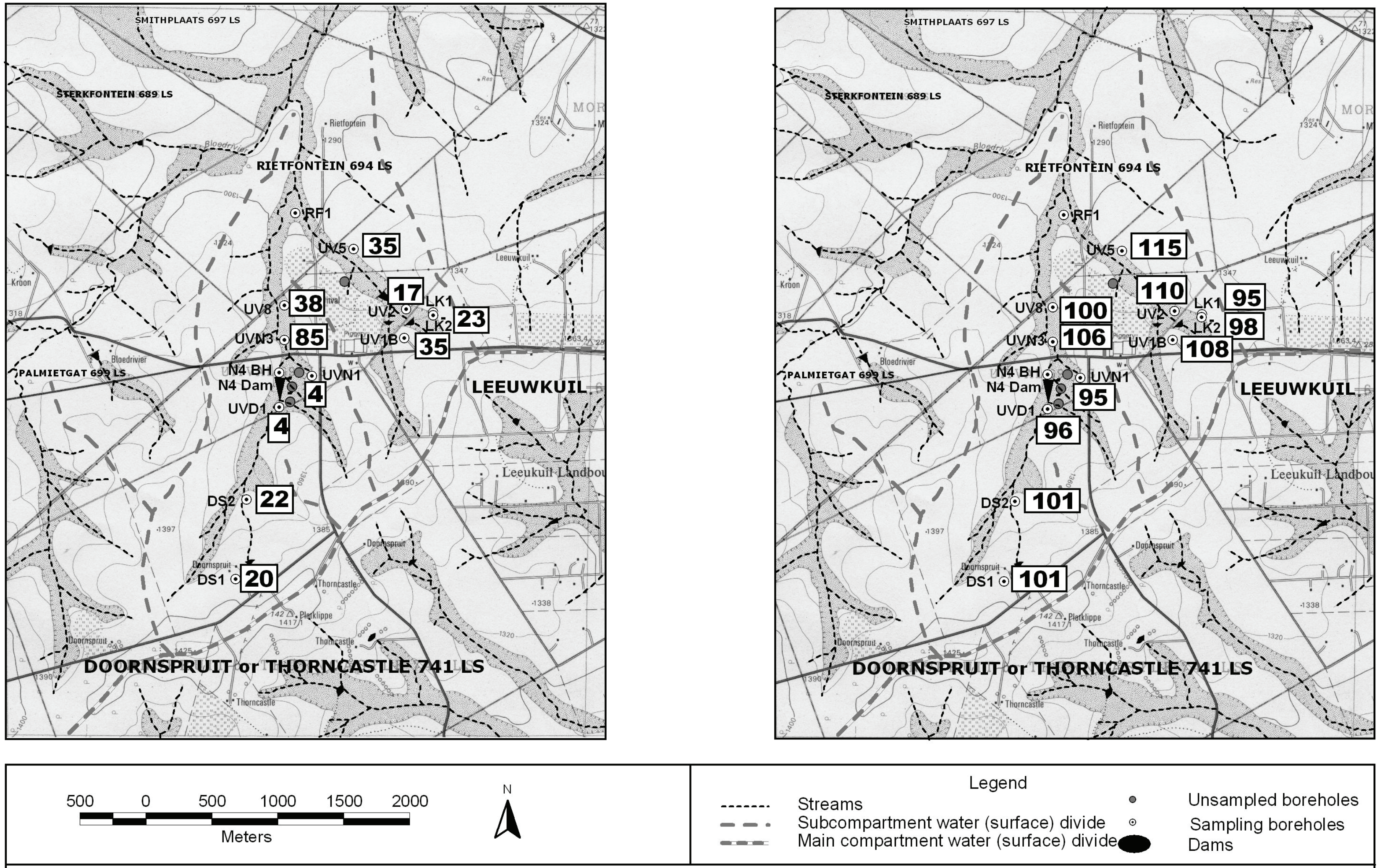


Figure 3.3 Leeukuil. Isotope and geochemistry distribution. (a) CFC-113 pmf (b)^{14}C pmc

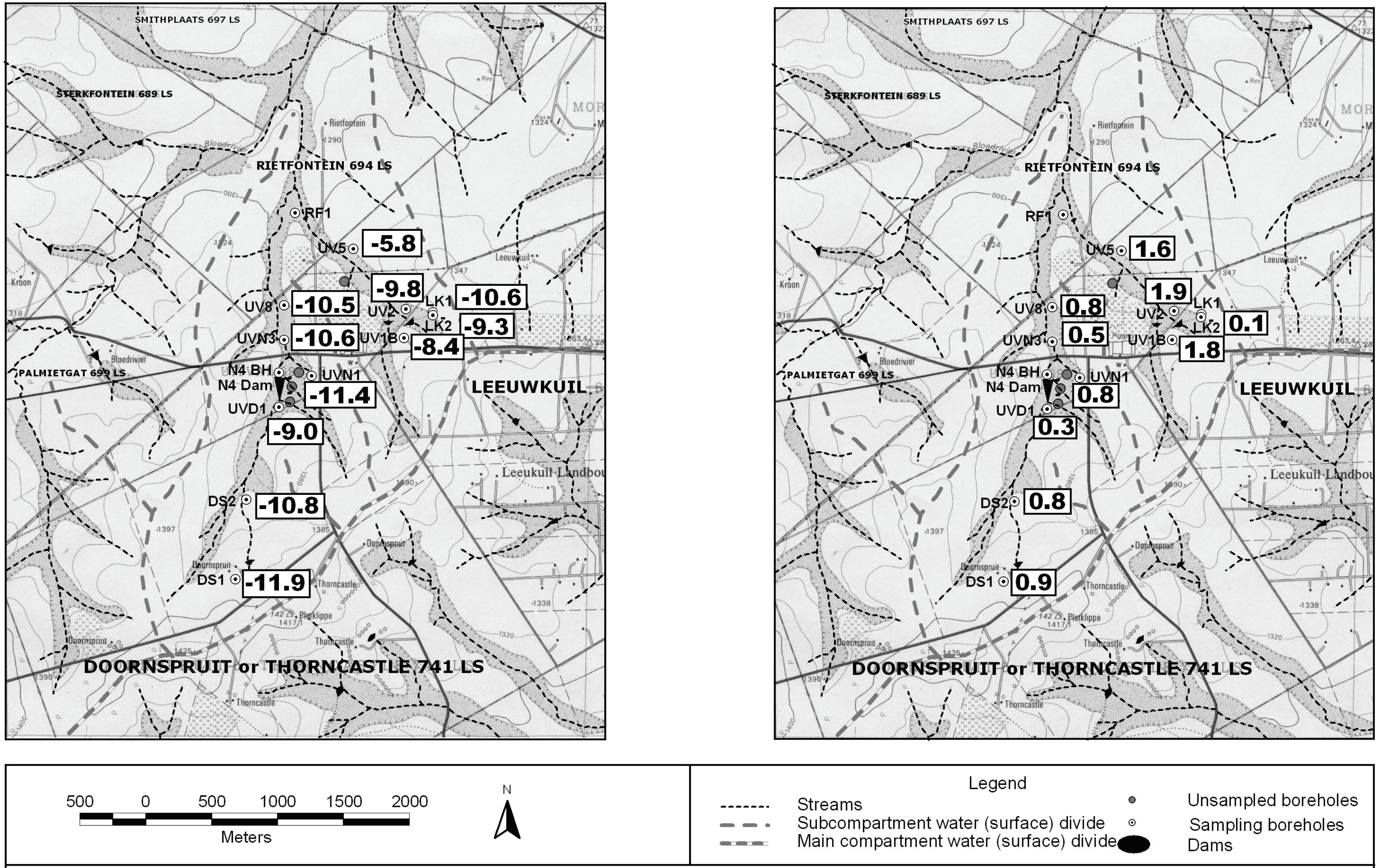


Figure 3.4 Leeukuil. Isotope and geochemistry distribution. (a) $\delta^{13}C$ ‰ PDB (b) TRITIUM TU

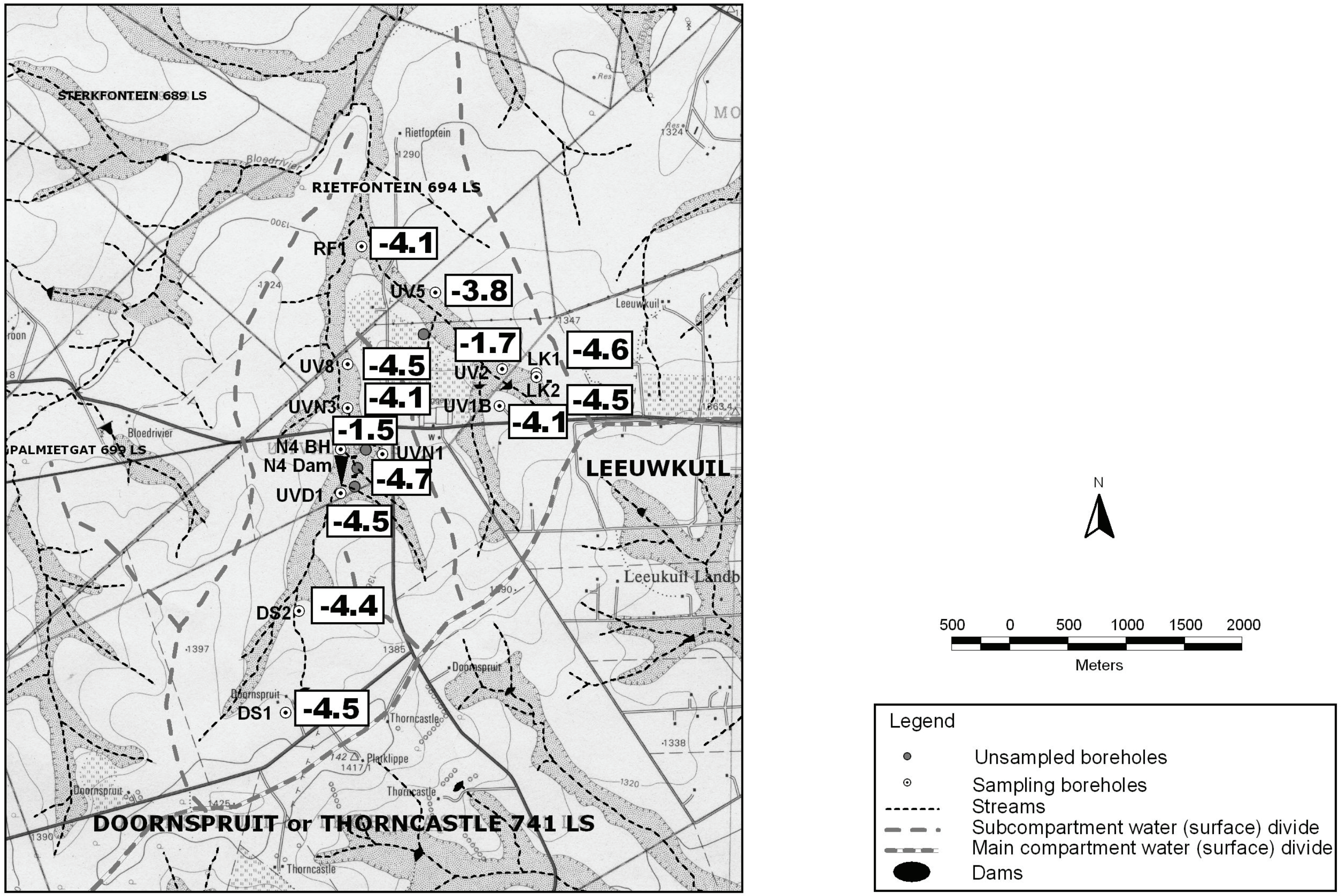


Figure 3.5 Leeukuil. Isotope and geochemistry distribution. (a) $\delta^{18}O$‰ SMOW

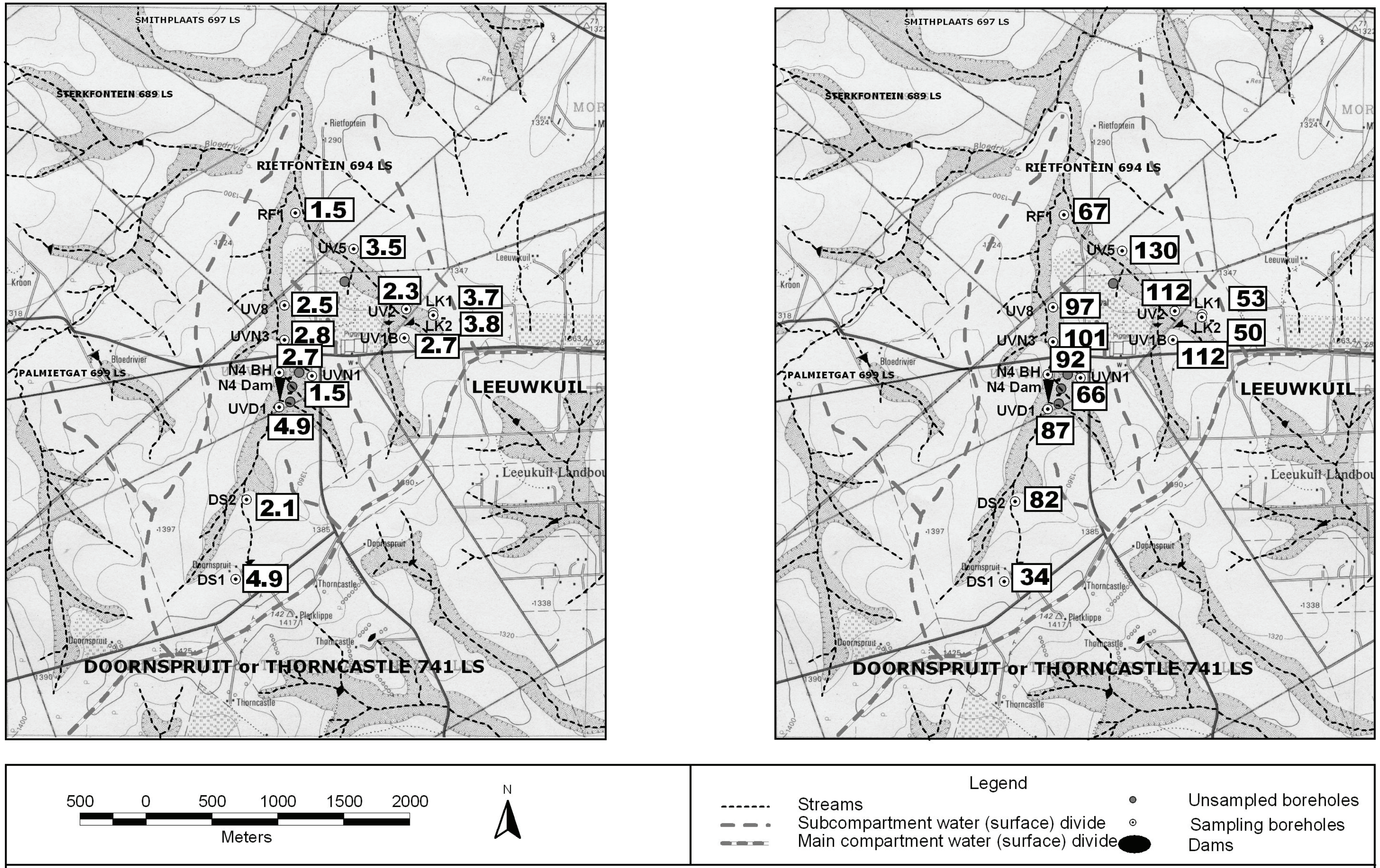


Figure 3.6 Leeukuil. Isotope and geochemistry distribution. (a) Potassium as K mg/L (b) Sodium as Na mg/L

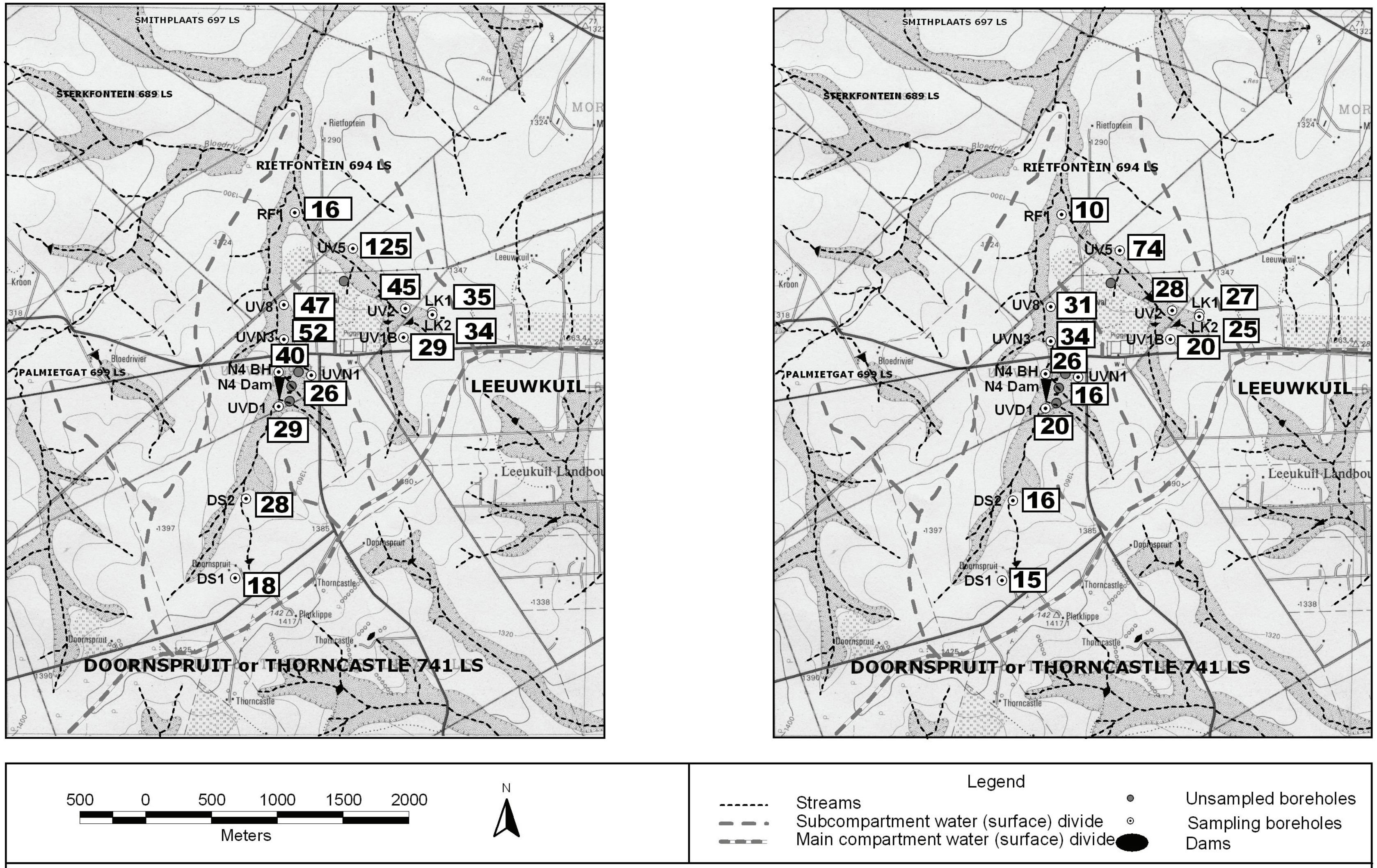


Figure 3.7 Leeukuil. Isotope and geochemistry distribution. (a) Calcium as Ca mg/L (b) Magnesium as Mg mg/L

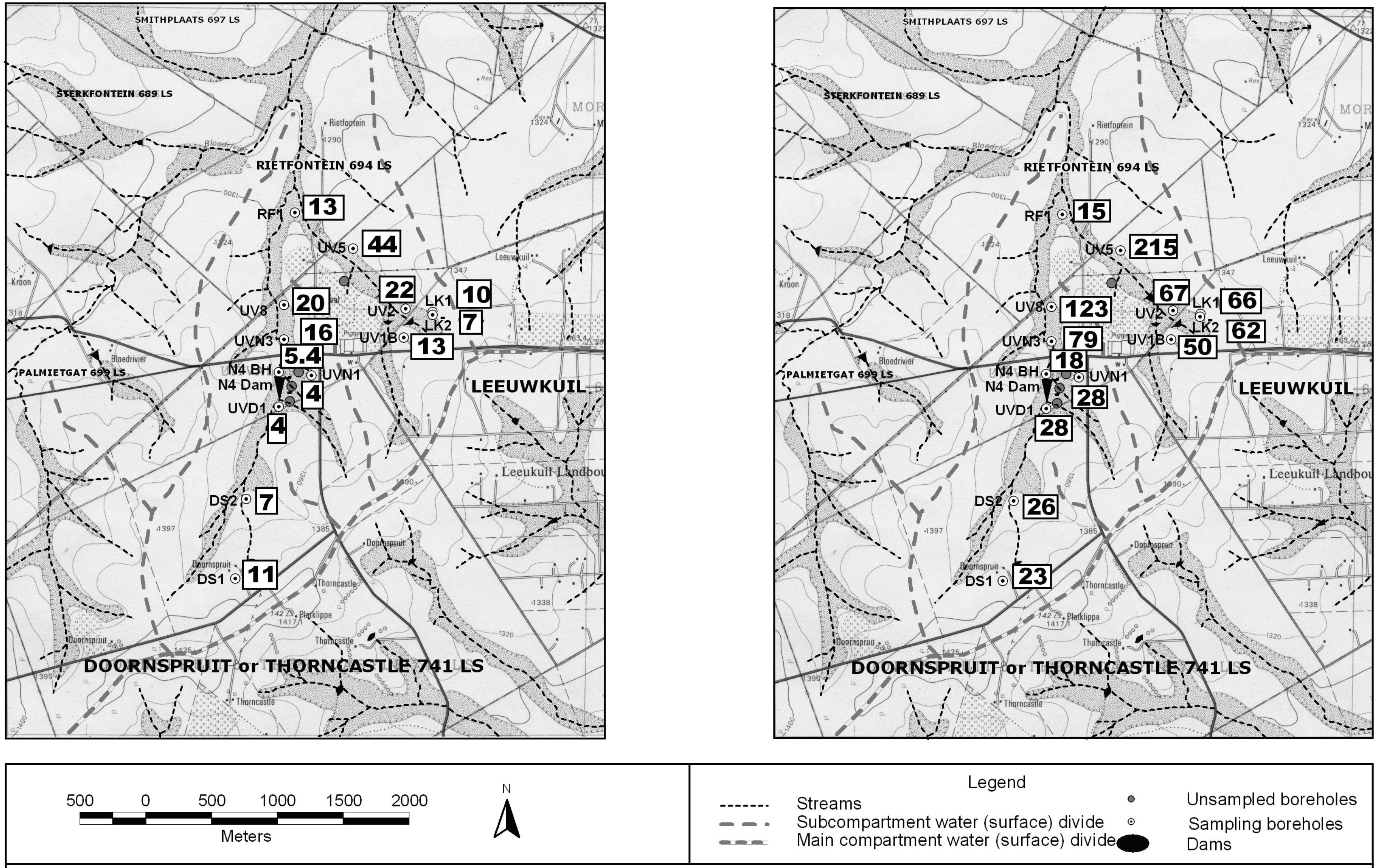


Figure 3.8 Leeukuil. Isotope and geochemistry distribution. (a) Sulphate as SO_4mg/L (b) Chloride as Cl mg/L

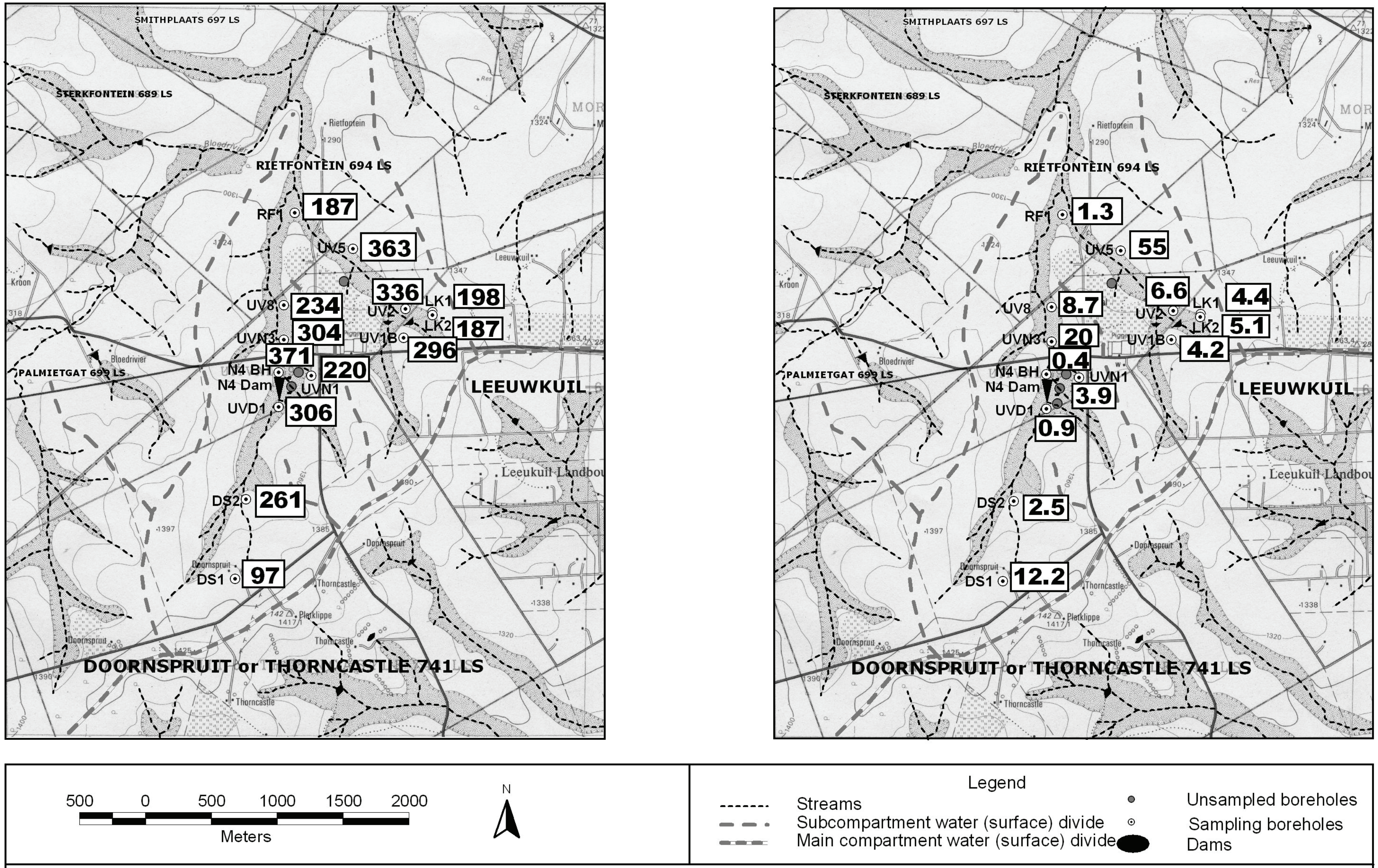


Figure 3.9 Leeukuil. Isotope and geochemistry distribution. (a) Alkalinity as $CaCO_3$ mg/L (b) Nitrate plus nitrite as N mg/L

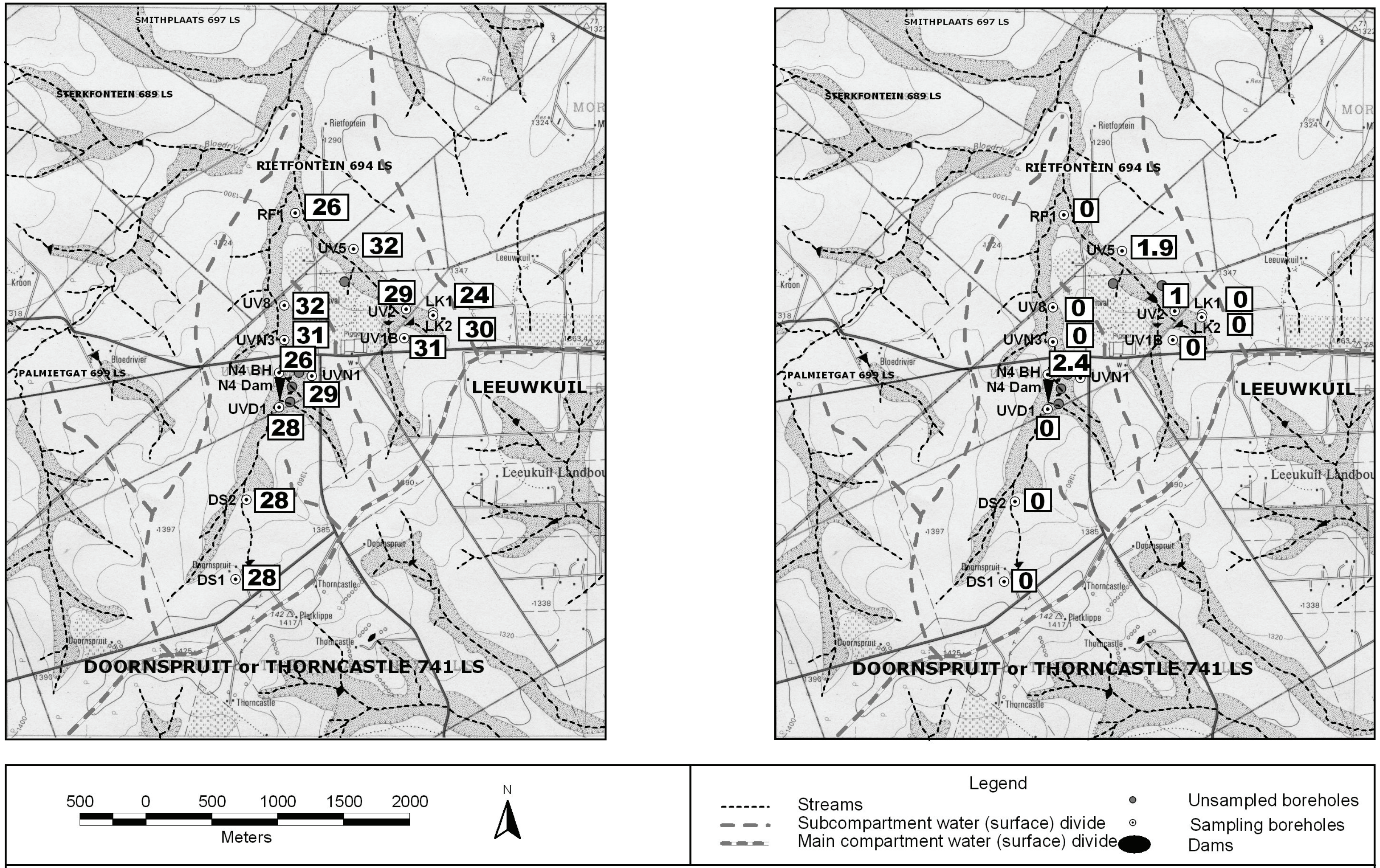


Figure 3.10 Leeukuil. Isotope and geochemistry distribution. (a) Silica as Si mg/L (b) Dissolved Organic Carbon mg/L

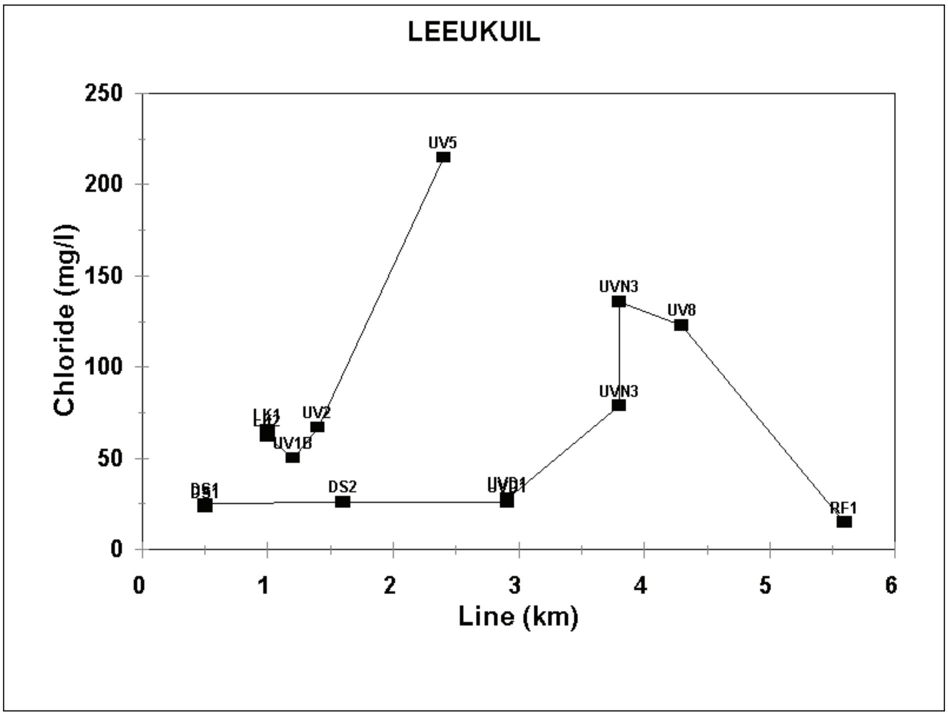


Figure 3.11 Variation of chloride along the two lines of boreholes in Leeukuil.

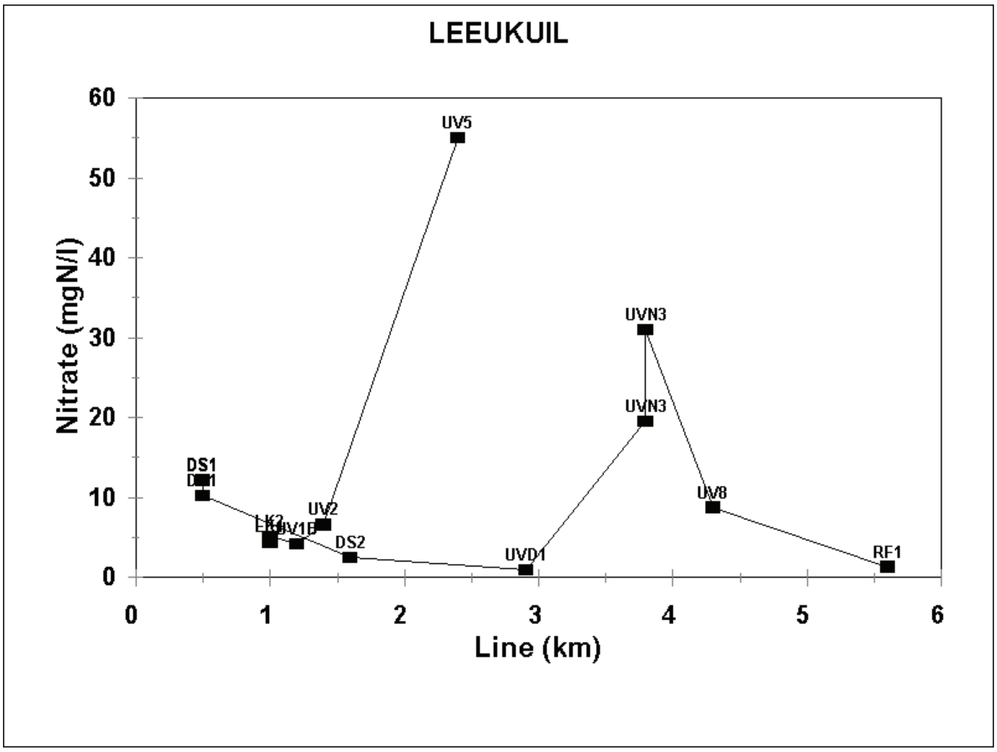


Figure 3.12 Variation of nitrate along the two lines of boreholes in Leeukuil.

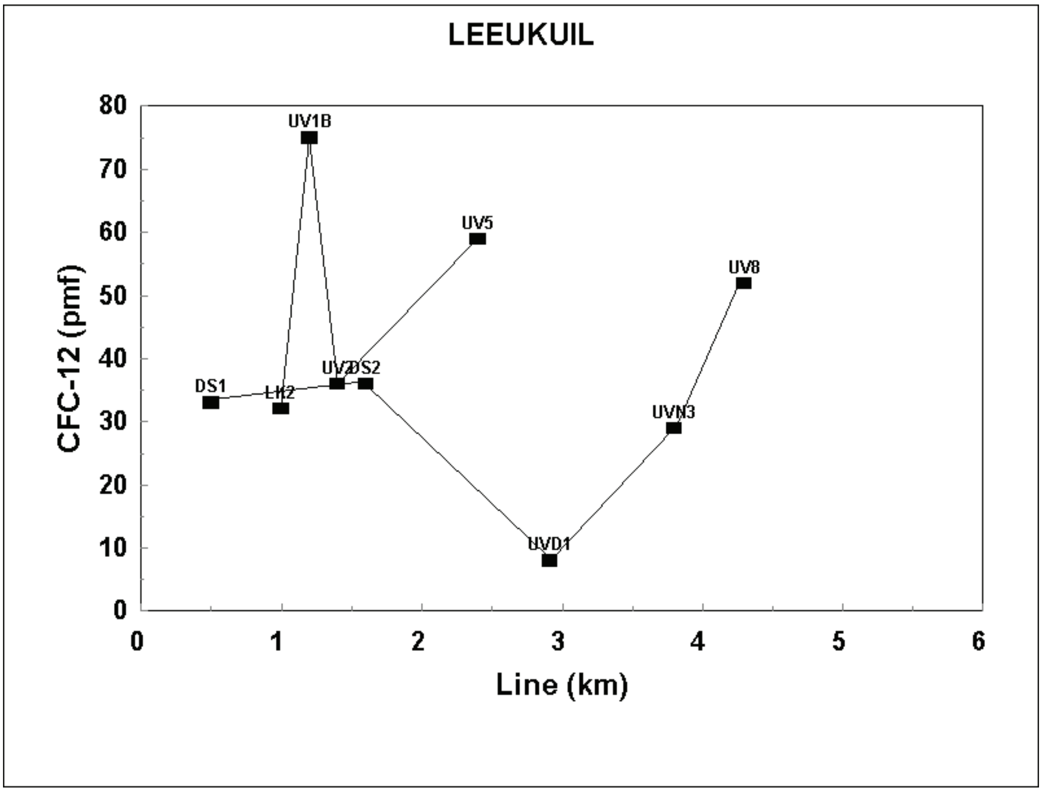


Figure 3.13 Variation of CFC-12 along the two lines of boreholes in Leeukuil.

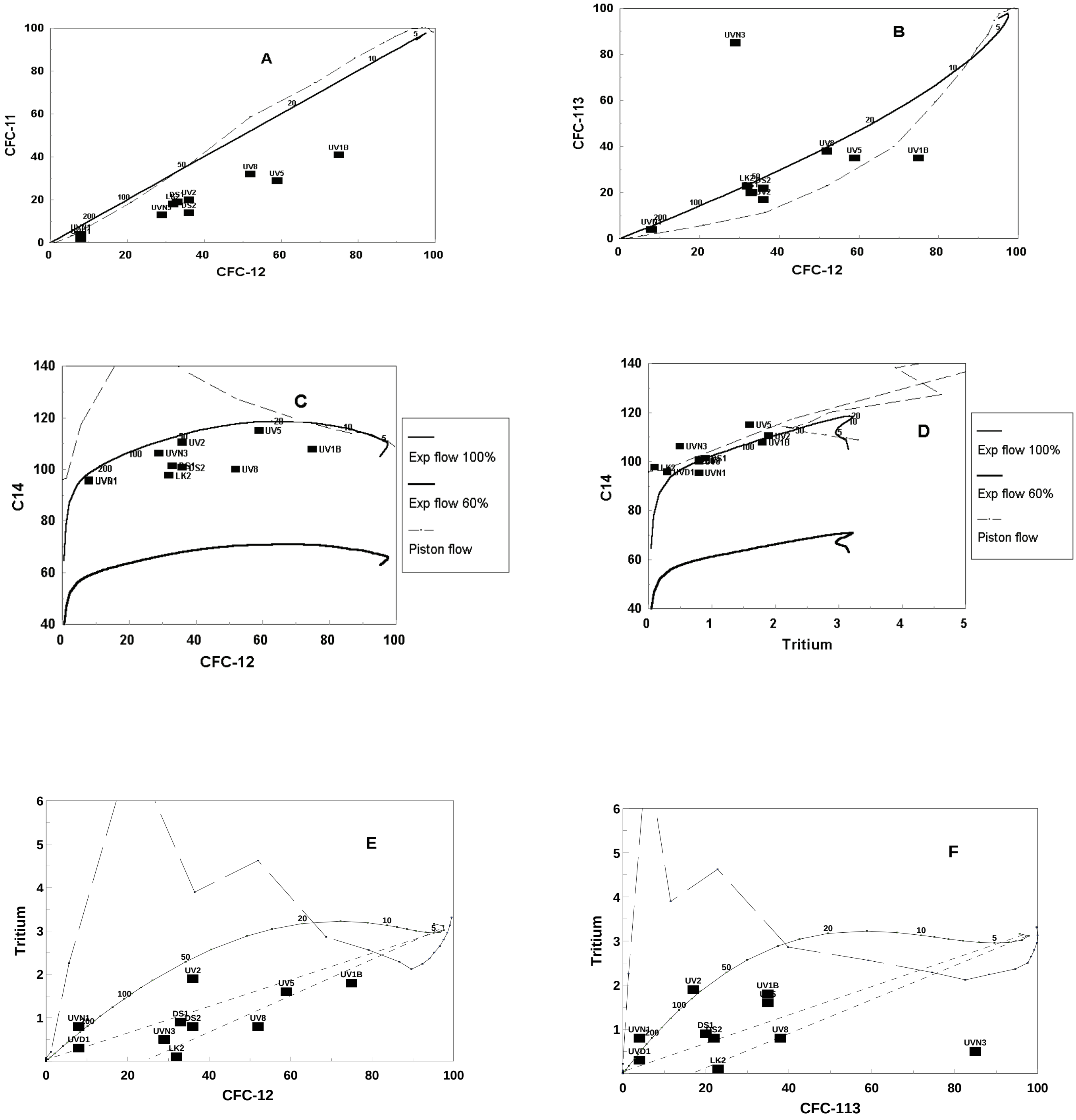


Figure 3.14 (A to F) Plots of ^{14}C, tritium and the three CFCs for the Leeukuil test site. Model relations for the exponential flow (solid line) and piston flow (dashed line) are also shown. The dotted lines in E and F suggest likely binary mixing processes. Numbers along the solid lines indicate the mean residence times of the exponential flow model.

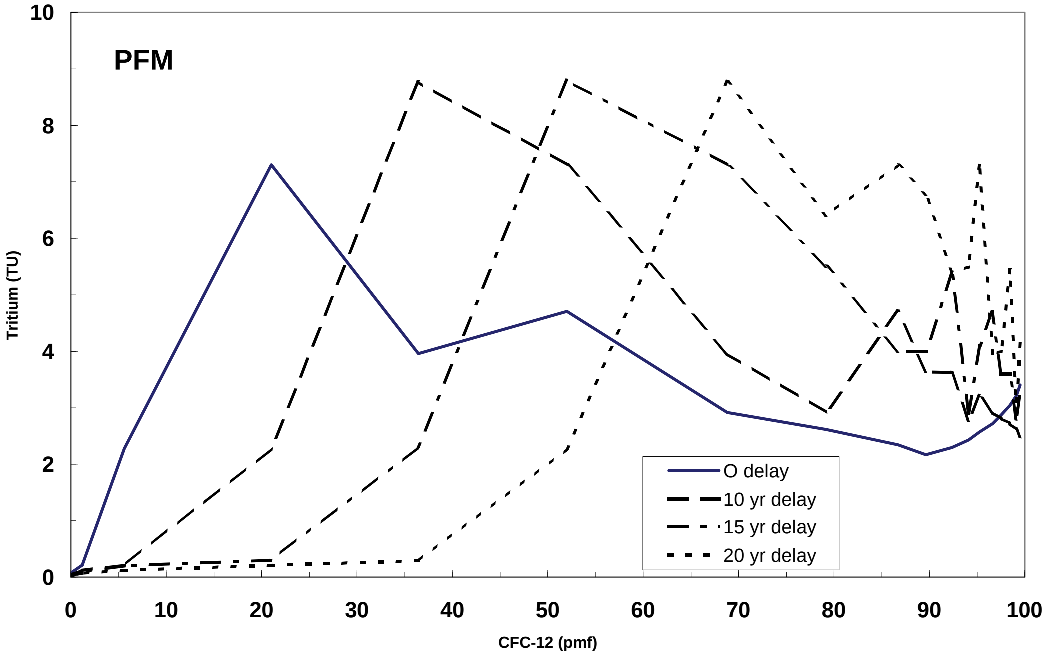


Figure 3.15 Model plots of tritium as function of CFC-12 with variable delays (up to 20 years) for tritium built in. This is intended to display the likely effect when tritium is held up in the unsaturated zone.

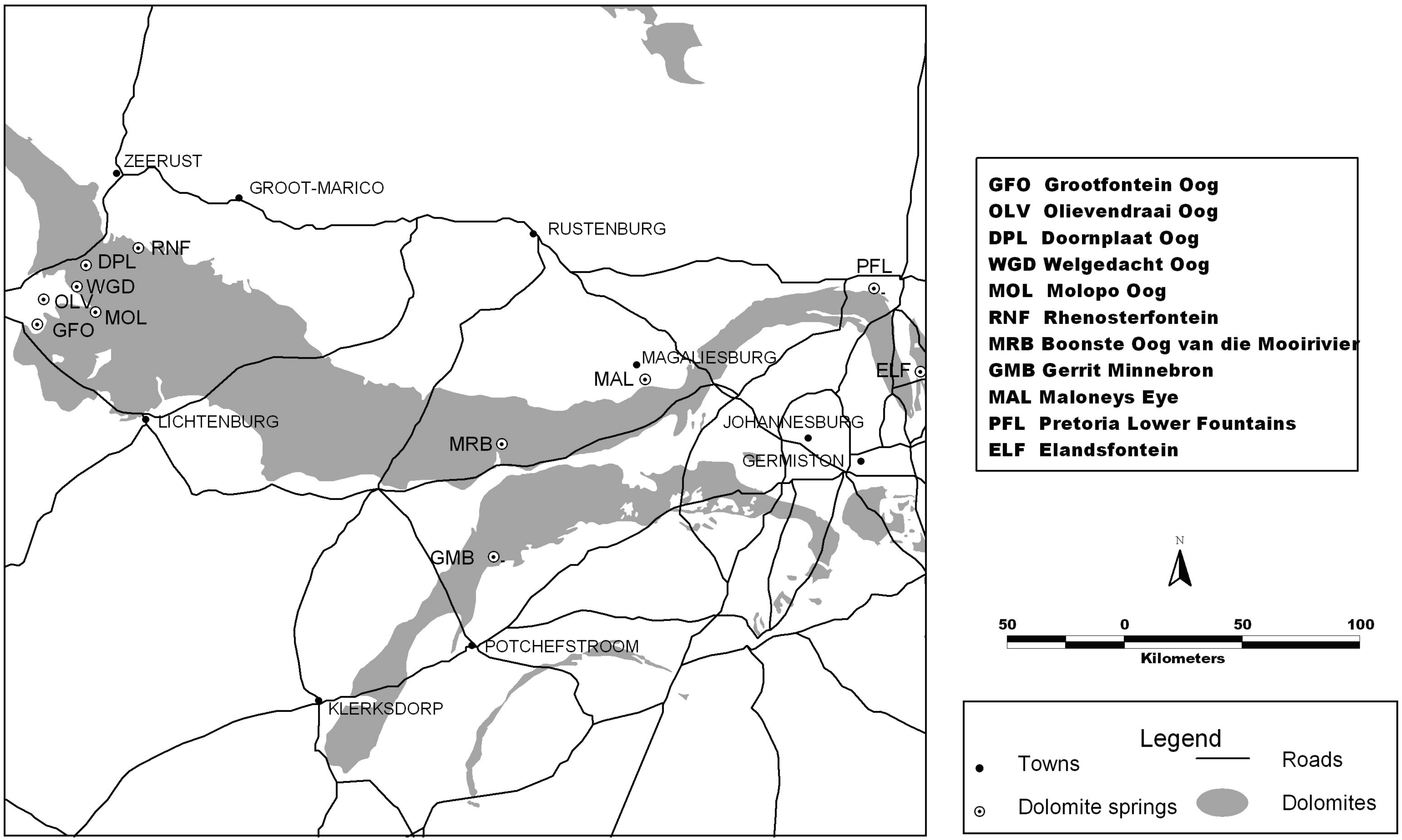


Figure 4.1 Dolomite springs. Site map showing sampling points.

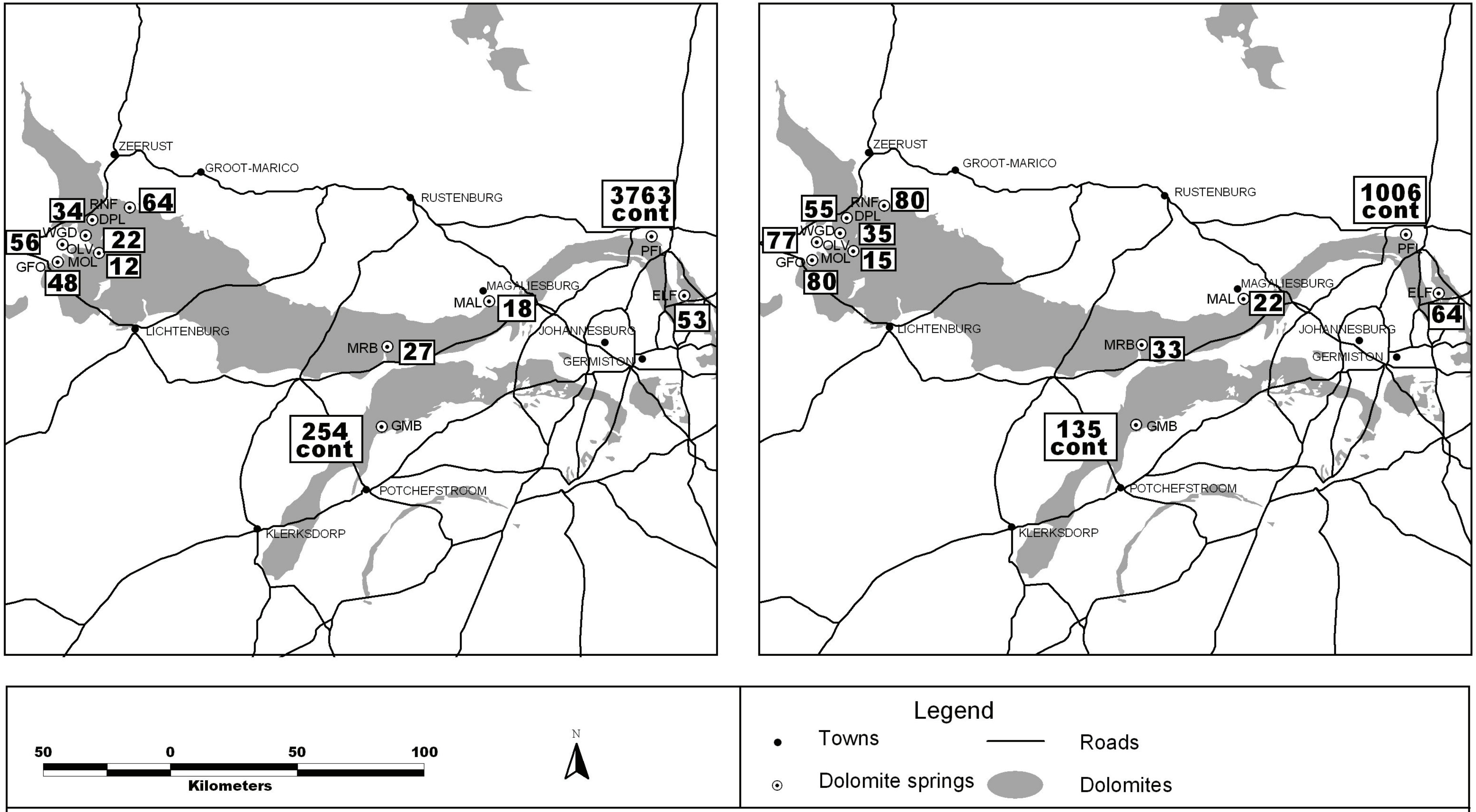


Figure 4.2 Dolomite. Isotope and geochemistry distribution. (a) CFC-11 pmf (b) CFC-12 pmf

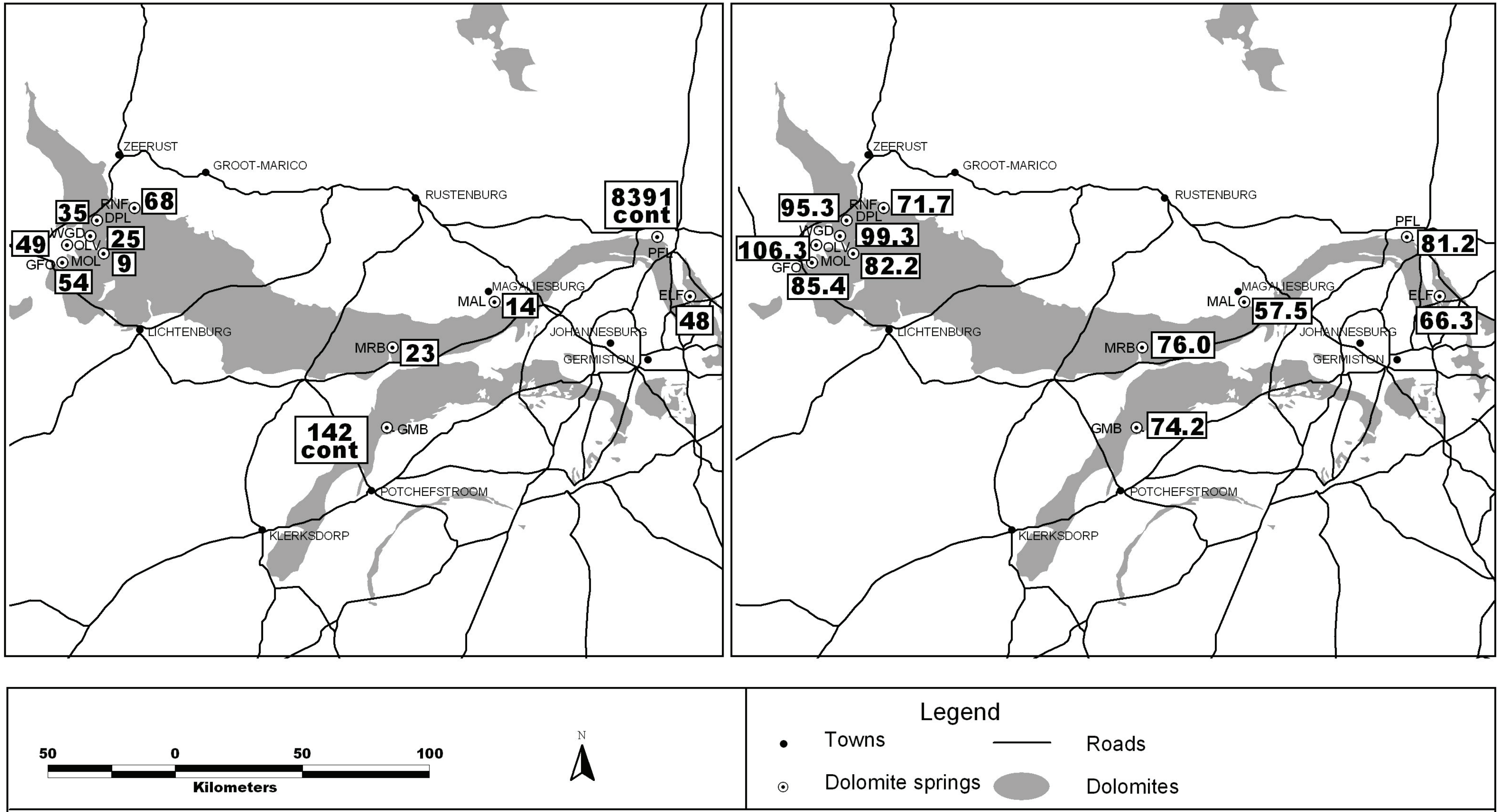


Figure 4.3 Dolomite. Isotope and geochemistry distribution. (a) CFC-113 pmf (b)^{14}C pmc

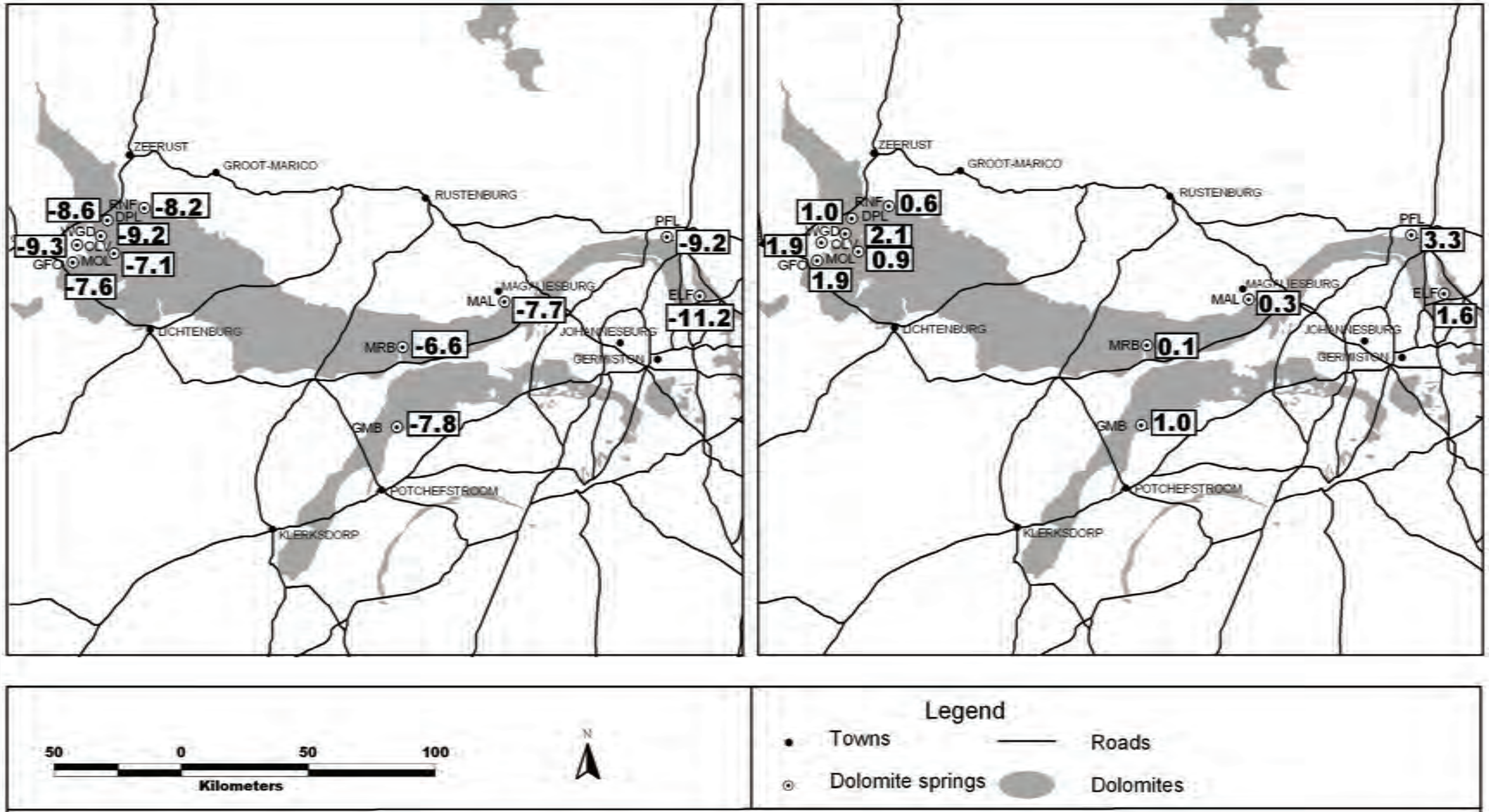


Figure 4.4 Dolomite. Isotope and geochemistry distribution. (a) $\delta^{13}C$ ‰ PDB (b) TRITIUM TU

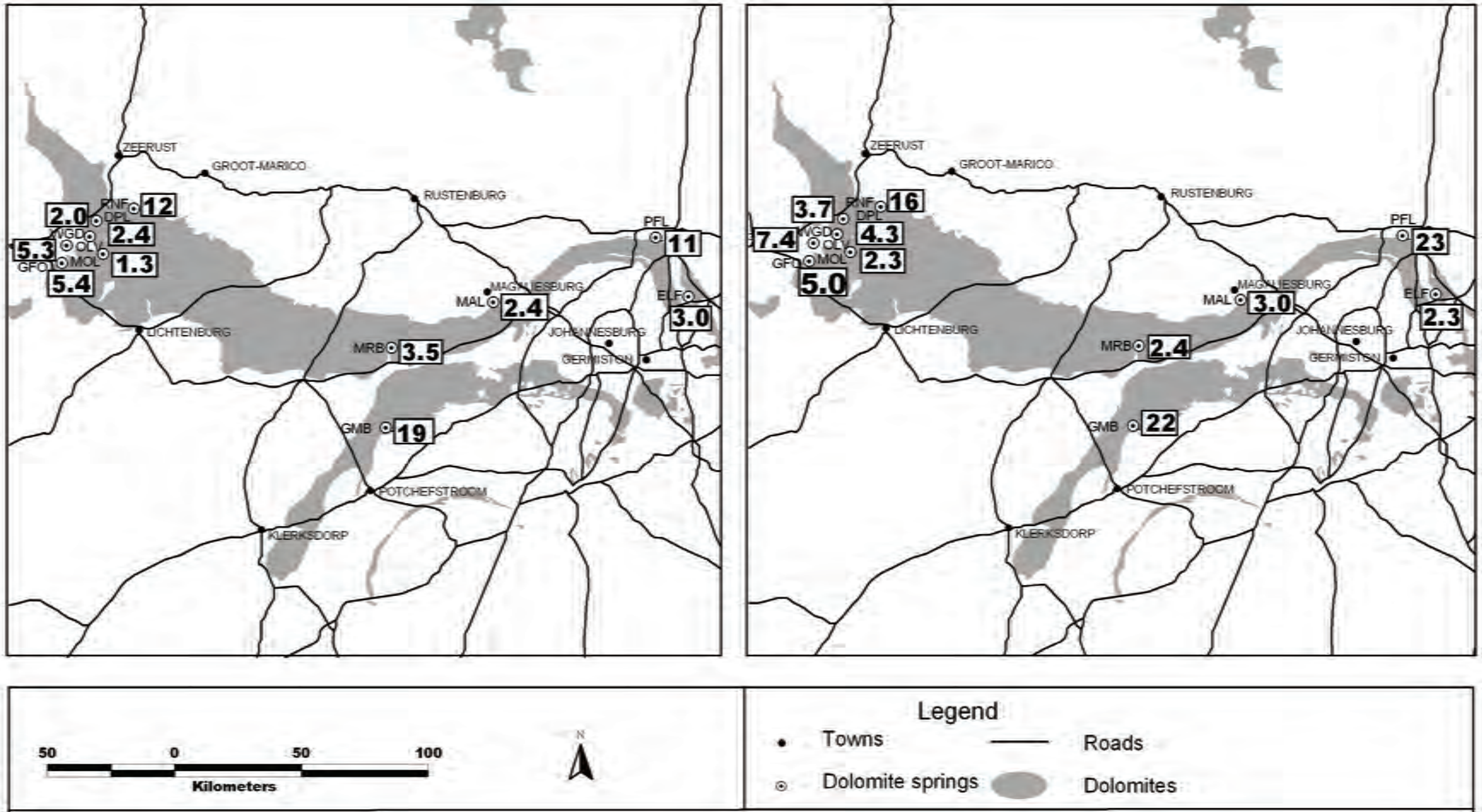


Figure 4.5 Dolomite. Isotope and geochemistry distribution. (a) Sodium as Na (mg/L) (b) Chloride as Cl (mg/L)

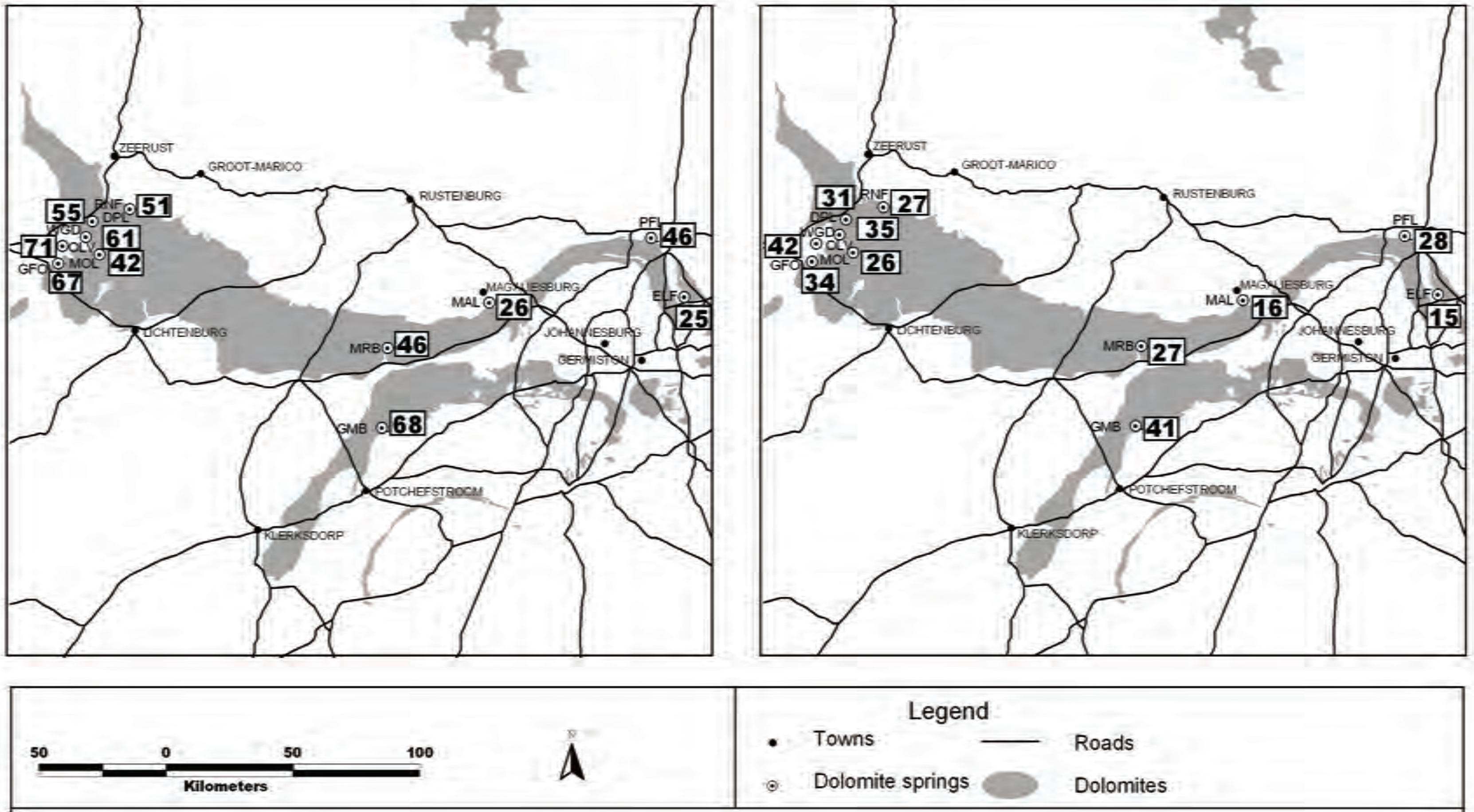


Figure 4.6 Dolomite. Isotope and geochemistry distribution. (a) Calcium as Ca (mg/L) (b) Magnesium as Mg (mg/L)

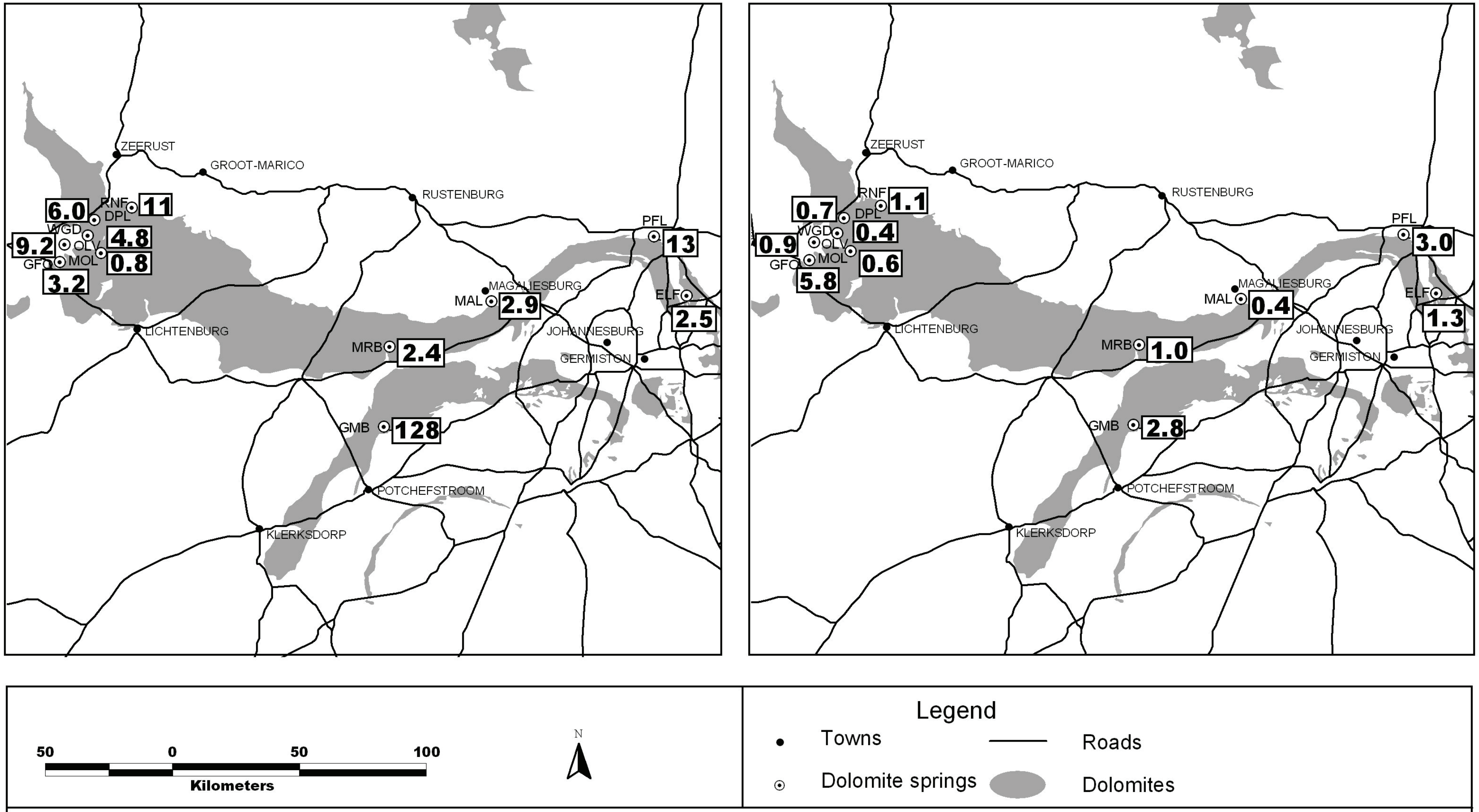


Figure 4.7 Dolomite. Isotope and geochemistry distribution. (a) Sulphate as SO_4 (b) Nitrate plus nitrite as N (mg/L)

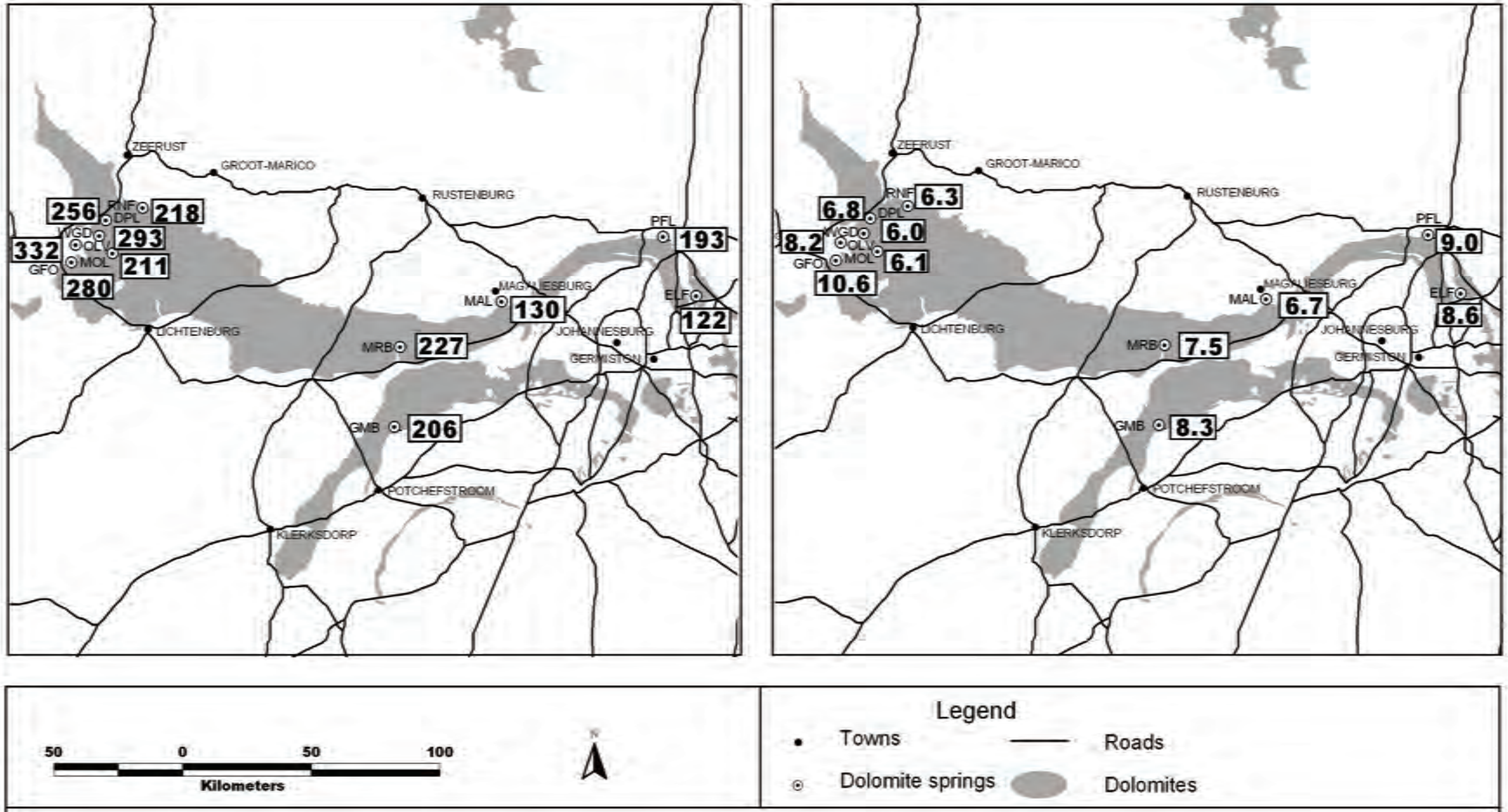


Figure 4.8 Dolomite. Isotope and geochemistry distribution. (a) Alkalinity as $CaCO_3$ (mg/L) (b) Silica as Si (mg/L)

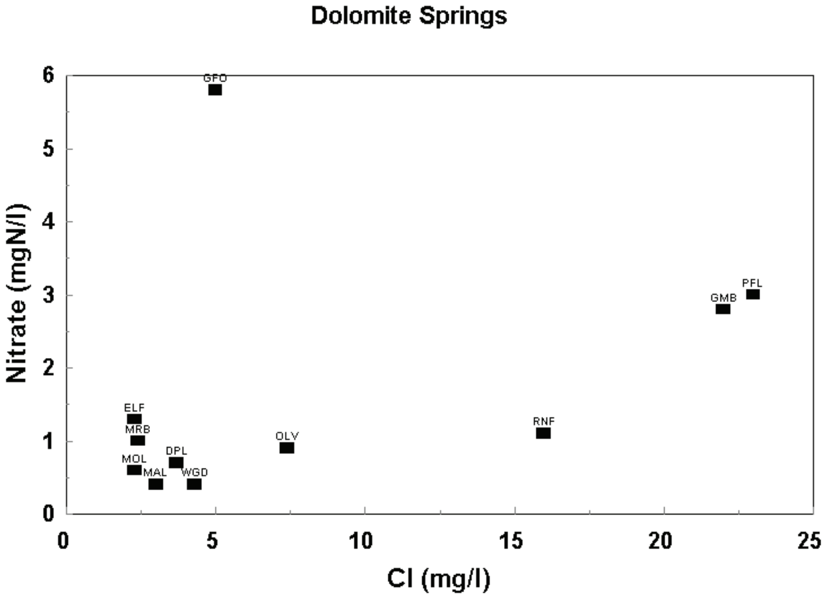


Figure 4.9 Plot of nitrate against chloride for the dolomite springs. Note the exceptions PFL (Pretoria Fountains lower), RNF (Rhenosterfontein) GMB (Gerrit Minnebron) and GFO (Grootfonteinoog)

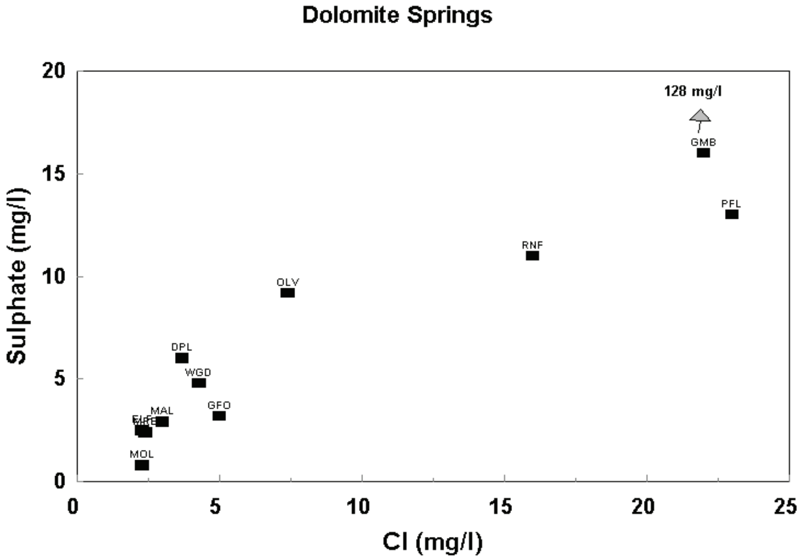


Figure 4.10 Plot of sulphate against chloride for the dolomite springs. Note the exceptions PFL (Pretoria Fountains lower), GMB (Gerrit Minnebron), RNF (Rhenosterfontein) and OLV (Olievendraai).

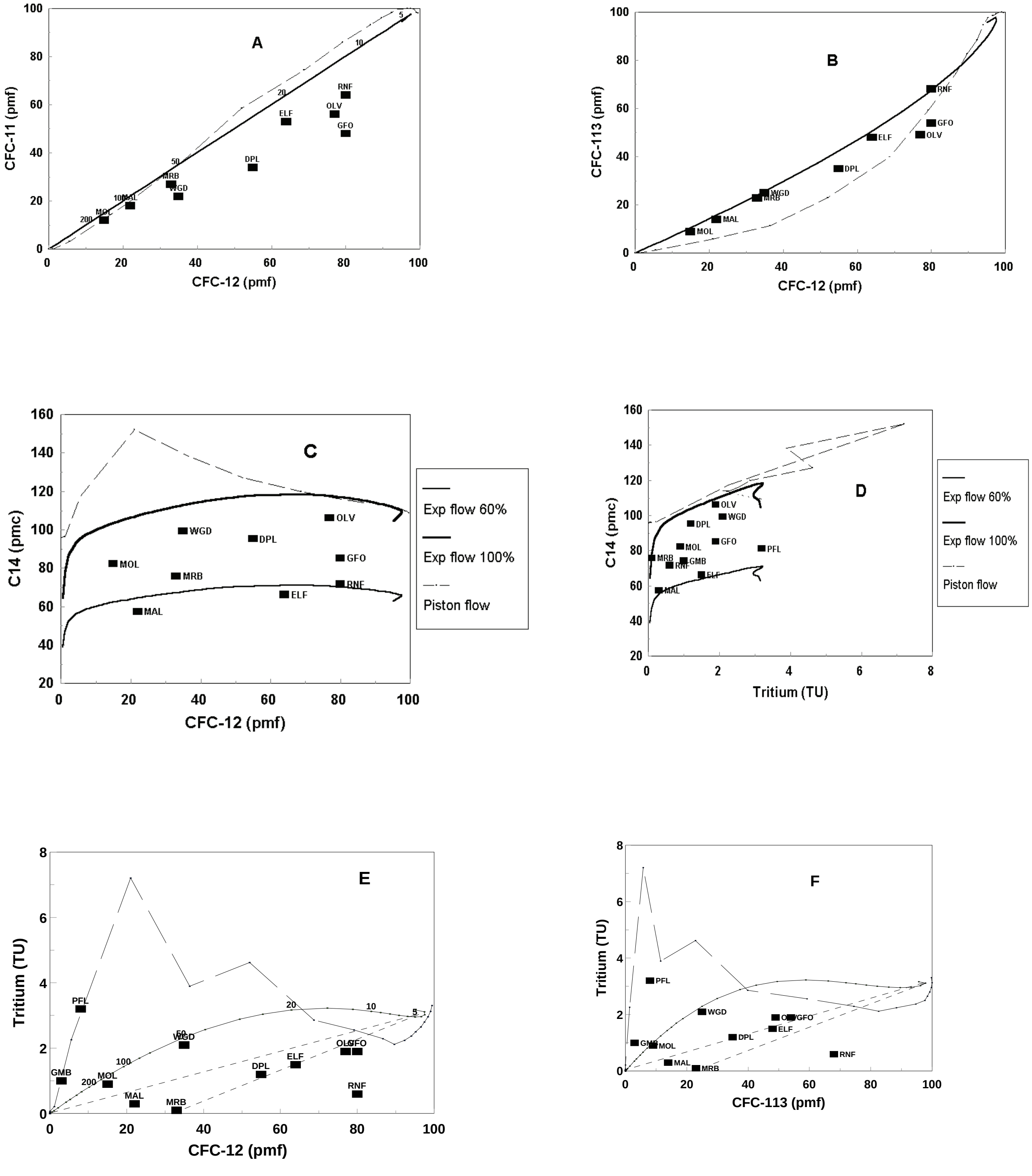


Figure 4.11 (A to F). Plots of ^{14}C, tritium and the three CFCs for the Dolomite springs that were sampled. Model relations for the exponential flow (solid line) and piston flow (dashed line) are also shown. The dotted lines suggest likely mixing processes. Numbers along the solid lines indicate mean residence times for the exponential flow models.

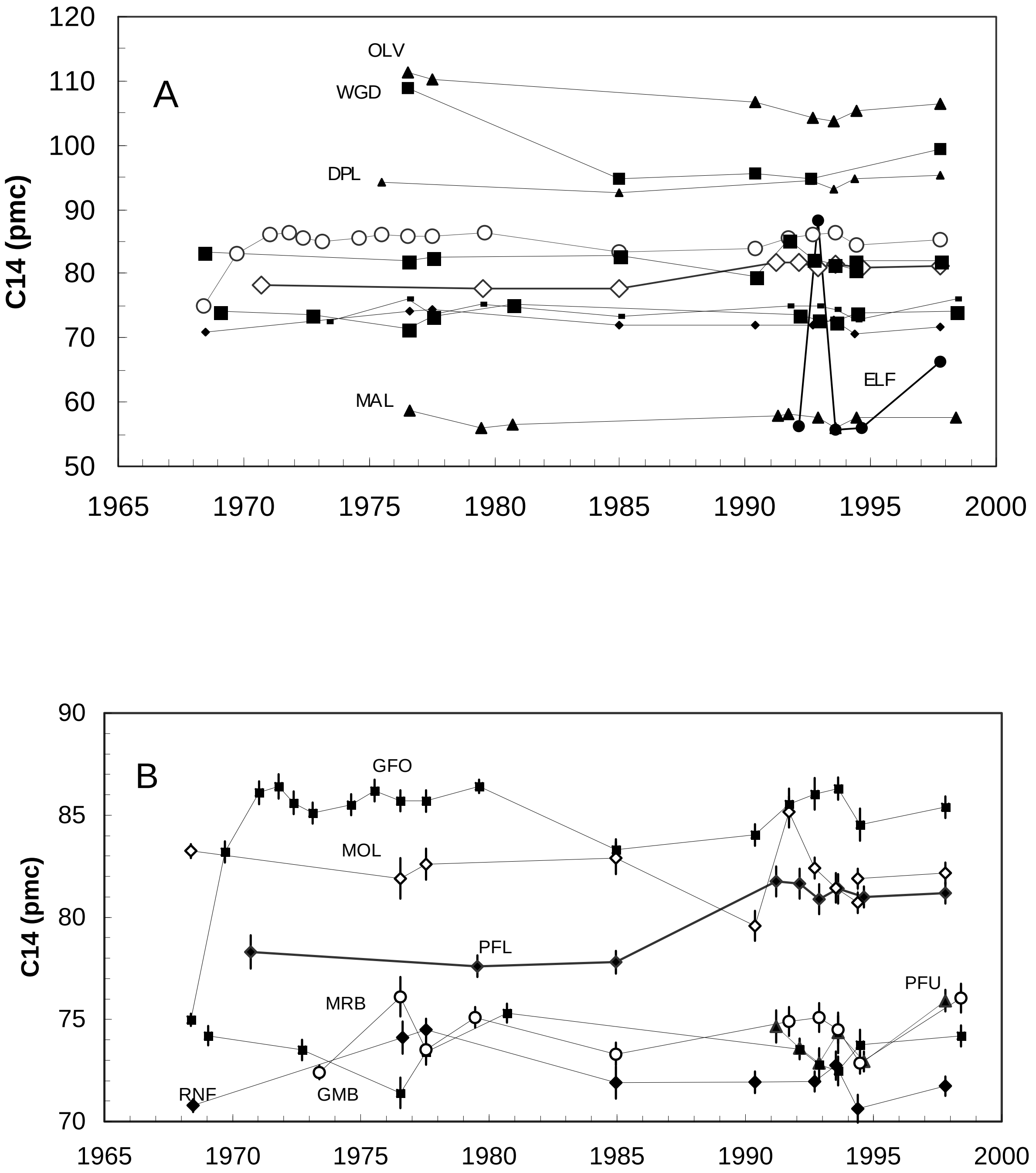


Figure 4.12 Plots of ^{14}C with time of the springs sampled in the course of the present project. A: all the time series. B: selected time series that vary slowly. Data from Talma and Vogel (2001) and report of Talma to DWAF (in preparation).

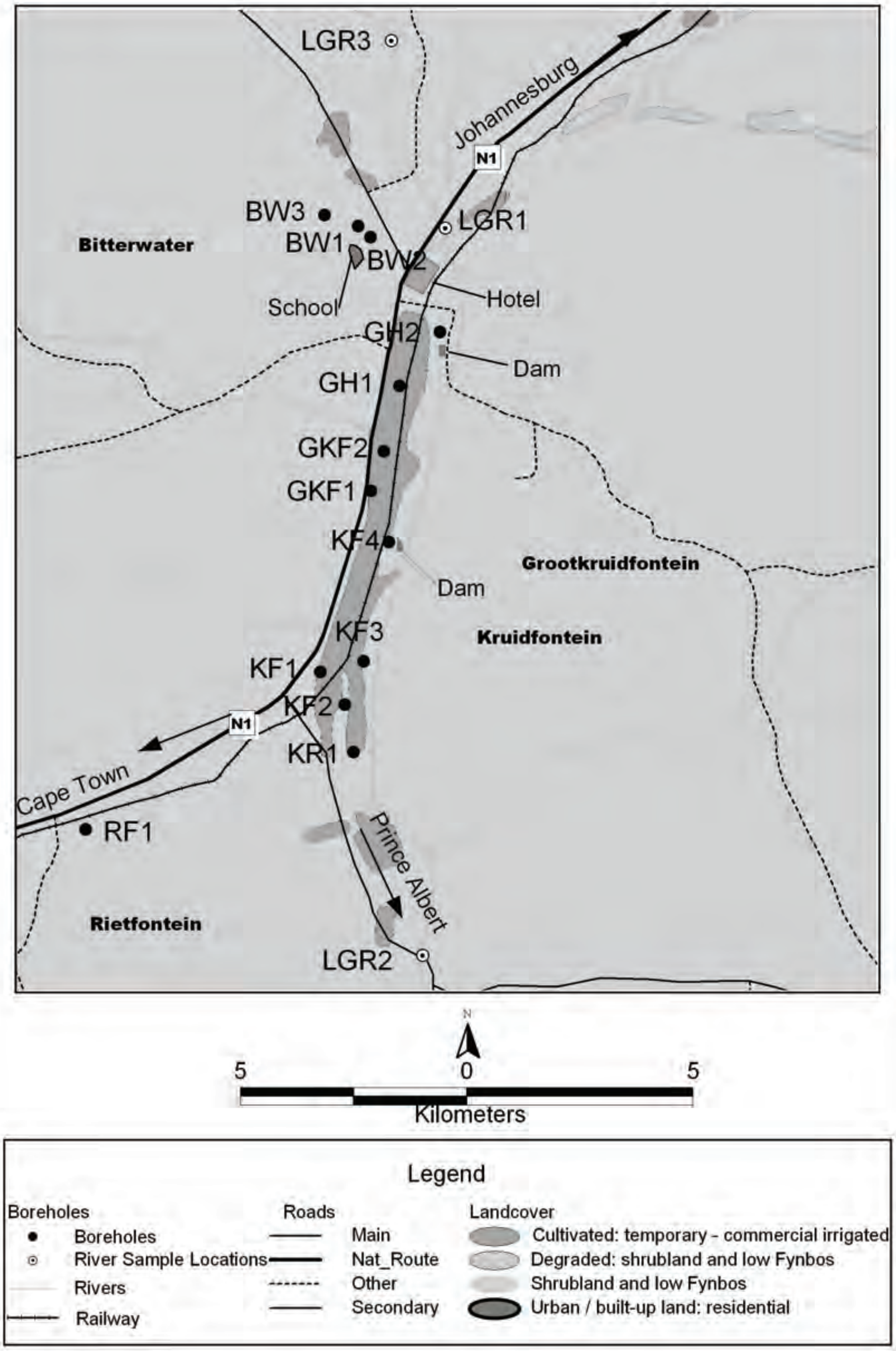


Figure 5.1 Leeu Gamka. Site map showing points.

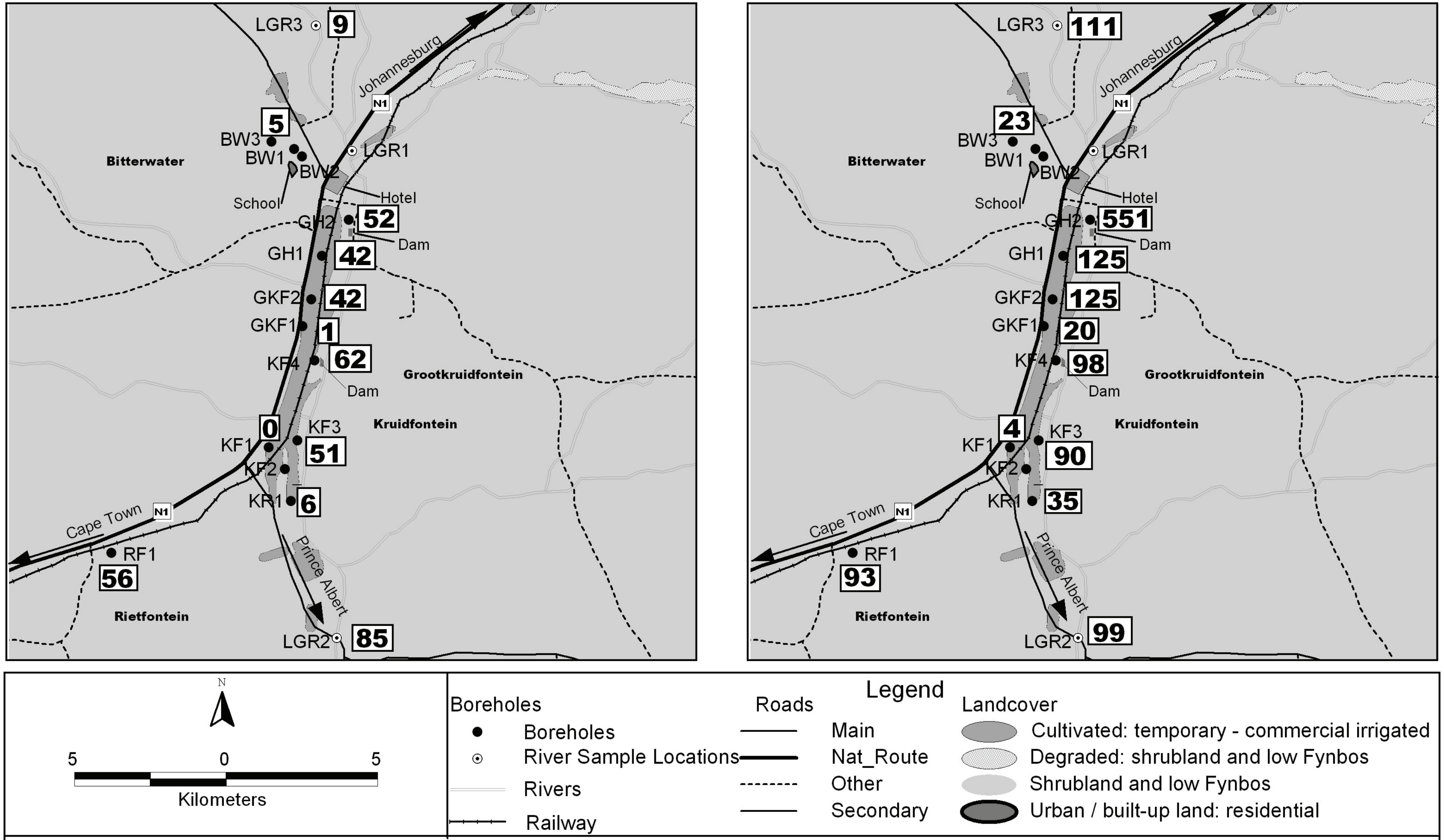


Figure 5.2 Leeu Gamka. Isotope and geochemistry distribution. (a) CFC-11 pmf (b) CFC-12 pmf

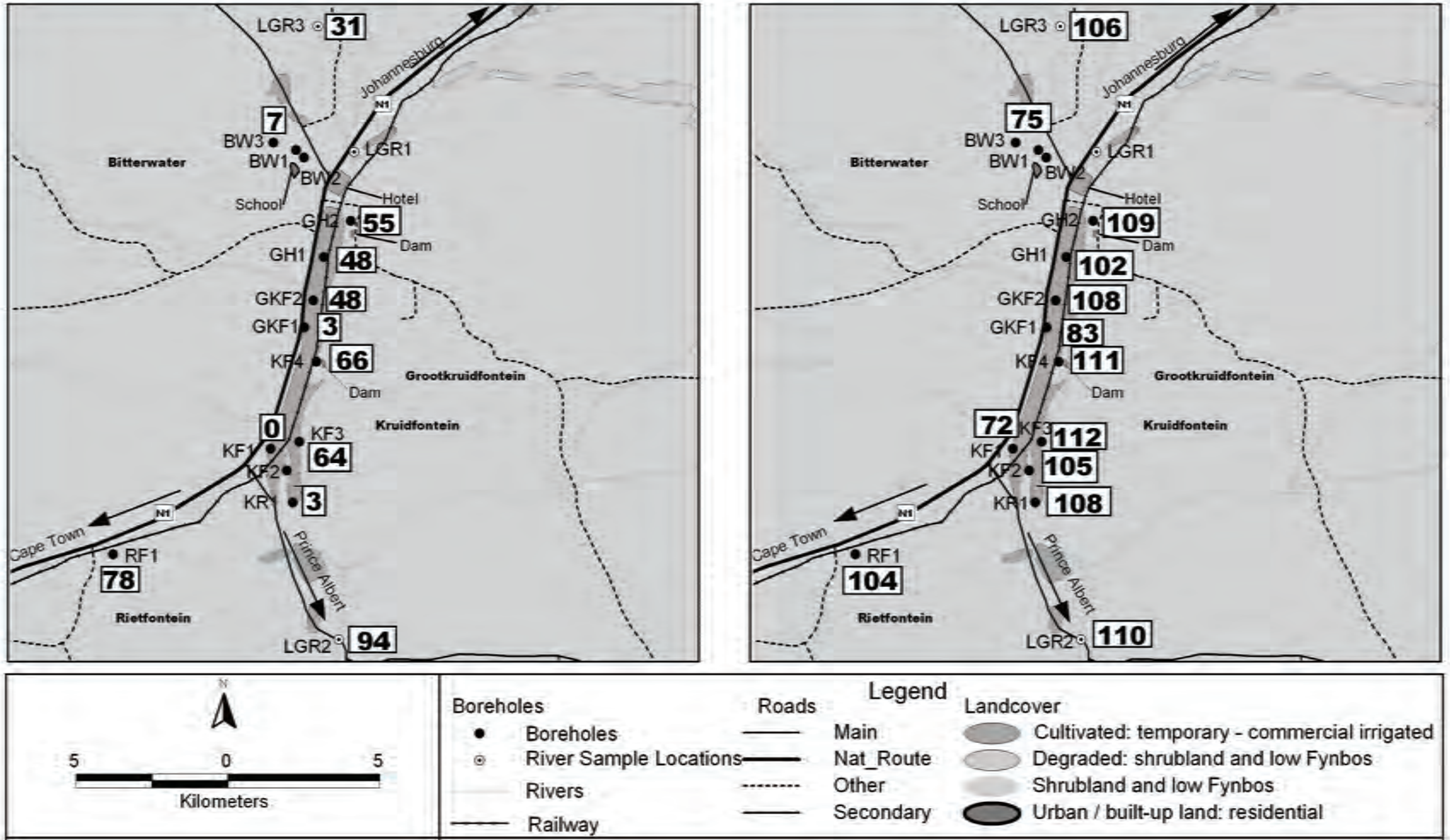


Figure 5.3 Leeu Gamka. Isotope and geochemistry distribution. (a) CFC-113 pmf (b)^{14}C pmc

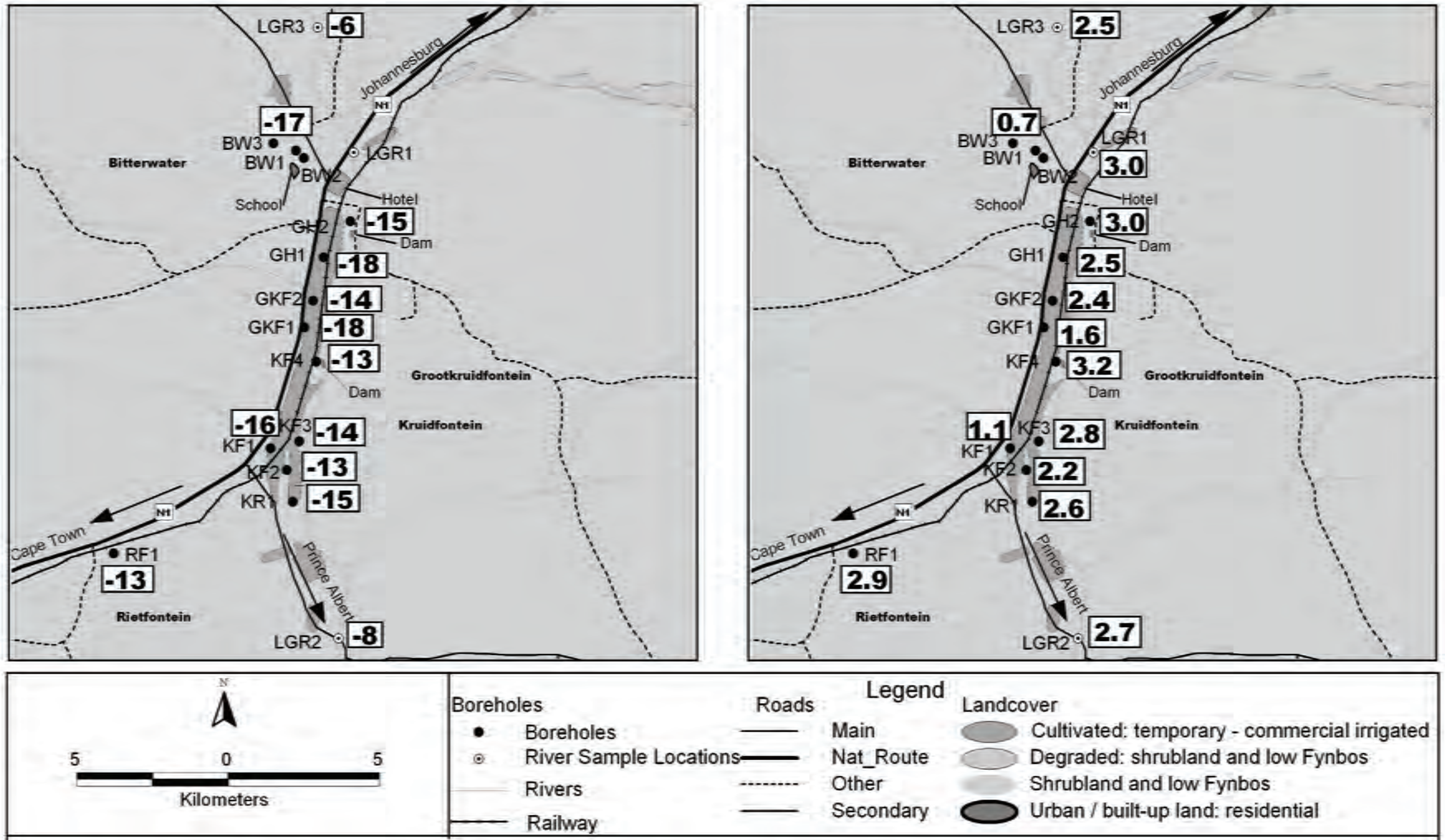


Figure 5.4 Leeu Gamka. Isotope and geochemistry distribution. (a)$\delta^{13}C$‰ PDB (b) TRITIUM TU

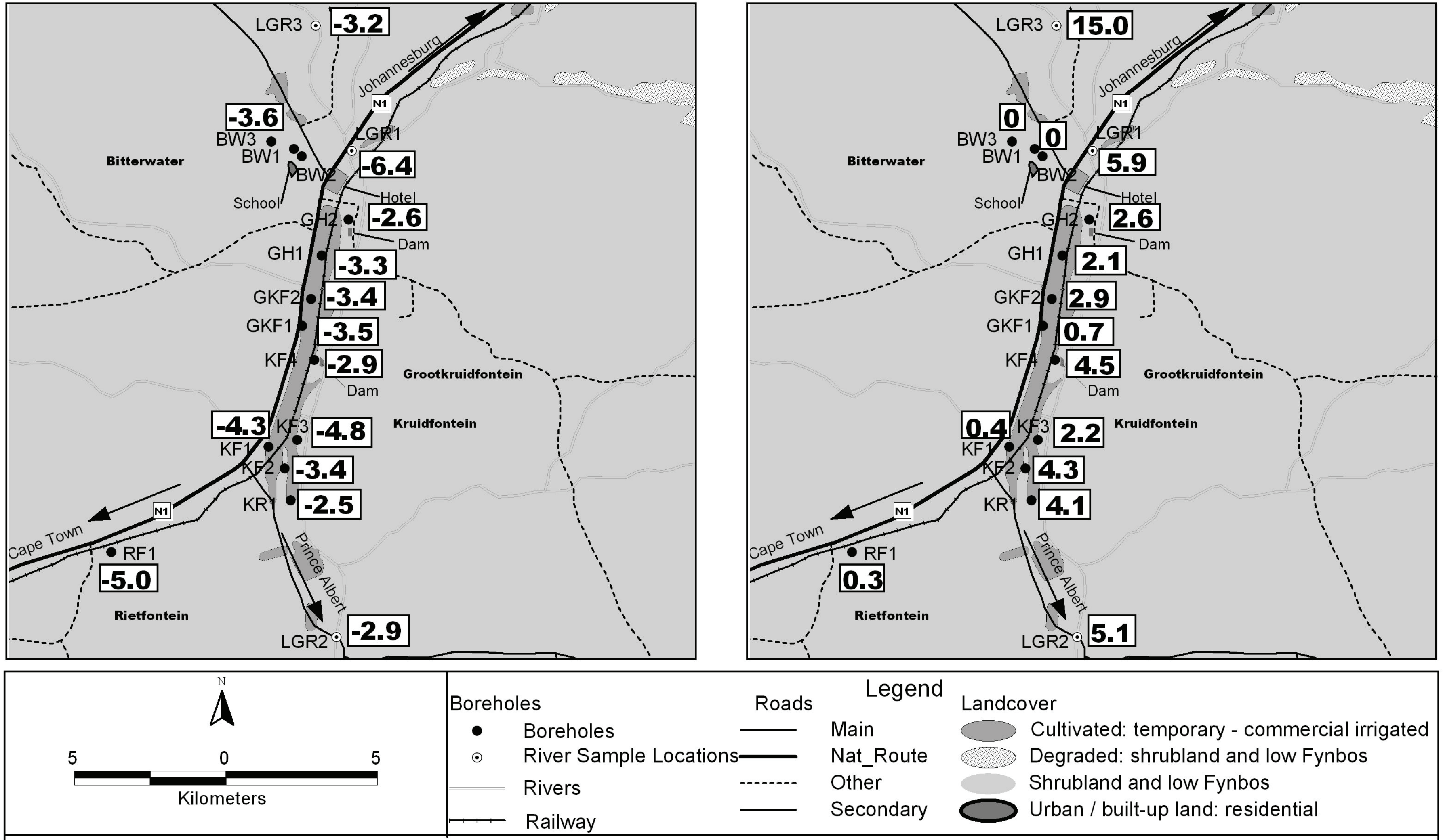


Figure 5.5 Leeu Gamka. Isotope and geochemistry distribution. (a) δ^{18}O‰SMOW (b) Dissolved Organic Carbon (mg/L)

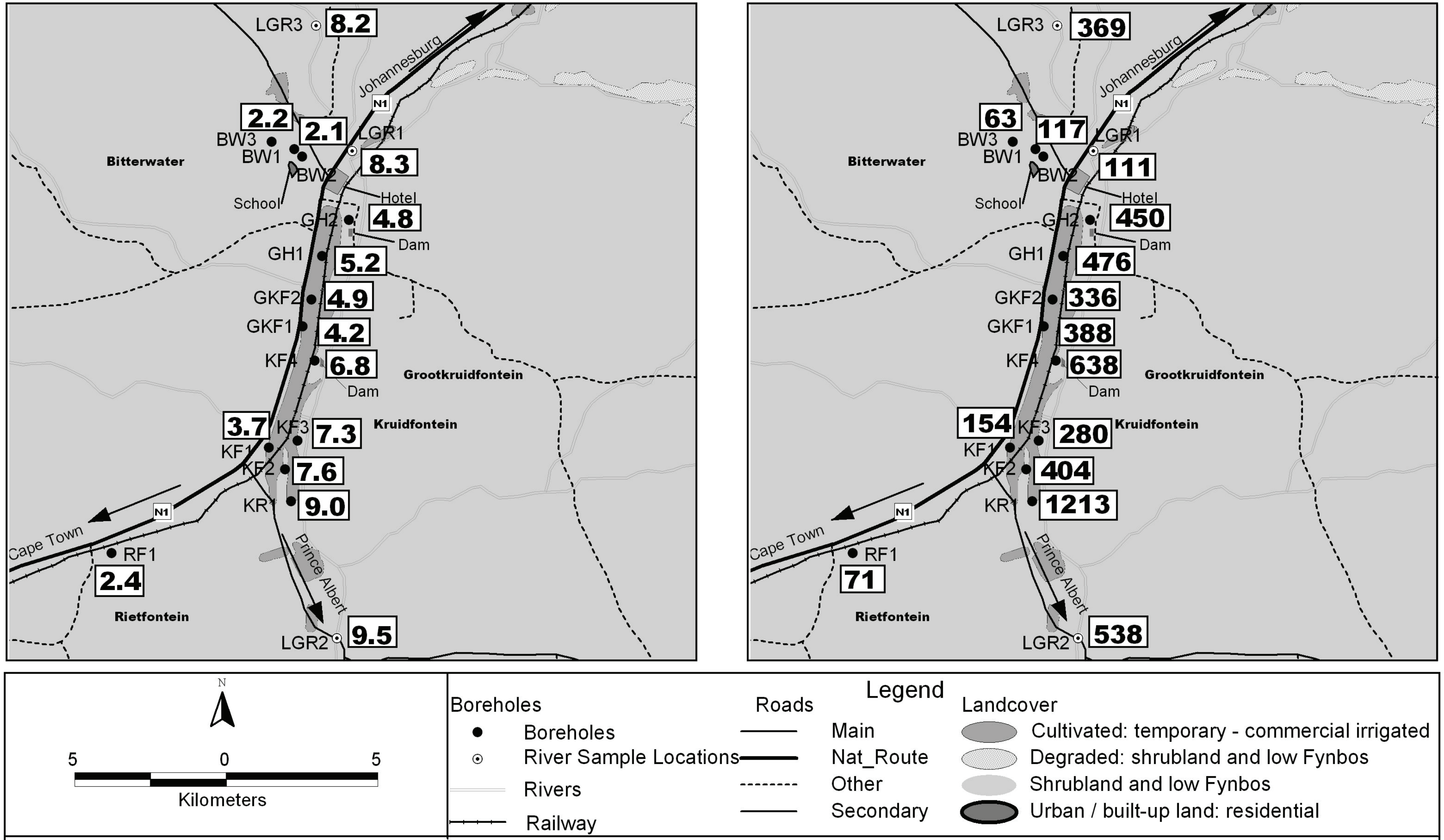


Figure 5.6 Leeu Gamka. Isotope and geochemistry distribution. (a) Potassium as K (mg/L) (b) Sodium as Na (mg/L)

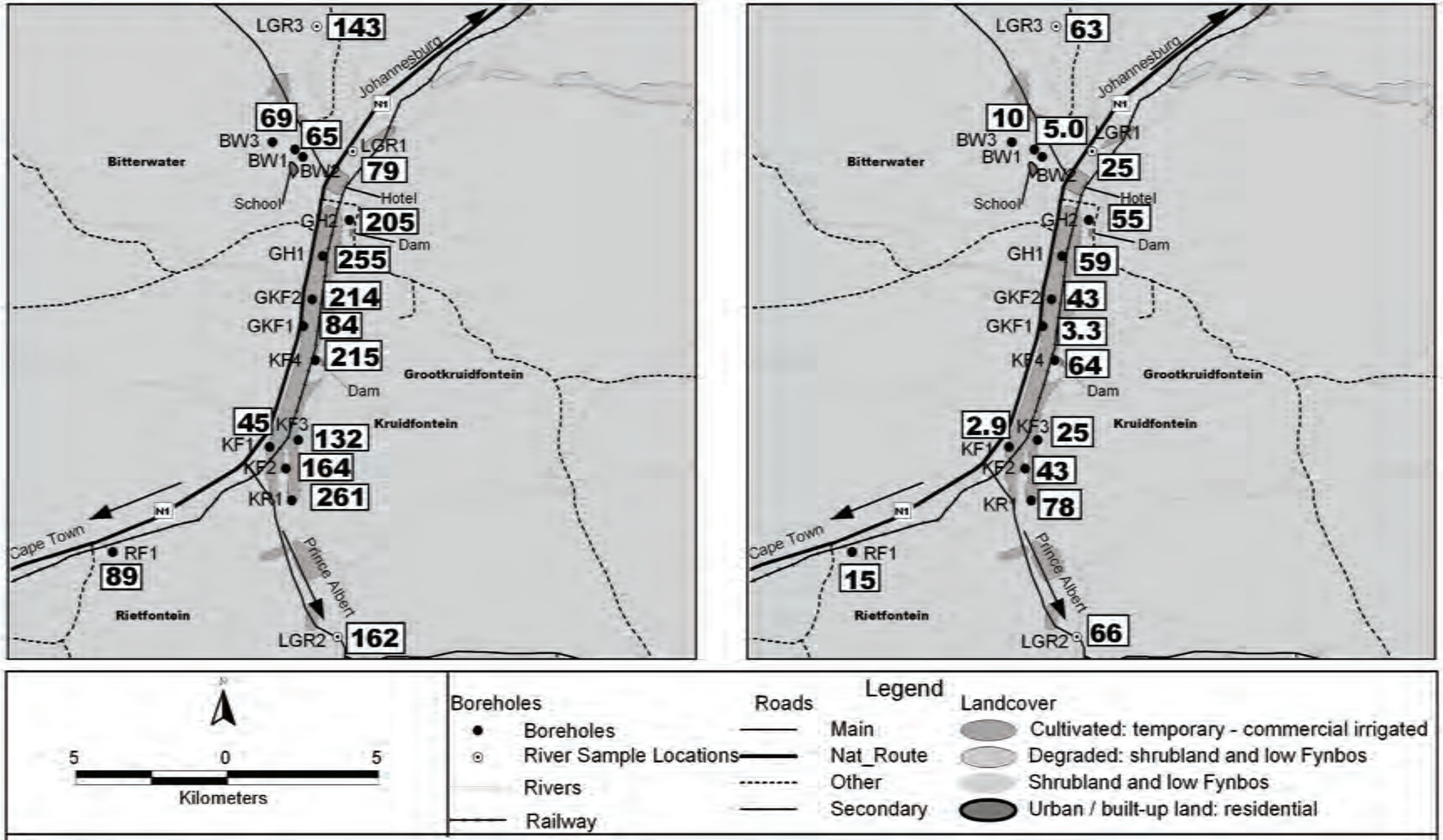


Figure 5.7 Leeu Gamka. Isotope and geochemistry distribution. (a) Calcium as Ca (mg/L) (b) Magnesium as Mg (mg/L)

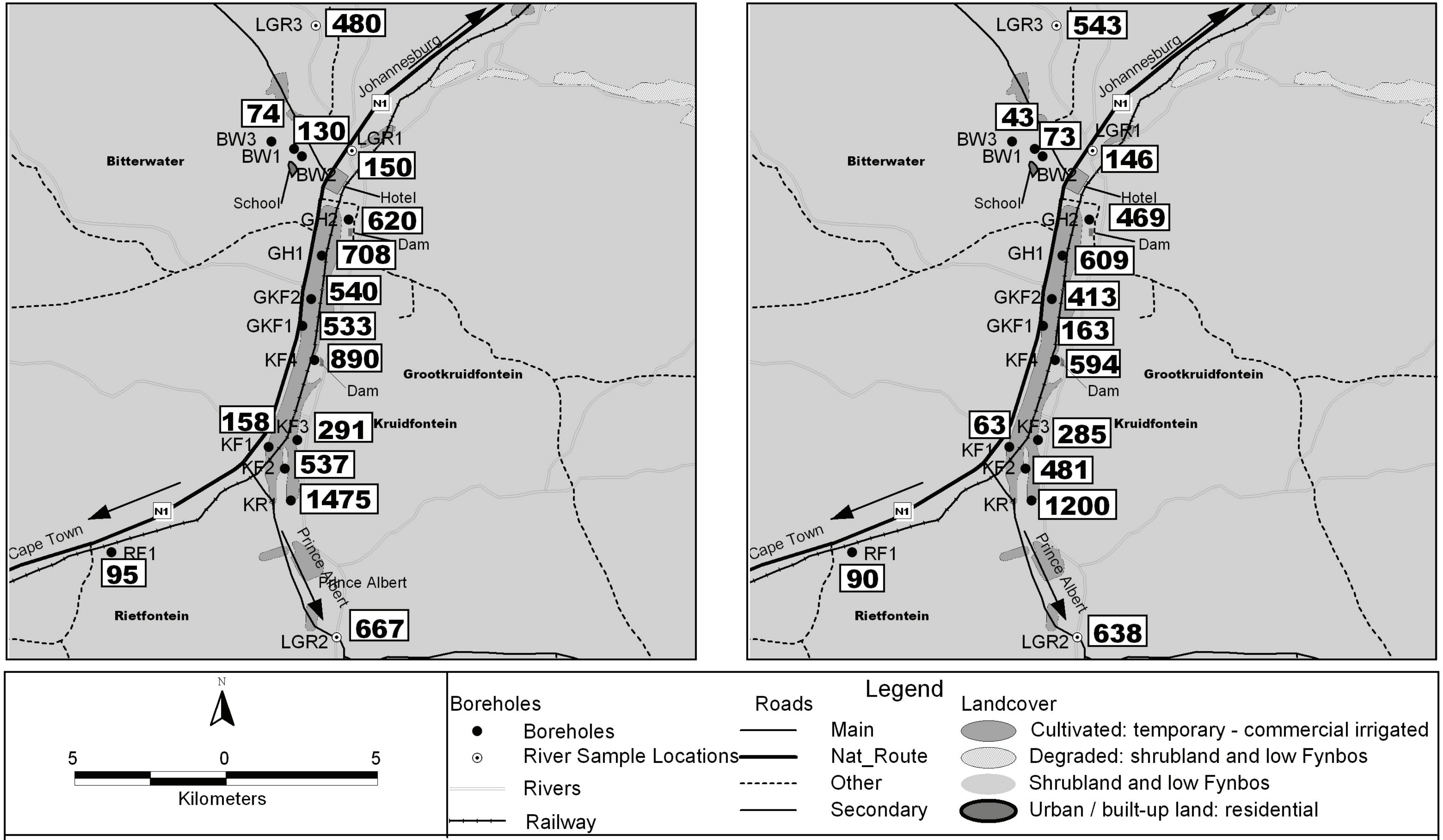


Figure 5.8 Leeu Gamka. Isotope and geochemistry distribution. (a) Sulphate as SO_4 (mg/L) (b) Chloride as Cl (mg/L)

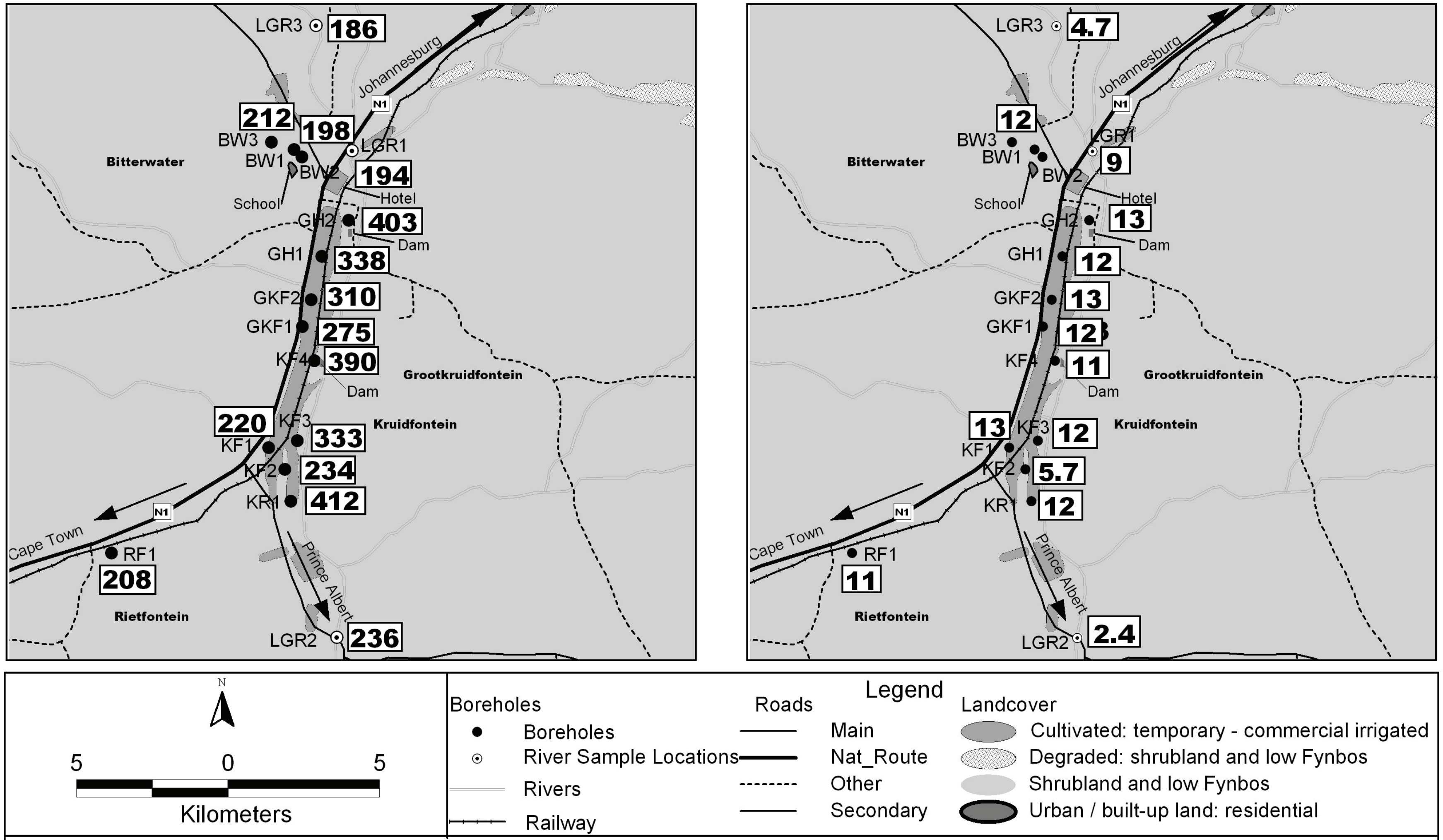


Figure 5.9 Leeu Gamka. Isotope and geochemistry distribution. (a) Alkalinity as $CaCO_3$ (mg/L) (b) Silica as Si (mg/L)

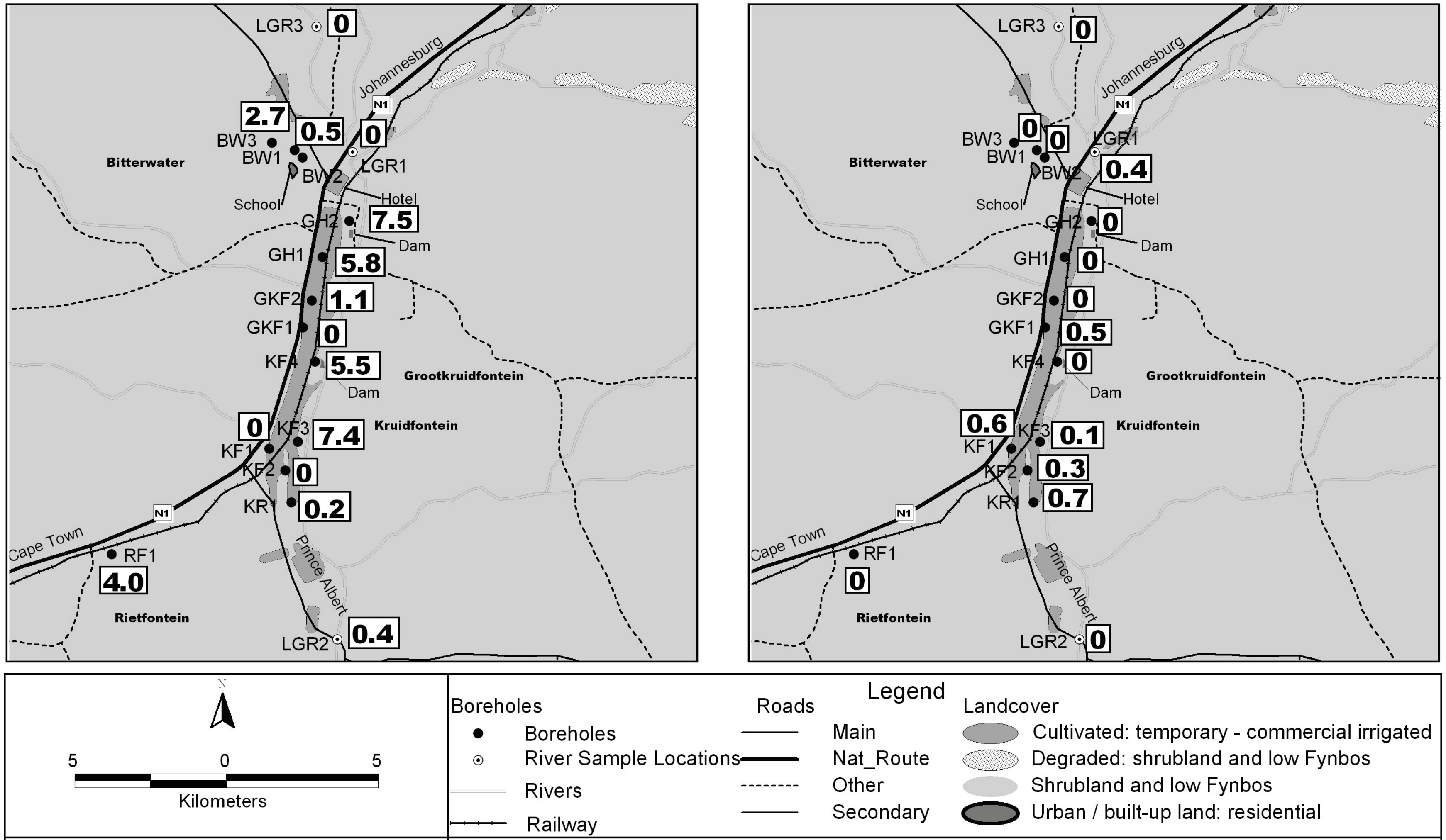


Figure 5.10 Leeu Gamka. Isotope and geochemistry distribution. (a) Nitrate plus nitrate as N (mg/L) (b) Ammonia as NH_4 (mg/L)

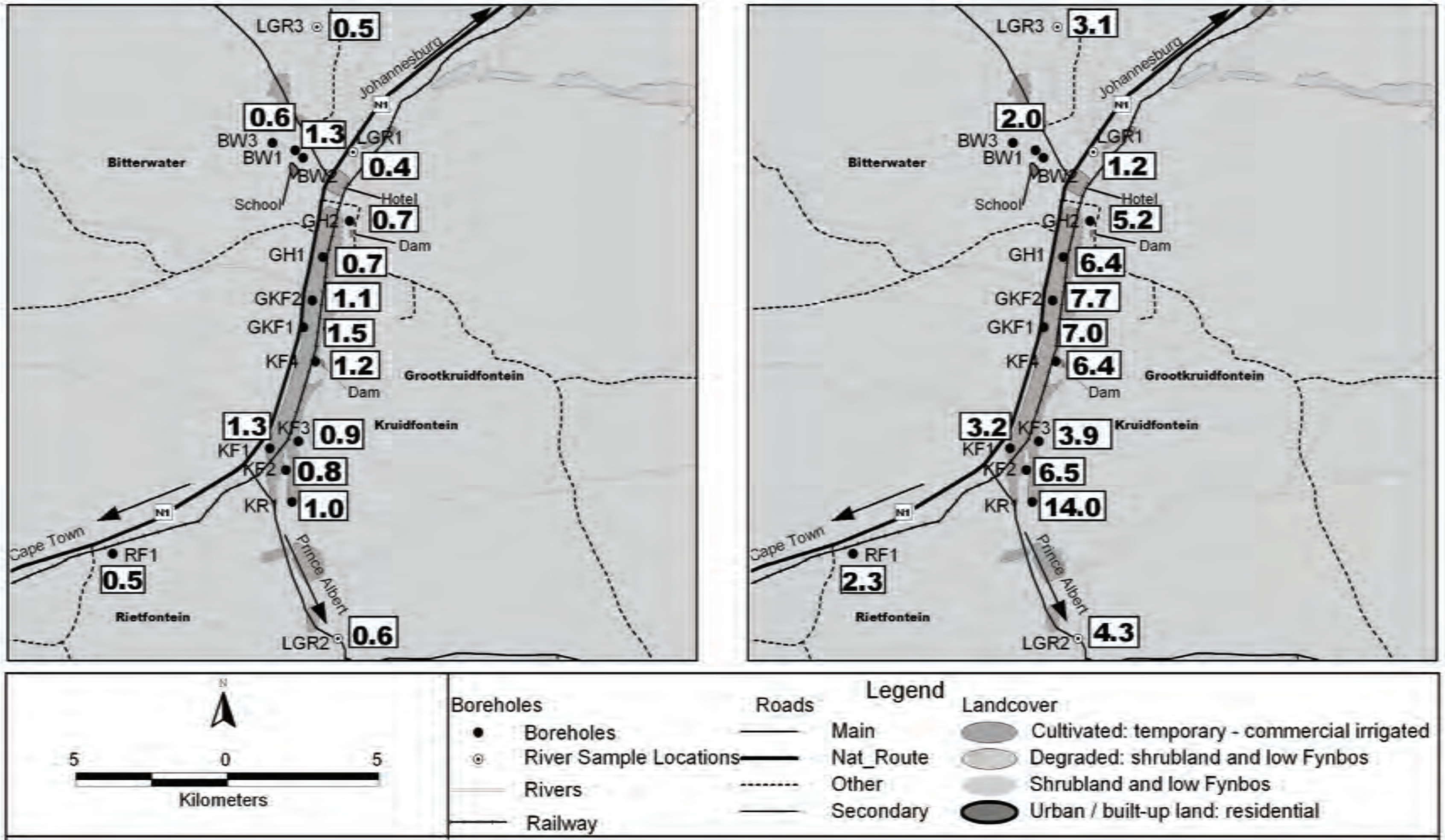


Figure 5.11 Leeu Gamka. Isotope and geochemistry distribution. (a) Fluoride as F (mg/L) (b) Strontium as Sr (mg/L)

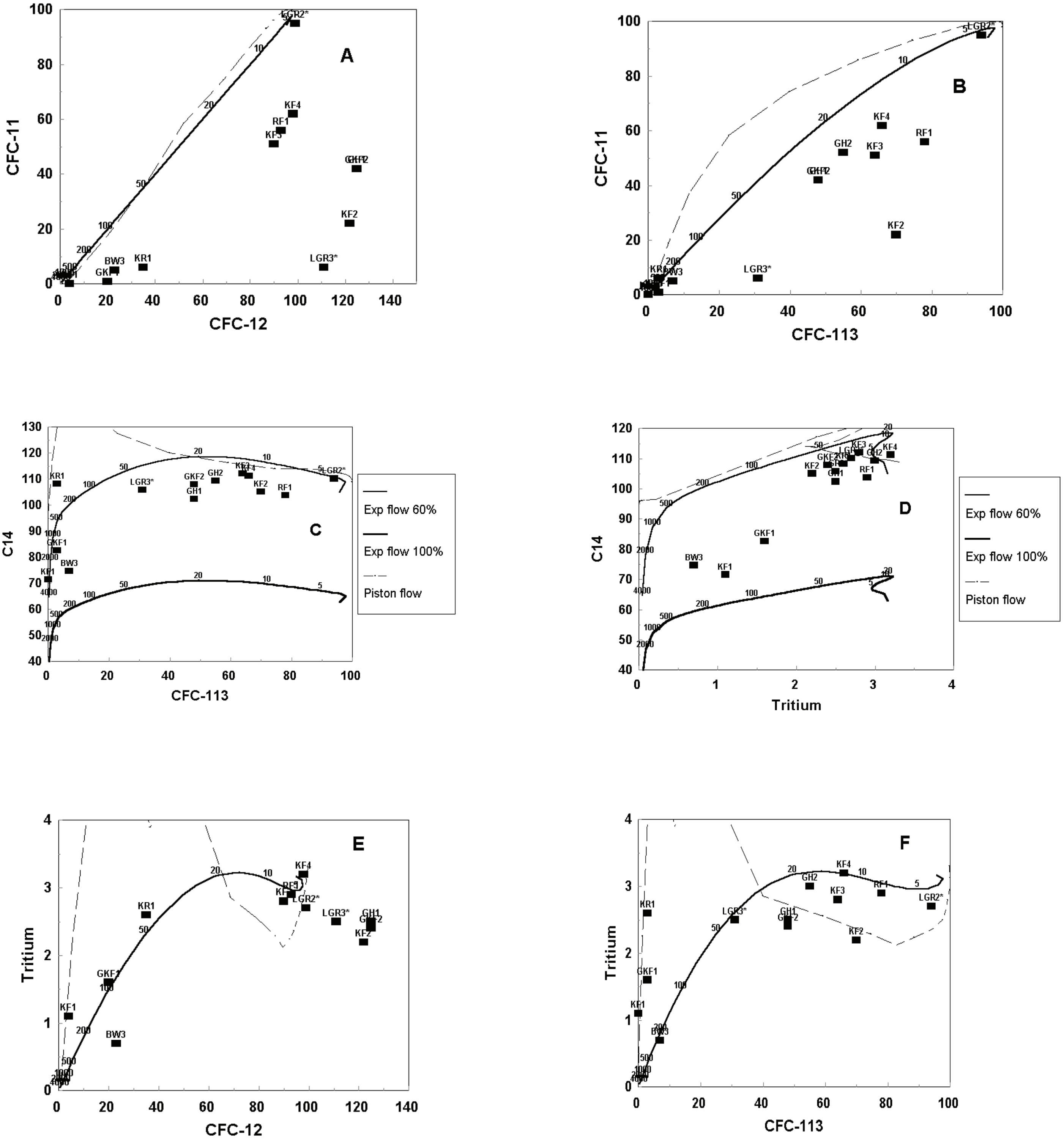


Figure 5.12 (A to F). Plots of ^{14}C, tritium and the three CFCs for the LeeuGamka study site. Model relations for the exponential flow (solid line) and piston flow (dashed line) are also shown. Numbers against the solid lines indicate the mean residence times.

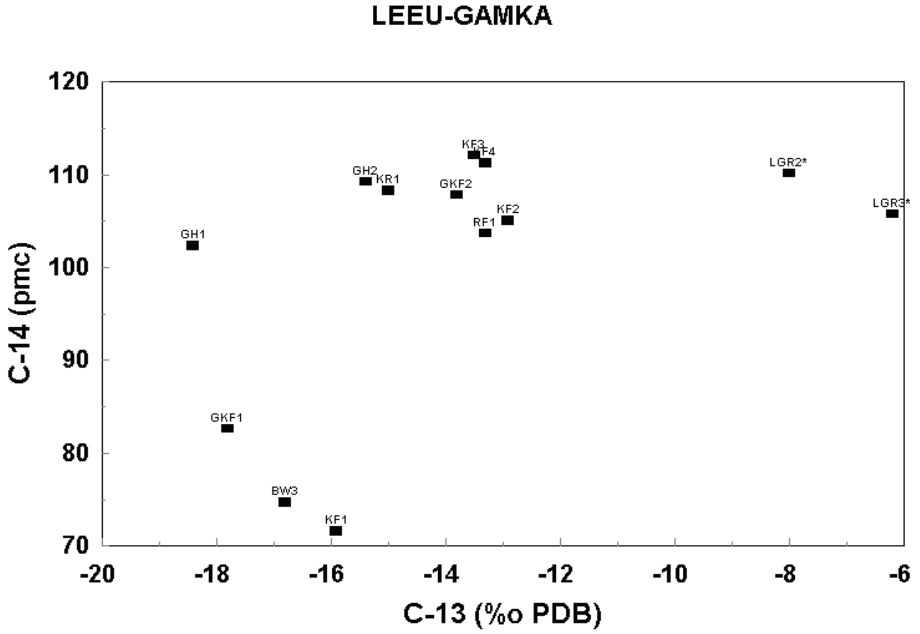


Figure 5.13 Plot of ^{14}C as function of ^{13}C in LeeuGamka. Note the grouping of the young and old water and the clear distinction of the two river waters (LGR2 and LGR3).

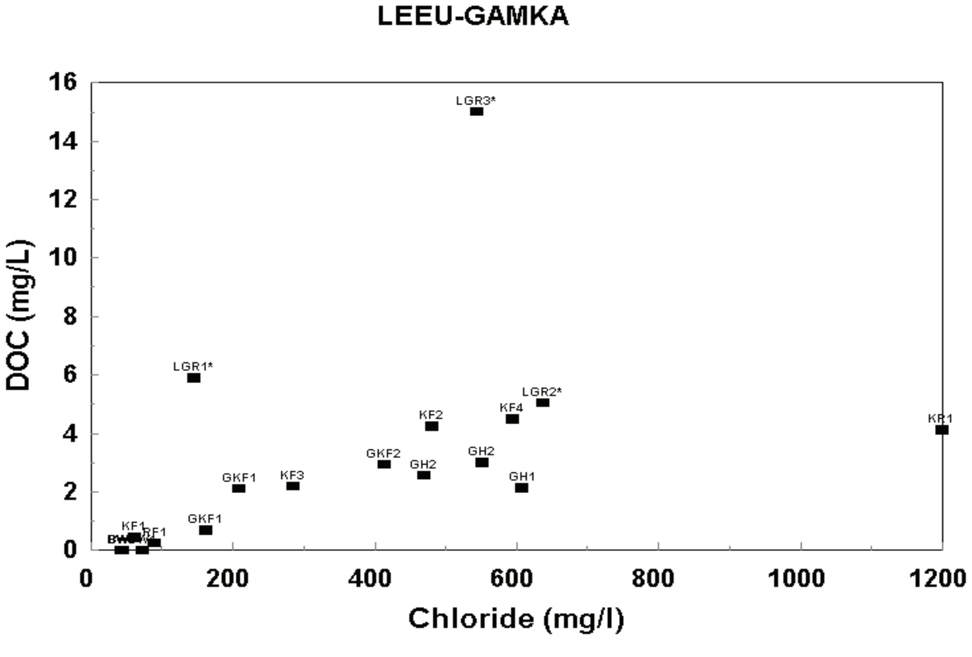


Figure 5.14 Plot of dissolved organic carbon (DOC) as function of chloride. Note the clear relation between old and young samples (excluding the rivers, LGR2 and LGR3).

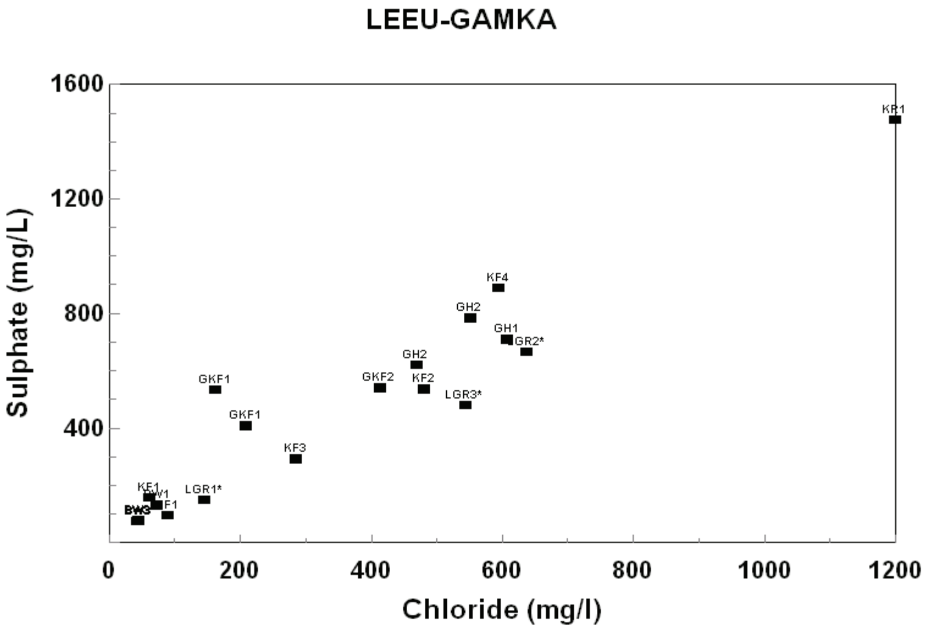


Figure 5.15 Plot of sulphate against chloride in Leeu Gamka.

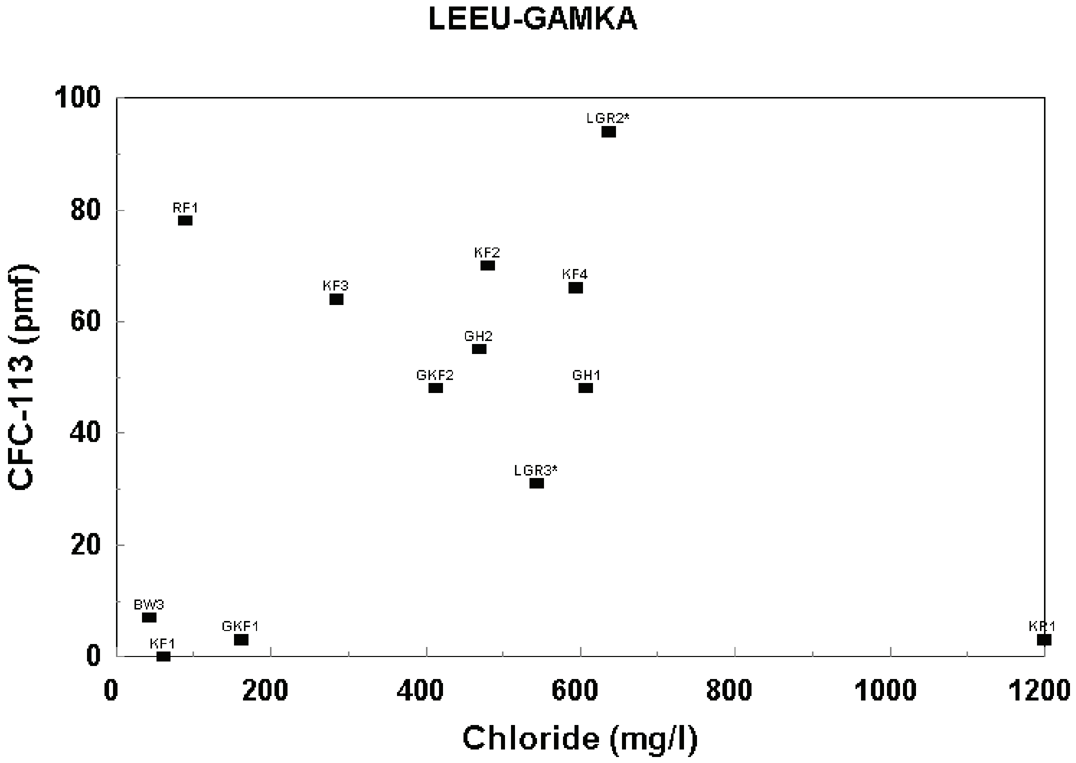


Figure 5.16 Plot of CFC-113 against chloride in Leeu Gamka.

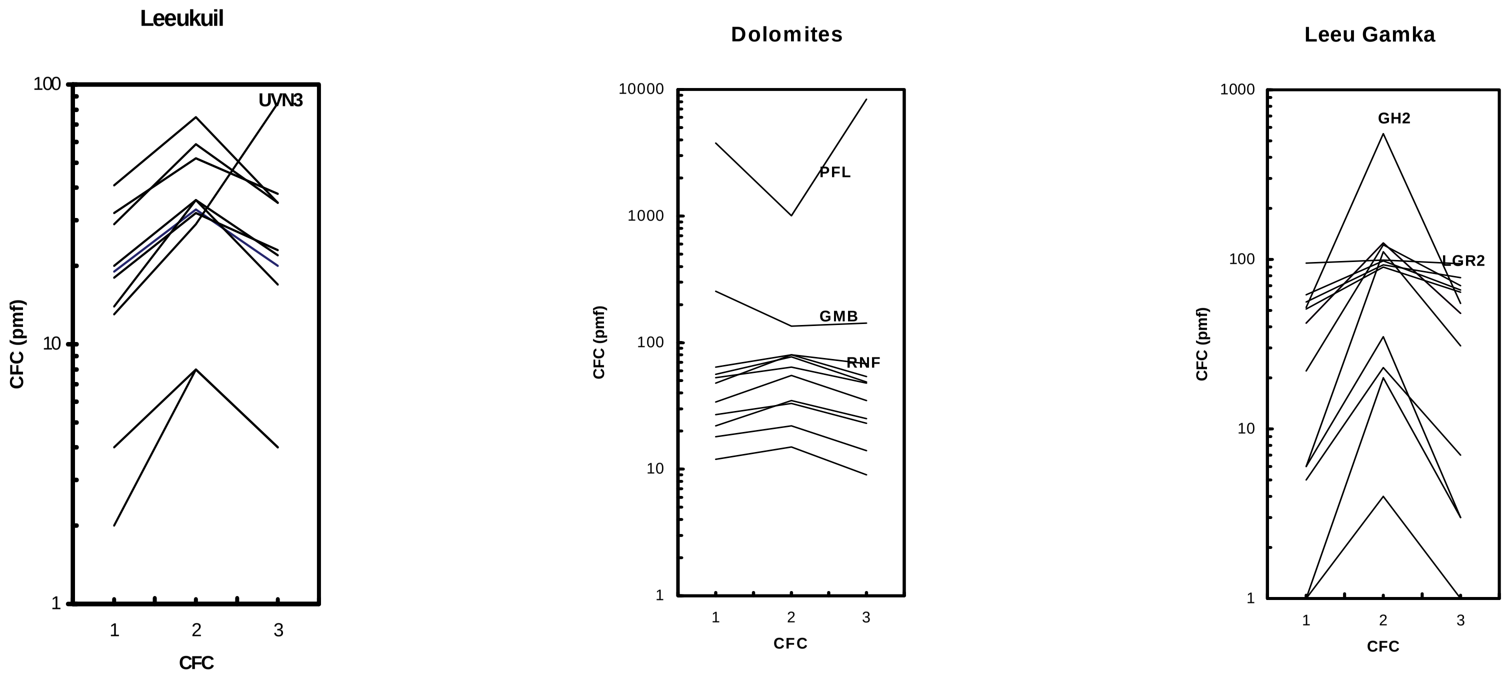


Figure 6.1 Logarithmic plots of the three CFCs to show pollution patterning. The numbers on the X-axis (1,2,3) indicate CFC-11, CFC-12 and CFC-113 respectively.

Other related WRC reports available:

Field studies of chlorofluorocarbons (CFC's) as a groundwater dating tool in fractured rock aquifers

JMC Weaver • AS Talma

The chlorofluorocarbon gases CFC-11, CFC-12 and CFC-13 were developed during the 1930s. The known growth rates of atmospheric CFCs, the rapid mixing world-wide, their solubility in water and their good chemical stability have enabled CFCs to become a useful tool for hydrologists to trace water movement in the oceans, in surface water and in groundwater. The method was considered to hold great promise as a valuable tool for the hydrogeologist, in using dissolved CFC gases as groundwater age-dating tools for groundwater younger than 50 years of age.

Three case-study sites were used to test the CFC method of age dating in the South African fractured-rock environment. The Agter-Witzenberg and Klein Karoo Rural Water Supply Schemes both located in the Table Mountain Group quartzites, and the Dewetsdorp aquifer which is located in Karoo sandstones were the test sites. The use of CFCs has been demonstrated successfully in the environments investigated. By using CFCs, the mixing of young and old waters could be shown, including information on groundwater flow patterns. Because of the mixing of groundwater of various ages, the CFC results produced recharge dates of 1960/70, but carbon-14 isotope analysis recorded ages of 1 000 years and older. Thus, the application of this method in fractured-rock environments requires further investigation. In the South African context, the method was tested, but still needs to be proven.

The quick response of CFC in young and rapid flowing recharge water was seen in the TMG quartzites at Agter-Witzenberg. The CFC recharge dates were consistent within the ranges given by likely modelling parameters and other isotopes. Much more episodic recharge was indicated in the Dewetsdorp Karoo sandstone where CFC data indicated recharge during a few single high rainfall years and delays within the aquifer. However, to translate CFC concentrations into ages based on simple calculations is not feasible. Age determination requires an understanding of the mixing ratios of older and younger waters.

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