Measurement of neon in groundwaters – analysis and validation

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CONTENTS

FIGURES

TABLES

ABSTRACT

Nitrate is the most pervasive contaminant in New Zealand's groundwaters. Thus, understanding and managing nitrogen loads through New Zealand's aquifers is vital for maintaining the quality of groundwaters and connected surface waters.

Denitrification is a natural process that is mediated by the metabolism of aquifer microorganisms and by which dissolved nitrate is reduced eventually to nitrogen gas. However, the extent of denitrification occurring within New Zealand's groundwater system is largely unknown, because there has historically been no straightforward, reliable and accurate technique to measure it.

Calculation of the concentration of excess nitrogen in groundwaters is a promising technique to quantify the amounts of denitrification occurring in the groundwater system. The concentration of dissolved atmospheric nitrogen, according to the recharge conditions of the water, can be established by the measurement of two noble gases, such as neon and argon, that are part of the atmosphere. This enables differentiating the excess nitrogen gas produced via denitrification reactions from atmospherically derived dissolved nitrogen gas.

This report details the development and validation of an analytical method to simultaneously measure neon, argon and nitrogen.

KEYWORDS

Neon, denitrification, noble gas, groundwater

1.0 INTRODUCTION

1.1 NITRATE AND DENITRIFICATION

Nitrate is the most pervasive contaminant in New Zealand groundwaters. Approximately 40% of long-term groundwater monitoring sites show above-natural concentrations, with no conclusive evidence of improvements over the last decade (Daughney and Wall 2007; Moreau et al. 2016). Understanding and managing nitrogen loads through New Zealand's aquifers is therefore vital for maintaining and/or improving the quality of groundwater and connected surface waters.

Denitrification is a natural process that is mediated by the metabolism of microorganisms in the aquifers and by which dissolved nitrate is reduced eventually to nitrogen gas (Chapelle, 1993):

$NO_3 \rightarrow NO_2 \rightarrow NO_{(g)} \rightarrow N_2O_{(g)} \rightarrow N_{2(g)}$ Equation 1

Denitrification can therefore remove nitrate from groundwater by conversion to gaseous forms. This process can potentially lead to a significant nitrate reduction in the aquifer and lessening of nitrogen loads into receiving waters such as groundwater-fed streams, springs, wetlands, and lakes (Woodward et al. 2013).

1.2 MEASUREMENT OF DENITRIFICATION

The extent of denitrification within New Zealand's groundwater system is largely unknown. Denitrification is an anaerobic respiration process by which facultative heterotrophic denitrifying bacteria (e.g., *Pseudomonas* sp and *Bacillus* sp) simultaneously oxidise organic carbon compounds (as an electron donor) and utilise nitrogen oxides as the terminal electron acceptor, (Delwiche, 1981) i.e.,

$4N0_3^- + 5CH_2O \rightarrow 2N_{2\,(g)} + 5CO^-_{2\,(g)} + 3H_20^+ 4OH^-$ Equation 2

Denitrification primarily occurs under reducing (e.g., oxygen depleted) conditions, after the dissolved oxygen is consumed. Much emphasis has been placed on identifying where optimal redox conditions are present to allow for the facilitation of denitrification (Stenger et al. 2008). However, assessment of the redox status of the groundwater only suggests whether denitrification could be possible in an aquifer, not whether it has actually occurred (Langmuir 1997). For example, a comparison of groundwater age versus redox status suggests that many reduced (anoxic) zones are, in effect, stagnant or very slow moving (Morgenstern et al. 2014), and hence any potential for denitrification may have little effect on reducing nitrogen loads to receiving waters because the water does not flow through these zones.

Several other methods for investigating denitrification in groundwater systems exist. This includes comparisons of the isotopic composition of N and O in nitrate and nitrogen gas, a method which has been used to estimate denitrification in the groundwater system (Heaton et al. 2005). However, this method is complicated by low nitrate concentrations, lack of knowledge of flow paths, and/or multiple sources of nitrate that have overlapping isotopic signatures (Clague et al. 2015). 'Push-pull' or 'recirculating well' tests have also been used to measure the amount of nitrate that is removed from injected and subsequently extracted groundwater samples. Such tests are complicated by local groundwater flow and, because the system is perturbed artificially, do not indicate the extent of denitrification that is likely to occur under natural conditions (Burberry et al. 2013; Kim et al. 2005).

Measurement of ‘excess N_2’, the product of the denitrification reaction ($N_{2(g)}$ in Equation 2), is the most promising method for directly measuring denitrification that has occurred in an aquifer (Stenger et al. 2013; Wilson 1990). All groundwaters contain dissolved gases derived from the atmosphere during recharge, including N_2. In addition to the dissolved atmospheric N_2, groundwaters can also contain excess N_2 that has accumulated from denitrification reactions. The dissolved atmospheric N_2, according to the recharge conditions of the water, can be established by the measurement of two noble gases that are part of the atmosphere, usually argon (Ar) and neon (Ne). This enables differentiating the excess N_2 produced via denitrification reactions from atmospherically derived dissolved N_2.

Despite its potential, the excess N_2 technique, as based on measurement of dissolved N_2, Ar and Ne, has never previously been applied to quantify denitrification in New Zealand groundwater systems. This is because, historically, there has been no straightforward, reliable and accurate approach for measuring the concentration of Ne in groundwater.

In this report, the development and validation of a technique to measure Ne in New Zealand groundwaters is outlined. The simultaneous measurement of dissolved Ne and Ar will allow us to determine the recharge temperature of groundwater, concentration of excess air (Heaton 1981), and consequently the concentration of nitrogen from atmospheric sources. Measurement of the N_2 concentration in the groundwater will then allow us to establish the excess N_2 and, for the first time, directly assess the amount of nitrogen from denitrification.

2.0 ANALYTICAL SET UP

2.1 NEON MEASUREMENT

Ne is a noble gas with a low solubility relative to Ar and N_2, and is present in the atmosphere at a concentration of 0.001818%. The standard procedure for measuring dissolved gases (SF_6 CFCs, Ar, and N_2) in the GNS Science Water Dating Laboratory is by a “purge and trap” procedure (e.g., Swinnerton et al. 1962, van der Raaij 2003). However, this method is not suitable for Ne measurement because Ne is not condensable by commonly used trapping methods such as using liquid N_2 (-196 °C). Analysis of Ne using a thermal conductivity detector (TCD) on a gas chromatograph (GC) has been applied for measurement of Ne in gaseous mixtures (e.g., Sugisaki et al. 1982), but TCDs are generally not sensitive enough for measurement of low concentrations of dissolved Ne in groundwaters without pre-concentration of Ne in the sample. To achieve adequate sensitivity, methods using gas chromatographs equipped with mass spectrometers (GC-MS) (e.g., Beyerle et al. 2000; Brennwald et al. 2013) have been developed. To minimise analytical costs, and in order to encourage future uptake of the method by stakeholders, the GC-MS approach was not investigated in this study. Instead, a head space analysis approach using a thermal conductivity detector (TCD) simultaneously with a pulse discharge helium ionisation detector (PDHID) has been used. The PDHID has been adapted for measurement of Ne following the methodology of Lasa et al. (2004). When used in this fashion the PDHID has been shown to have a sensitivity to Ne an order of magnitude higher than that of the TCD (Lasa et al. 2004).

2.2 DESCRIPTION OF THE MEASUREMENT SYSTEM

The system developed for the measurement of Ne is shown in Figure 2.1. Two detectors, a PDHID (Valco Instruments D-4-I-SH14-R) and a TCD (Shimadzu TCD-2014), are used, requiring two independent carrier gas flows (HF1 and HF2) of ultra high purity helium gas. The He is supplied from two gas cylinders, both of which flow through respective in-line regulators, set to 695 psi, and subsequent molesieve and oxygen scrubbers. HF1 flows through a pressure controller set to 414 kpa before being purified by a Valco Instuments He purifier. A flow restrictor, reducing the flow to 30 ml min^{-1}, is in place before HF1 reaches a 6 port valve, V1, and the PDHID. HF2 flows through a pressure controller set to 190 kpa. This flow controller is manually adjusted between sample measurements to ensure the flow is always 20.0 standard cubic centimetres per minute. HF2 flows through a 6 port valve, V2, to the standard loop.

A standard curve for Ne, Ar and N_2 is needed to measure groundwater samples. This is produced by evacuating the sample loop before allowing an air standard to enter the sample loop to the desired pressure. The air standard in the sample loop is then injected into the column via V2. Moisture is removed by Nafion tubing before the standard passes through an eight metre molesieve 5A column, which is cooled in an ethanol-dry ice bath to -30 °C. Ne is largely unrestricted through the column, taking approximately 4 minutes to pass through to the PDHID. After passing through PDHID, HF2 then flows through the TCD resulting in the Ne being measured on two different detectors. After 5 min 30 sec V2 is switched so that HF2 flows directly through the TCD and not through the PDHID. The column remains in the ethanol-dry ice bath for another twelve minutes to allow for the separation of Ar and O_2, after which it is placed in a hot water bath, of approximately 90 °C, to remove N_2 from the column.

The measurement of a sample uses the principles of head space analysis and Boyle’s Law. Samples are collected in evacuated 1 L flasks (shown in Figure 3.1 and described further in section 3.0), whereby the flask is partially filled to leave a headspace of approximately 100 mL.

The flask is attached to the inlet system via a Cajon fitting. The connection to the flask is then evacuated, as is the 200 mL stainless steel syringe which is extended to its maximum volume. The outlet valve on the headspace sample is opened to allow the headspace to spread between the flask and the syringe. The outlet valve is then closed and the syringe is compressed, reducing the volume of the sample. The compressed sample is then injected from the sample loop and follows the same subsequent processes as the air standard for measurement. The area of the integrated peaks from the sample are used to calculate the concentration of each individual gas (Ne, Ar, and N_2) in the headspace.

The original sample concentration (C_i) of a particular gas can be calculated using equation 3:

$$C_i = C_g(K + r) \qquad \text{Equation 3}$$

Where C_g is the measured concentration of the gas in the headspace, K is the partition coefficient between the gas phase and water, and r is the ratio of the headspace to the volume of water in the sample flask (Sliwka and Lasa 2000)

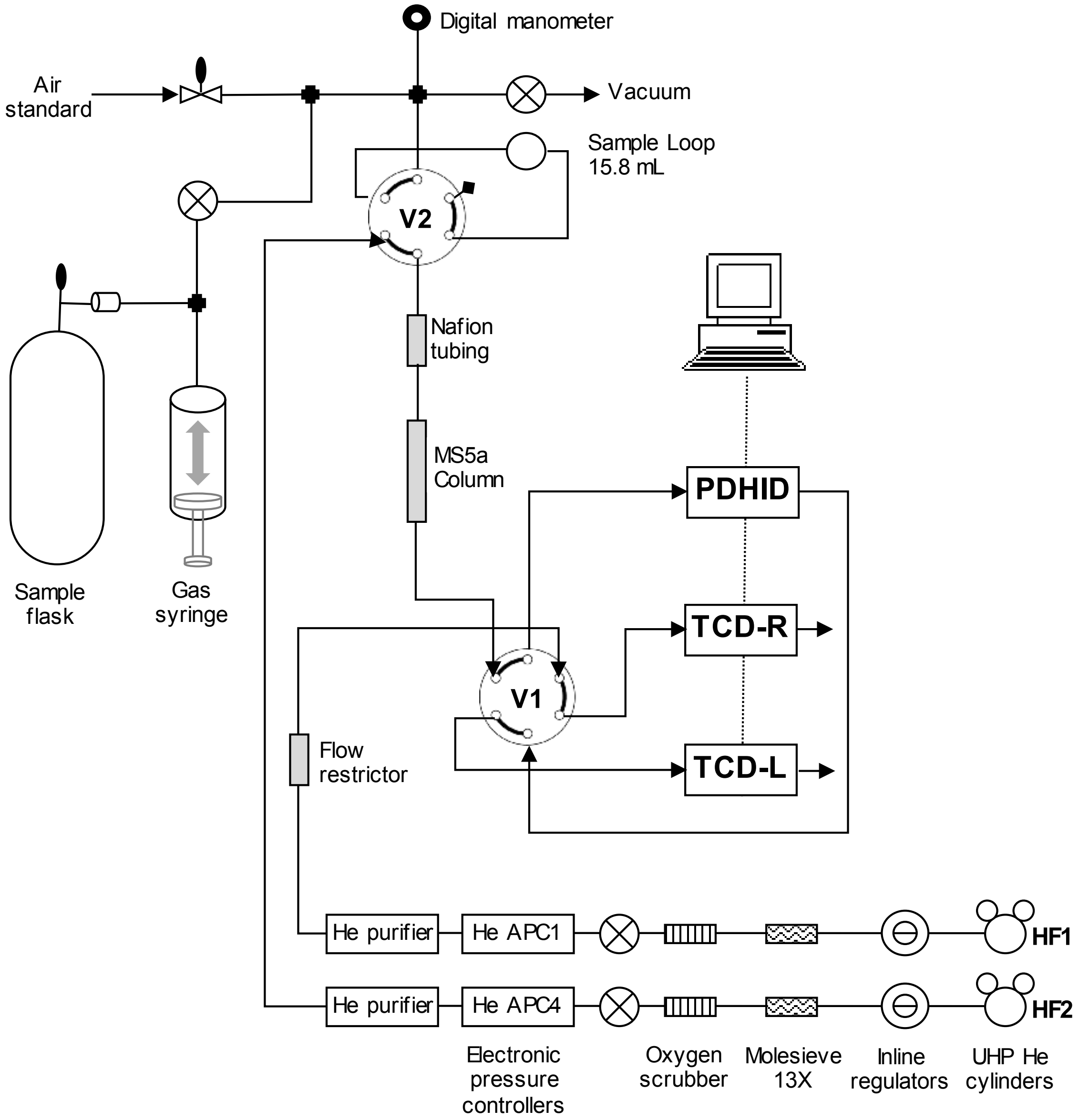

Figure 2.1: Schematic of the analytical set up of the neon measurement system.

3.0 SAMPLING PROCEDURE

Evacuated 1 L glass flasks are used for groundwater sample collection (Figure 3.1). Sample tubing from the sample source outlet is attached to one of the side-arms on the bottom of the flask. On the opposite side arm, exhaust tubing with a clamp is attached. The sample inlet valve is narrow enough to allow water to pass from the sample source to the exhaust tubing when the sample inlet valve is closed. When it is visible that no air bubbles are passing through the tubing, the clamp is closed and the sample inlet valve is opened, allowing sample water to enter the flask. When approximately 900 mL of sample has entered the flask the sample inlet valve is closed, leaving a headspace of approximately 100 mL.

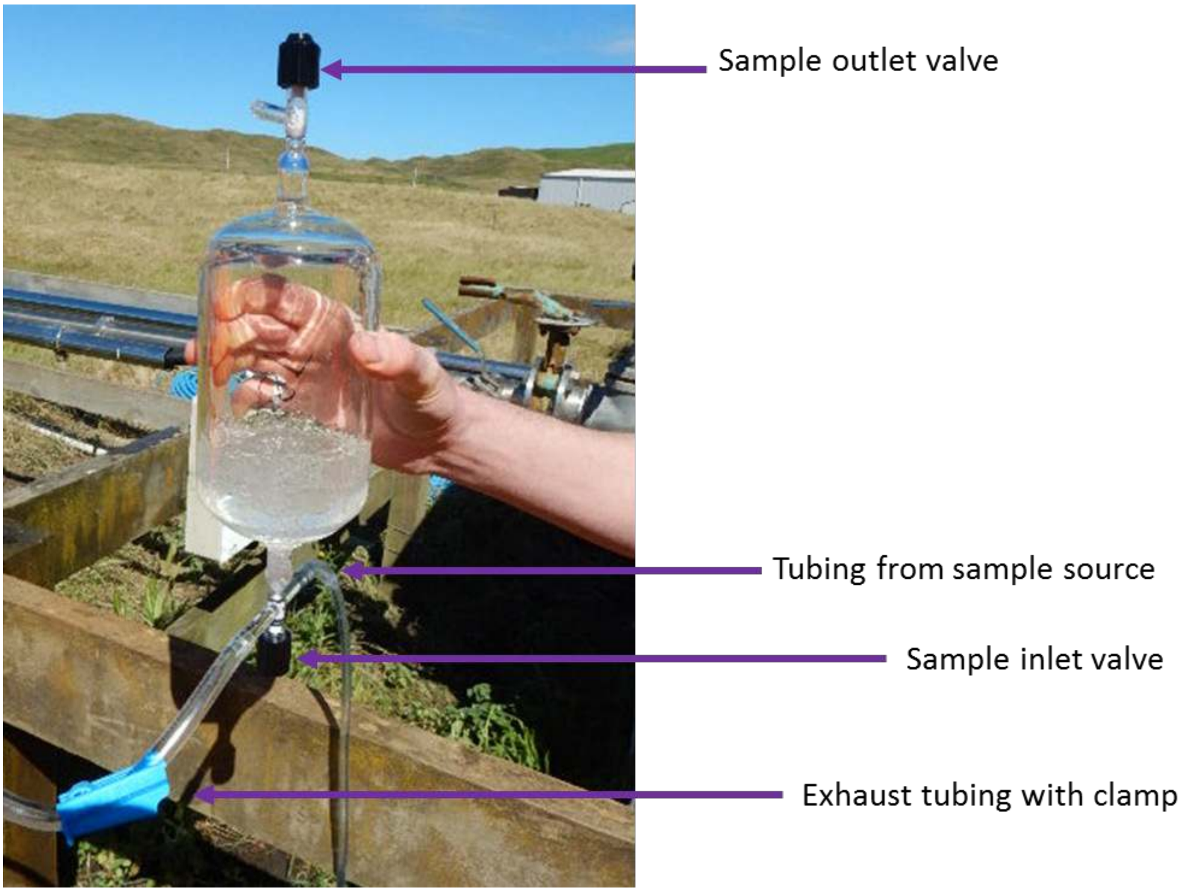

Figure 3.1 Annotated photograph of the neon sample flask.

4.0 VALIDATION OF SAMPLING AND MEASUREMENT PROCEDURE

To validate the analytical method for simultaneous measurement of Ne, Ar, and N_2, groundwater samples were collected from three deep wells with known Ne concentrations from previous measurements. In 2013, Seltzer et al. (2015) measured noble gases, including Ne and Ar, in “paleo” groundwaters in Taranaki, Marlborough, and Tasman via noble gas mass spectrometry. The mean age of these groundwaters ranged from 14,000 to 40,000 years (Seltzer et al. 2015). It is unlikely that concentrations of Ar and Ne in these paleo groundwaters would differ significantly between now and 2013. A comparison between Seltzer’s Ar and Ne results with the newly developed analytical set up will assist validating the new method. In addition to samples from the three paleo wells, samples from two shallower wells, also previously sampled by Seltzer et al. (2015), were collected.

As a further verification of the gas measurement system (that includes Ne), the measured Ar and N_2 concentrations were cross-calibrated against the Ar and N_2 measured in the gas measurement system used for CFC analysis.

4.1 SAMPLE COLLECTION AND MEASUREMENT

Samples were collected in triplicate from three artesian wells in Taranaki and Marlborough which contained paleo groundwater (Table 4.1); see Seltzer et al. (2015) for a further description of the sampling sites. A submersible piston pump was used to sample shallow well P28w/398, and the other shallow well was sampled using a pre-installed pump. No difference is expected to be observed on the dissolved gas concentration from the different sampling methods. All wells were purged for three well volumes before sampling. Ne samples were collected following the procedure outlined in section 3.0. CFC samples were also collected at the sampling sites following standard groundwater sampling procedure (Daughney et al. 2006). Samples for measurement of Ne, Ar, and N_2 were measured within 24 hours after collection via the procedure outlined in section 2.2. Ne samples were also collected in copper tubes, following the procedure of Weiss (1968), and were sent to the Environment Tracer and Noble Gas Laboratory at CSIRO in Adelaide, Australia for comparison. The results from the copper tube samples were not available at the time of writing this report.

Table 4.1 Summary of well information and sampling details. (*Ages as published in Seltzer et al. (2015)).

Site Name	Location	Age (kyr BP)*	Screen depth	Sampling Date	Easting (NZTM)	Northing (NZTM)	Dissolved Oxygen (mg/L)	Temperature (°C)	pH
GND585	South Taranaki	17.5 – 22.4	122.8 – 140.5	15/11/17	1748265	5588832	0.17	17.9	8.17
P28w/0980	Marlborough	39.8 – 43.3	n/a	20/11/17	1678884	5401360	0.13	15.0	7.64
P28w/3278	Marlborough	23.1 – 27.3	102 –187	20/11/17	1673937	5402672	0.07	15.7	8.05
GND524	South Taranaki	<1	64 – 76.2	15/11/17	1726436	5606436	5.13	15.2	5.70
P28w/398	Marlborough	<1	n/a	20/11/17	1667689	5406335	8.65	12.0	6.10

4.2 ANALYTICAL RESULTS

4.2.1 Validation of Ne and Ar results

The measured Ne and Ar concentrations from the three wells containing paleo groundwater are compared to the published results of Seltzer et al. (2015) (Figure 4.1 – Figure 4.3). The uncertainty shown in Figure 4.1 – Figure 4.3 is the standard measurement error (combined standard uncertainty) u_c of the measurements. This is the summation of all significant uncertainties involved in the analysis (Ellison and Williams 2012) such that the uncertainty for measurement *x* is given by:

$$u_c(x) = \sqrt{u(s)^2 + u(r)^2 + u(b)^2 + u(m)^2} \qquad \text{Equation 4}$$

where:

- *u(s) is the uncertainty from the calibration procedure arising through the use of least squares regression (Hibbert 2006).*
- *u(r) is the repeatability which is derived from the relative standard deviation (RSD) of multiple measured standards.*
- *u(b) is the uncertainty from the blank correction.*
- *u(m) is the uncertainty from physical parameters such as standard loop and dead space volumes, pressures, temperatures, sample weights and sample volumes.*

Uncertainties for the Ne measurement range between 2 – 3%, while the Ar uncertainties are slightly higher at ca. 4%. It is expected that the standard measurement error will be higher than a measurement undertaken on a GC-MS, due to the higher sensitivity of the GC-MS measurement. However, improvements to the analytical system, such as increasing the syringe size, and further refining measurement uncertainties, including *u(m)* and *u(r)*, are planned to reduce overall uncertainty.

The measured noble gas concentrations in all three wells agree with those of Seltzer et al. (2015), confirming the validity of the Ne analytical method. The results for well P28w/3278 do not agree with the published measurements as well as those of wells GND585 and P28w/0980. This is likely due to difficulty during sampling. The 2016 Kaikoura earthquake had caused the hydraulic head of P28w/3278 to increase by approximately 6 metres, causing a high pressure sampling flow. Even when the outflow from the well was fitted with a "T" fitting to reduce the sampling flow, the sample could visibly be seen degassing through the sampling tubes while sampling. Another possibility for the discrepancy in P28w/3278 is that the well was not purged sufficiently.

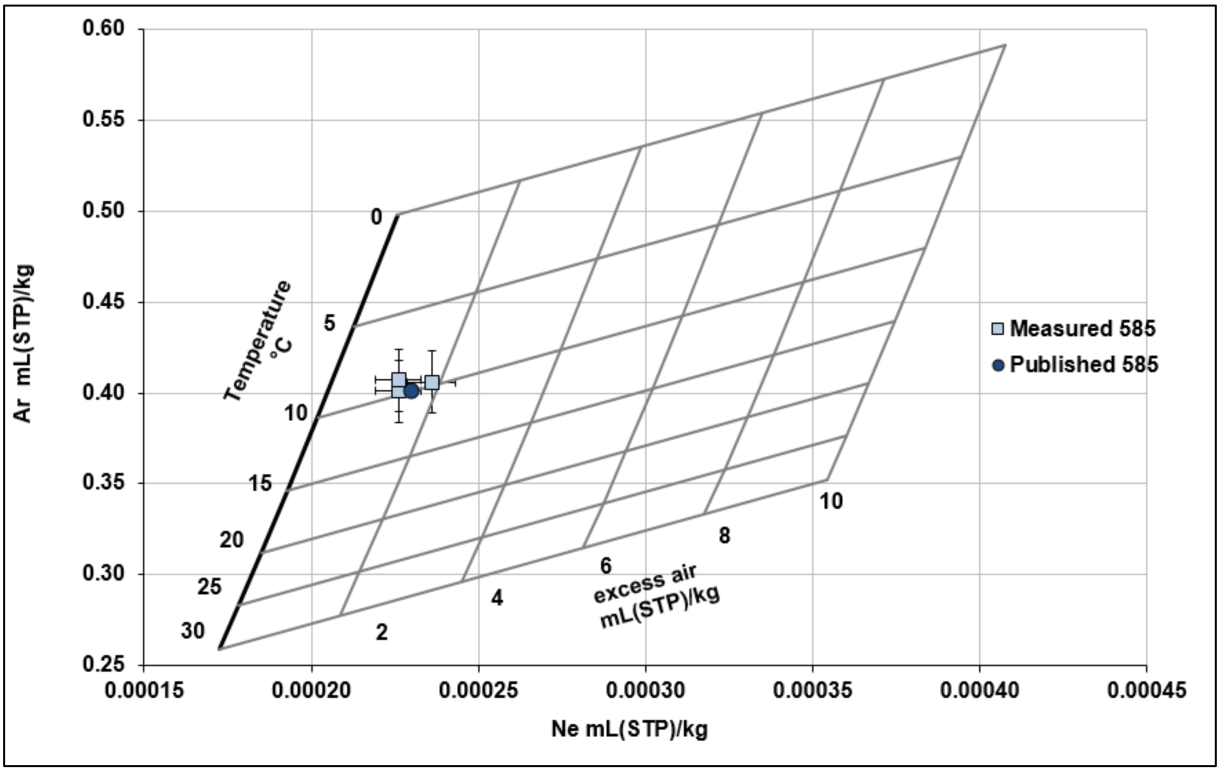

Figure 4.1 Comparison of the measured Ne and Ar concentrations (square symbols) at well GND585 to Seltzer et al. (2015) published result (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

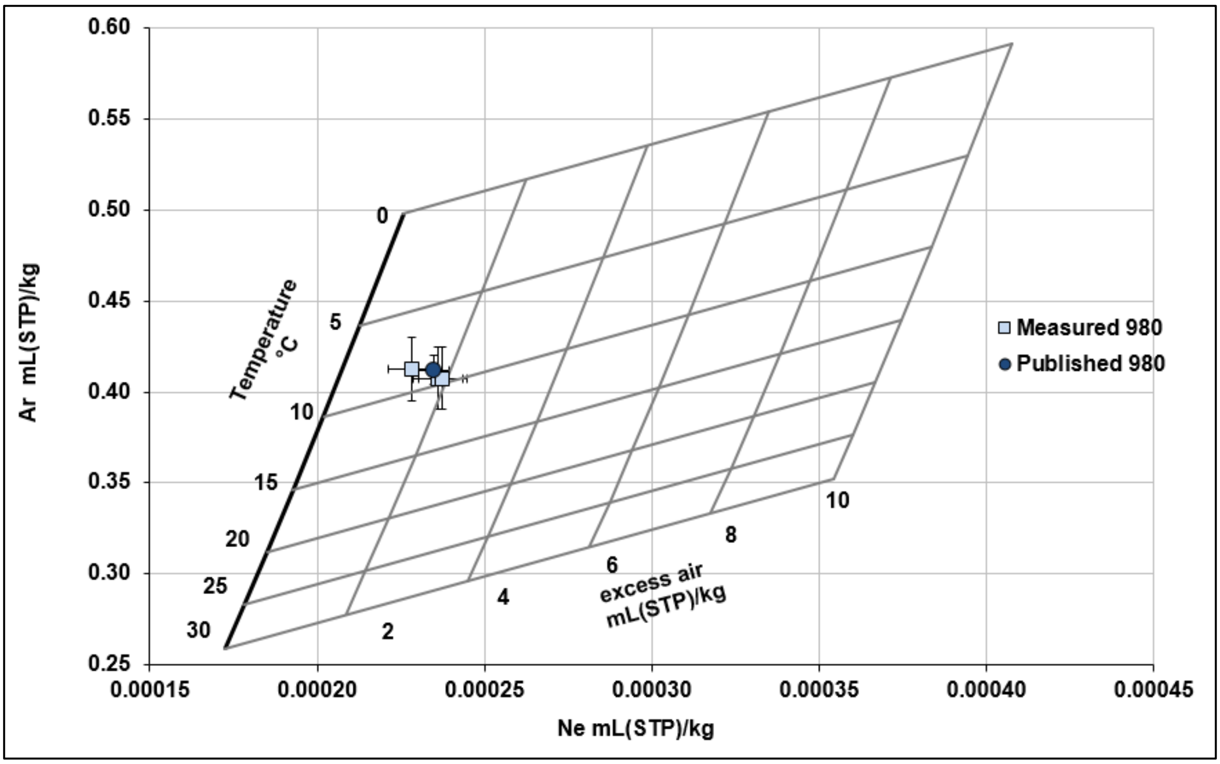

Figure 4.2 Comparison of the measured Ne and Ar concentrations (square symbols) at well P28w/0980 to Seltzer et al. (2015) published result (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

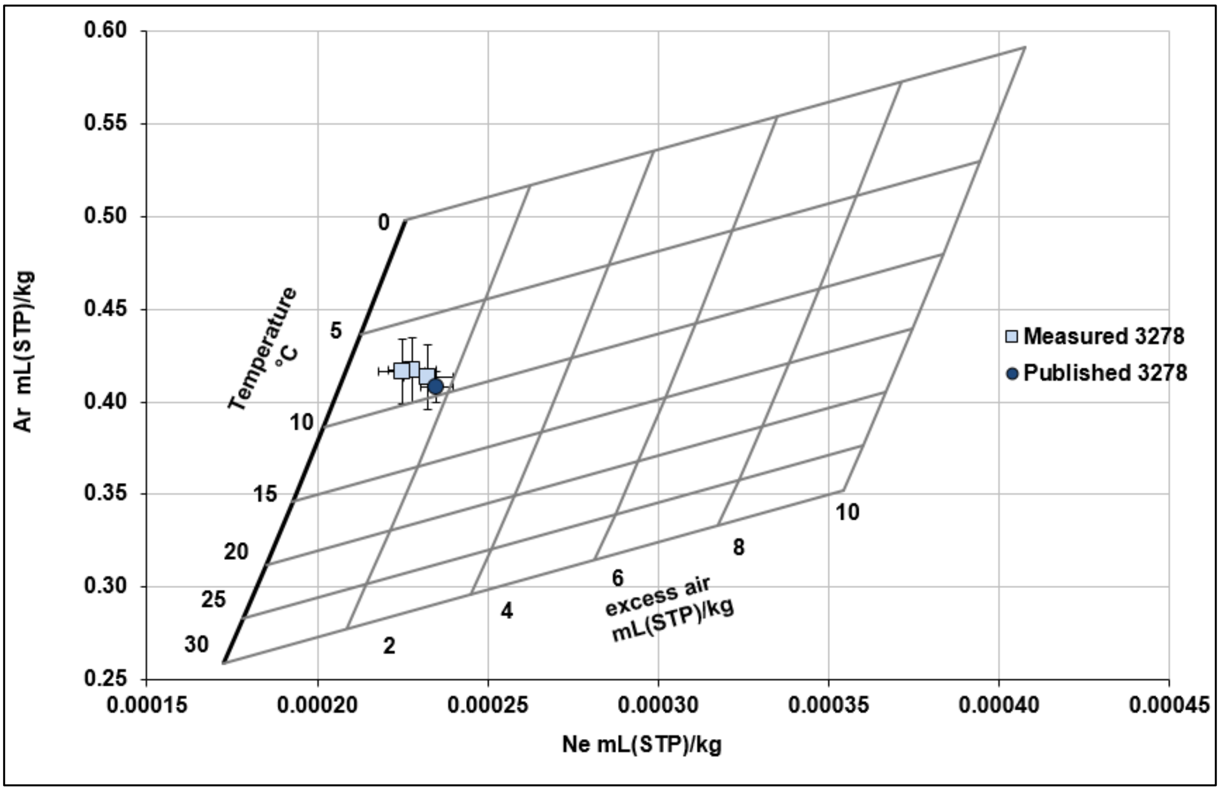

Figure 4.3 Comparison of the measured Ne and Ar concentrations (square symbols) at well P28w/3278 to Seltzer et al. (2015) published result (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

4.2.2 Validation of Ar and N_2 results

The measured Ar and N_2 concentrations from the new analytical (headspace) method are compared in Figure 4.4 – Figure 4.7 to those measured using the established methodology for CFC analysis. CFC measurements were not possible for well P28w/0980 because it was subject to a considerable amount of degassing during sample collection, rendering the result unreliable. There is good agreement between the two measurement methods for Ar concentrations. However, the uncertainty associated with the N_2 measurement using the Ne analytical set up is relatively high and needs improvement.

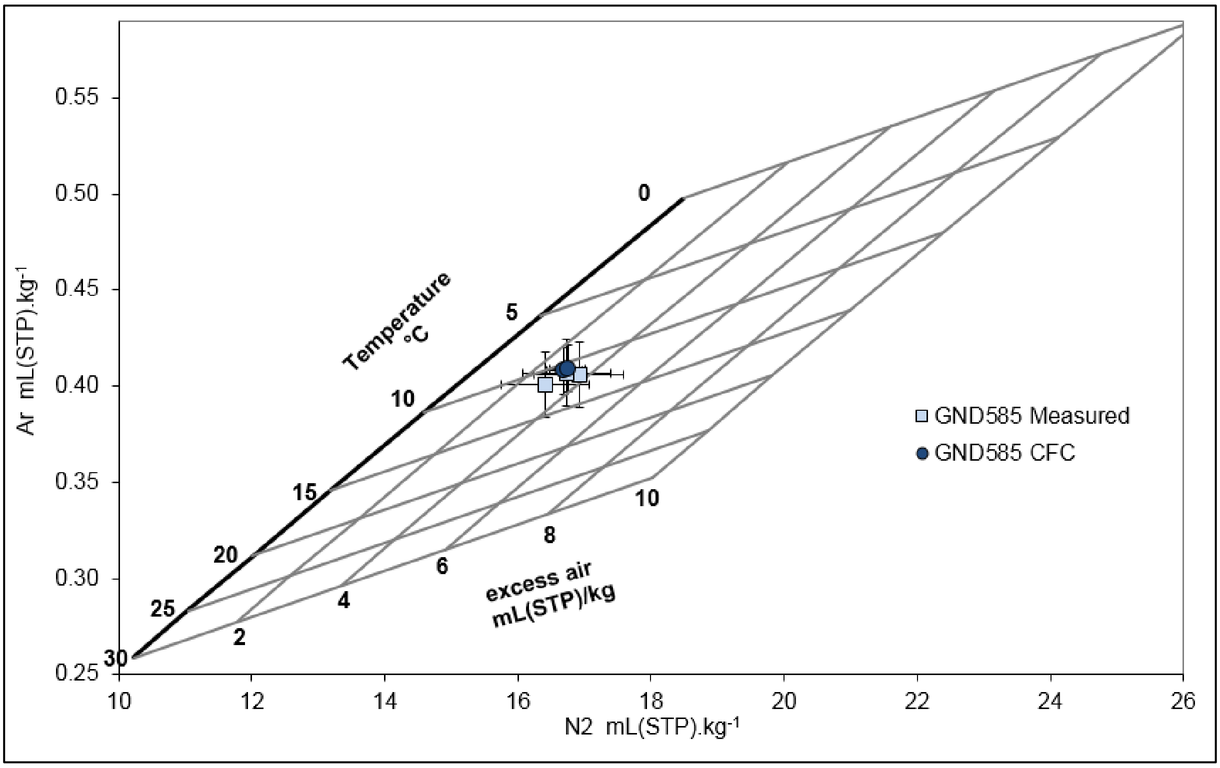

Figure 4.4 Comparison of the measured Ar and N_2 concentrations measured simultaneously with the Ne measurement (square symbols) at well GND585 to the Ar and N_2 concentrations measured during CFC analysis (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

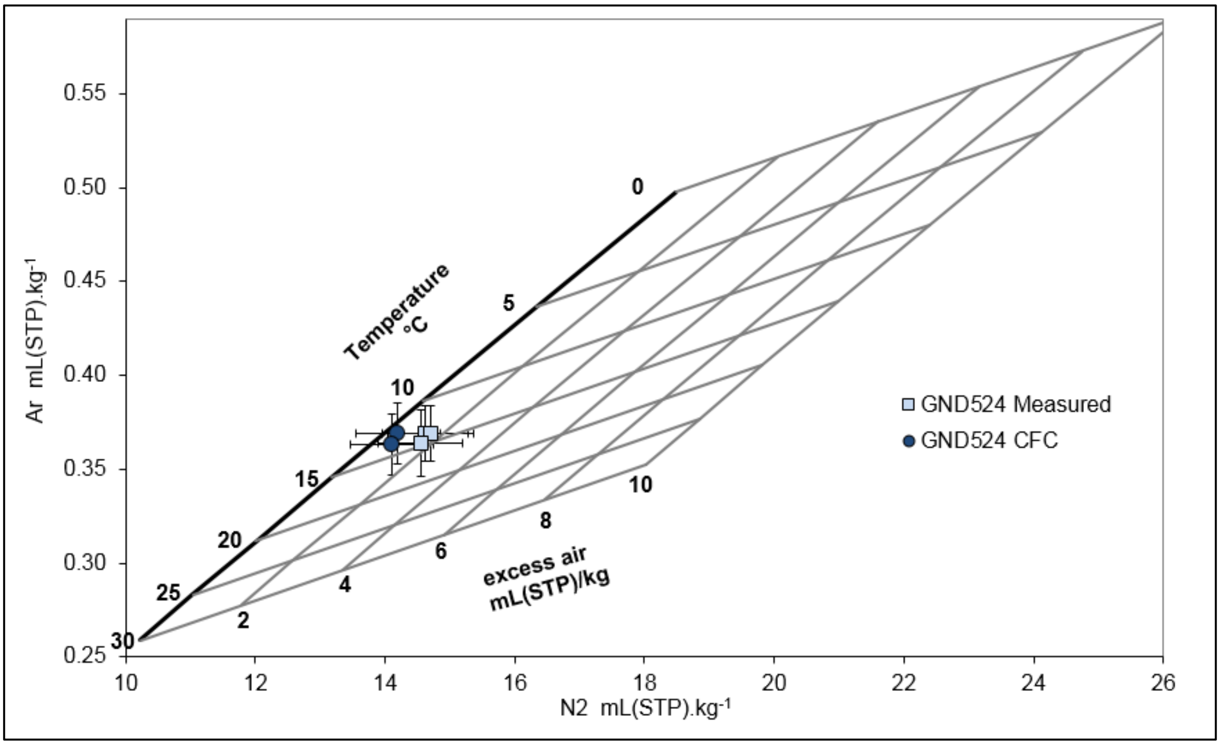

Figure 4.5 Comparison of the measured Ar and N_2 concentrations measured simultaneously with the Ne measurement (square symbols) at well GND524 to the Ar and N_2 concentrations measured during CFC analysis (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

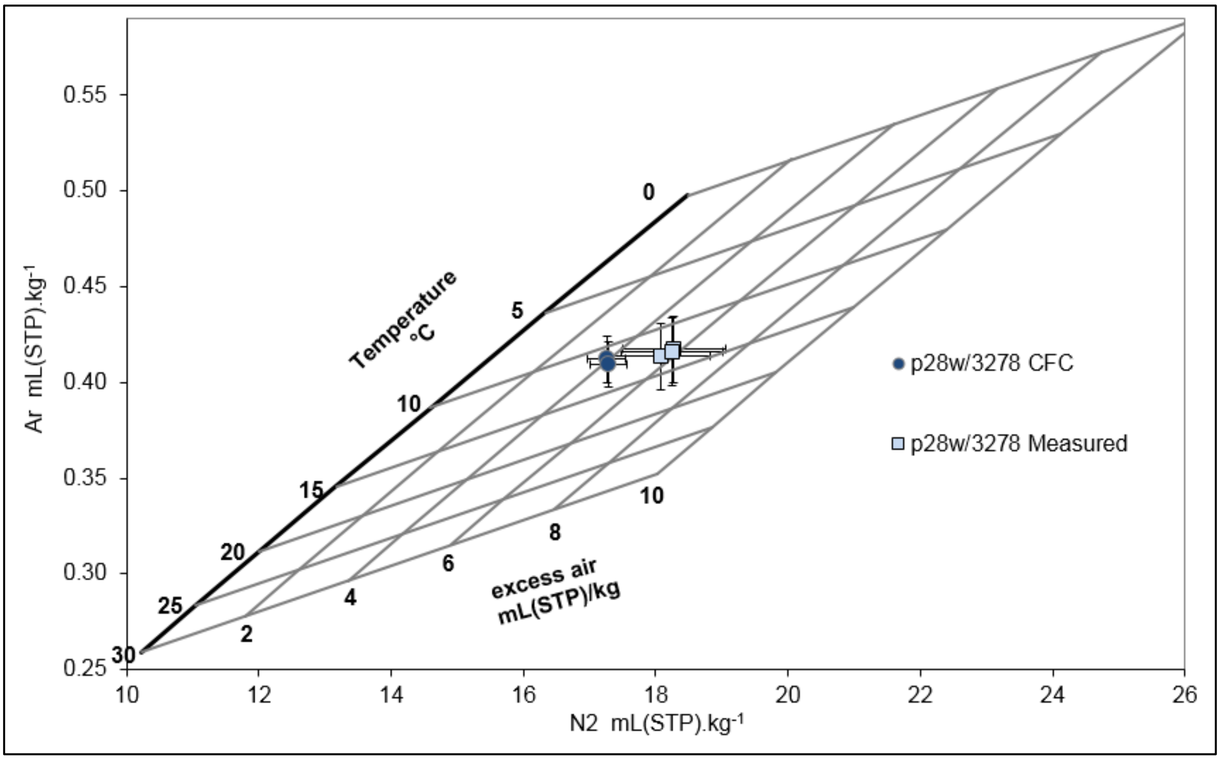

Figure 4.6 Comparison of the measured Ar and N_2 concentrations measured simultaneously with the Ne measurement (square symbols) at well P28w/3278 to the Ar and N_2 concentrations measured during CFC analysis (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

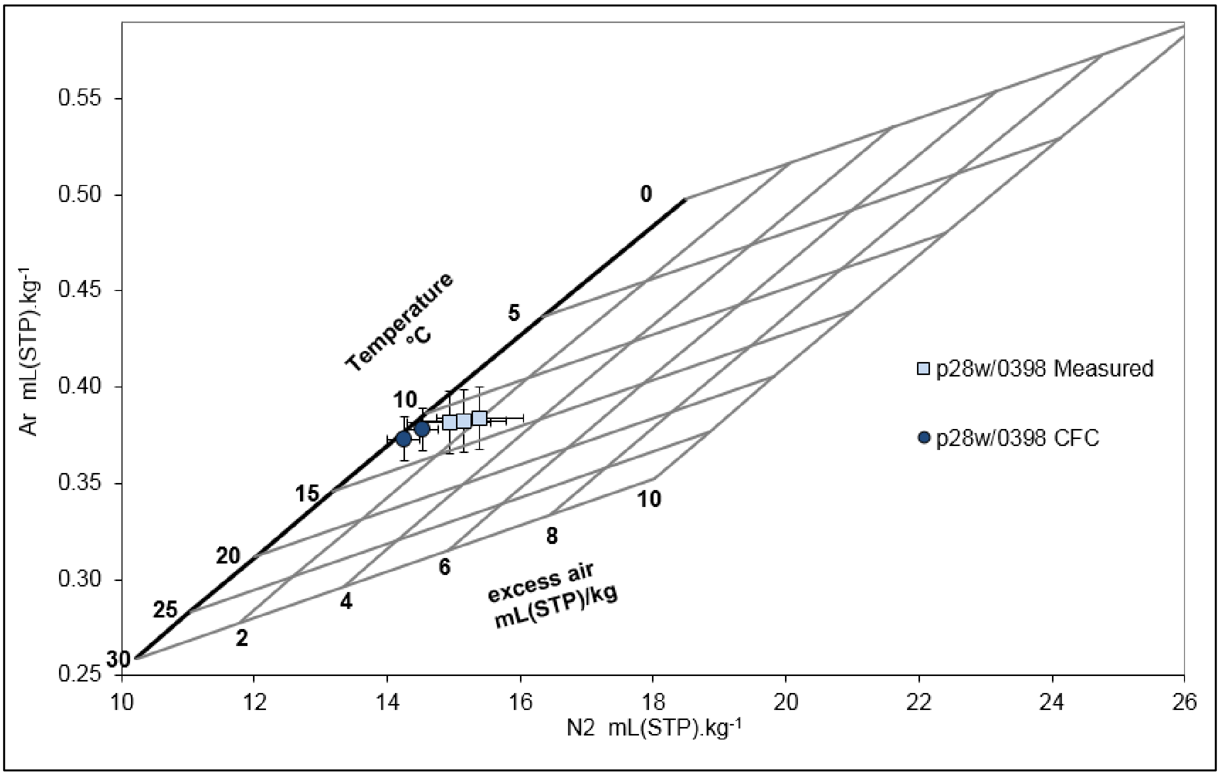

Figure 4.7 Comparison of the measured Ar and N_2 concentrations measured simultaneously with the Ne measurement (square symbols) at well P28w/0398 to the Ar and N_2 concentrations measured during CFC analysis (circle symbols). The error bars represent measurement uncertainty calculated according to Equation 4.

5.0 CONCLUSIONS AND FUTURE WORK

An analytical system to measure Ne in groundwater has been developed to accurately calculate groundwater recharge temperature and concentration of excess nitrogen. The comparison of Ne in paleo groundwaters using this methodology to those previously published by Seltzer et al. (2015) correlate well, validating the newly developed analytical system. This system has the capability to simultaneously measure dissolved Ar and N_2 in groundwaters. Cross-calibration between the newly developed analytical system and Ar/N_2 measured on the established CFC measurement system provided promising results: the measured Ar concentrations correlate well; however, the uncertainty of the N_2 measurements using the Ne analytical set up is relatively high and requires some more refinement before it can replace the N_2 measurement using the CFC analytical set up.

The next phase of the project will have two aspects; to reduce the uncertainty of our Ne, Ar and N_2 measurements and to collect further groundwater samples for analysis. The analytical measurement uncertainty can be improved by increasing the syringe size, and further refining measurement uncertainties. The additional groundwater samples will be collected from groundwater bores covering a range of redox conditions, in particular using bores that are known to have redox stratification with depth or redox alterations by season. Samples will be collected from the Waikato and Horizons regions, where various other methods have been previously applied in an attempt to measure denitrification (Stenger et al. 2013). Samples covering the range of redox conditions will be measured for dissolved gases (Ar, Ne and N_2) and also for forms and concentrations of dissolved nitrogen (NO_3, NO_2, NH_4), other redox indicators (O_2, Fe, Mn, SO_4), and isotopic ratios of N and O in nitrate. The purpose of these tests is to demonstrate that the calculated values of excess N_2 are broadly consistent with expectations based on other proxies for the extent of denitrification, using the samples collected from the different sites as a time-for-space substitution.

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