



Resolving groundwater sources to a coastal lagoon using major ions, nutrients and stable isotopes

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Abstract

Coastal lagoons are important for ecological, cultural, economic and recreational reasons. Globally, they are subject to significant anthropogenic pressures. Our understanding of the importance of groundwater discharge into coastal lagoons for water and solute budgets is evolving, yet key gaps remain. This study resolves sources of groundwater seepage and estimates nutrient loads from direct groundwater discharge into a large hypertrophic coastal lagoon in New Zealand. We analysed major ions, stable water isotopes and nutrients in lagoon surface water, porewater, groundwater wells and springs. Groundwater and porewater samples split into two distinct groups: (1) inland samples that were MgHCO_3 dominated with more negative $\delta^2\text{H}:\delta^{18}\text{O}$ ratios and lower ion concentrations, and (2) permeable barrier samples that were NaCl dominated with more positive $\delta^2\text{H}:\delta^{18}\text{O}$ ratios and higher ion concentrations. Porewater entering the lagoon is sourced from alpine river and rainfall recharge on the plains. Barrier porewater appears to be sourced from infiltration from the lagoon through the barrier and local rainfall. Despite higher nitrate in deeper groundwater wells, low nitrate in shallow porewater indicates potential denitrification before groundwater discharges to the lagoon. Our observations support efforts to restore and construct wetlands around the lagoon to remove nutrients. However, wetland restoration will need to be carried out by maintaining a balance between enhancing denitrifying conditions while preventing phosphorus release from sediments. Nutrient load calculations revealed that direct groundwater seepage to the lagoon provides ~3% of dissolved inorganic nitrogen and ~30% of dissolved reactive phosphorus compared to river inputs, indicating that groundwater discharge may play an important role in phosphorus transport to the lagoon.

Keywords Coastal lagoon · Submarine groundwater discharge · Stable isotopes · Hydrochemistry · Nutrient transport

Introduction

Coastal lagoons are important features, found on coastlines on every continent except Antarctica (Barnes 1980). These shallow waterbodies range in their degree of connection to the sea, are typically turbid and well mixed, and have a salinity gradient from fresh to close to seawater (Kjerfve 1986, 1994). Coastal lagoons support rich biological

diversity, productive fisheries and extensive wetlands (Costanza et al. 1997) and provide fundamental ecosystem services, such as floodwater attenuation and nutrient cycling (Schallenberg et al. 2013). Coastal lagoons are at the nexus of many, often competing, human and ecological needs. As a result, coastal lagoons throughout the world face significant pressure from development, pollution and anthropogenic changes (Beer and Joyce 2013). Groundwater discharge into coastal lakes and lagoons has long been overlooked, but it has increasingly been found to be an important component of water and nutrient budgets (Lewandowski et al. 2015; Menció et al. 2017; Rosenberry et al. 2015; Santos et al. 2021). At some sites where groundwater was found to be a small component of the overall water budget, it was the biggest contributor of nutrient loads and other dissolved species (Santos et al. 2008). For effective management of groundwater-derived contaminants in coastal lagoons, the source of

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the groundwater discharge needs to be identified (Menció et al. 2017; Young et al. 2008).

The number of studies investigating groundwater sources and hydrological dynamics in coastal lagoons has increased in recent years. There have been studies examining coastal lagoons in the tropics (Young et al. 2008) and Mediterranean (Rocha et al. 2016; Stumpp et al. 2014), however fewer studies have been done in temperate climates in the Southern Hemisphere. A number of studies have specifically examined the role that groundwater plays as a source of nutrients (González-De Zayas et al. 2013; Liefer et al. 2014; McMahan & Santos 2017; Medina-Gómez and Herrera-Silveira 2006), dissolved ions (Santos et al. 2008) and trace elements (Ganguli et al. 2012) to coastal lagoons. Also, the connectivity between the lagoon and sea via the freshwater system underlying barriers remains difficult to quantify (Austin et al. 2013; Bratton et al. 2009; Rapaglia et al. 2010; Röper et al. 2012; Schmidt et al. 2011; Tamborski et al. 2019).

A variety of geochemical techniques can characterise groundwater sources including stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), radionuclides (namely ^{222}Rn and Ra isotopes), and major ions (e.g., Bratton et al. 2009; Kong et al. 2019; Petermann et al. 2018). Stable water isotopes offer insights into water sources contributing to submarine groundwater discharge (SGD) because they are simple to sample and the sources may have distinct signatures (Duque et al. 2019). Major ion chemistry can reveal geochemical processes that are relevant at a site and shed light on mixing water sources (Röper et al. 2012; Young et al. 2008). Many of these studies have lumped water samples into representative groups with similar hydro-chemical signatures. Techniques for doing this have typically included statistical correlations (e.g., linear regressions or Pearson coefficient correlations (see Santos et al. (2008) or Ji et al. (2013)), or mixing models using end-member mixing analysis (EMMA) (e.g., Moore 2003; Stumpp et al. 2014; Young et al. 2008). Mixing models often require a high density of samples to determine the chemical signature of each source (Duque et al. 2019) and tracers must be chemically conservative (Moore 2003).

Analysis of groundwater-derived nutrient transport and nutrient processes in coastal areas has revealed a major role of groundwater nutrients in coastal ecosystems (Andrisoa et al. 2019; Ibánhez et al. 2013; Santos et al. 2021). Nitrogen, phosphorus, carbon and silica concentrations in groundwater are required to estimate nutrient loads to receiving waters based on groundwater discharge estimates (e.g., Burnett et al. 2007; Ji et al. 2013; Kong et al. 2019; Maher et al. 2019). Several recent studies have examined nutrient processes within nearshore sediments and coastal waterbodies, such as denitrification and phosphorus release from sediments (Bernard et al. 2014; Duque et al. 2019; Santos et al. 2014). In coastal aquifers, denitrification often attenuates

the nitrogen flux via groundwater pathways (Loveless and Oldham 2010).

In this study, we aim to (1) resolve sources of groundwater seepage to a lagoon and (2) estimate nutrient loads from direct groundwater discharge to the lagoon. We analysed major ion chemistry, nutrients and stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) around a hypertrophic, temperate climate coastal lagoon in New Zealand including samples from lagoon surface water, porewater on the lagoon margins, groundwater wells and springs. We hypothesise that groundwater seepage comprises a mix of alpine river recharge, rainfall recharge and lagoon water recirculation in shallow sediments. Based on high nutrient concentrations in regional groundwater and rivers (Hayward and Ward 2009), we also hypothesise that direct groundwater seepage plays an important role releasing nutrients to the lagoon. This study addresses gaps in the literature around delineating groundwater sources to complex coastal waterbodies that are situated at the interface between terrestrial water sources and seawater mixing.

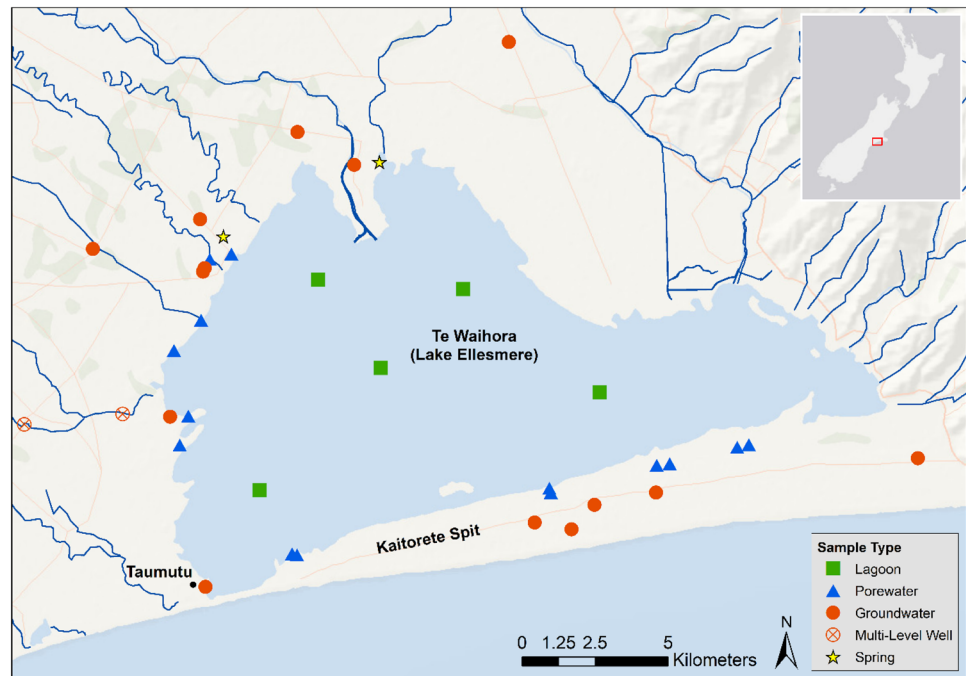
Methods

Site description

This study focuses on Te Waihora/Lake Ellesmere, a large ($\sim 150 \text{ km}^2$), shallow (mean depth = 1.4 m) coastal lagoon on the east coast of the South Island of New Zealand ($43^\circ 46' 40.3'' \text{ S } 172^\circ 28' 27.2'' \text{ E}$) (Fig. 1). This culturally significant site is important to a variety of stakeholders for its ecological, economic and recreational values. Local Māori tribe Ngāi Tahu consider Te Waihora a *taonga* (treasure) and have traditionally referred to the site as Te Kete Ika o Rākaihautū—The Fish Basket of Rākaihautū for its outstanding food and fibre-gathering resources. However, the water quality of the lagoon has significantly declined due to pressure from intensive agriculture, deforestation and wetland draining in the surrounding catchment. Te Waihora is hypertrophic with high turbidity, chlorophyll *a* and nutrients, however, the lagoon does not generally exhibit some of the classic characteristics of hypertrophic water bodies like severe oxygen depletion, fish kills or toxic algal blooms (Hayward and Ward 2009). In summer during periods of high temperatures and low wind speeds, there is some vertical stratification of temperature and oxygen levels in the water column, though stratification events appear to be infrequent (Schallenberg and Crawshaw 2017). There is also evidence of salinity-induced stratification in the water column close to the ocean outlet at the southwest end of the barrier (Larned and Schallenberg 2006).

The geology of the 2560 km^2 Te Waihora catchment comprises mainly alluvial sediments eroded from the Southern Alps to the west, which are composed of

Fig. 1 Location map of hydro-chemistry samples taken in November–December 2020 in and around Te Waihora/Lake Ellesmere. Map base layer credits: Land Information New Zealand and Eagle Technology. Map includes GIS data from Land Information New Zealand (Land Information New Zealand 2019,2020)



greywacke, a marine-derived sedimentary rock dominated by silicates (Brown and Weeber 1992). The catchment is bordered by two large gravel-bed braided rivers—the Waimakariri River to the north and the Rakaia River to the south, and to the southeast by Banks Peninsula volcanics overtopped by loess. Te Waihora formed in the depression between the alluvial fans of the adjacent braided rivers during interglacial Holocene sea level rise (Bird 1994), and it has fluctuated between an estuary and an enclosed coastal lake/lagoon (its present state). During the past several thousand years, sand and gravel transported by northward longshore drift formed a barrier that separated Te Waihora from the sea, referred to as Kaitorete Spit (Armon 1970). The lagoon is considered a “choked” lagoon in terms of Kjerfve’s (1986) lagoon classification and locally as a Waituna-type lagoon (Kirk and Lauder 2000), with features such as a narrow outlet to the sea; minimal tidal influence; salinity ranging from fresh to brackish; and relatively long water residence times. The lagoon entrance to the sea is mechanically opened to the sea on average 2–6 times per year when the lagoon height reaches set trigger levels. The regional hydrogeology largely consists of an unconfined mixed sand and gravel alluvial aquifer. The system becomes confined towards the coast where the alluvial gravels are interspersed by semi-confining marine deposits, which is referred to as the Christchurch artesian aquifer system (Brown 2001; Brown and Weeber 1992). Here, there are at least five confined aquifers in a stacked formation near the coast. In the area around Te Waihora, shallow groundwater levels vary less on a seasonal basis than in other parts of the catchment,

given the coast provides a constant head boundary, which limits fluctuations due to seasonality and climate (Williams 2009). Near the margins of Te Waihora, groundwater either emerges on land as springs, discharges directly into the lagoon or discharges offshore (Williams 2010). Over 40 rivers, small streams and drains flow into Te Waihora, many of which are spring fed.

While there are various studies investigating groundwater sources in and around Te Waihora in grey literature, there are few relevant published studies. Two previous studies examined the locations of groundwater seepage in the lagoon (Coluccio et al. 2020; Ettema and Moore 1995), while Coluccio et al. (2021) quantified groundwater discharge to the lagoon using a radon mass balance. Hanson and Abraham (2009) analysed major ion chemistry, stable oxygen isotopes and nutrients along a cross section of the Canterbury Plains, which intersected with Te Waihora. They found that $\delta^{18}\text{O}$ is the most reliable tracer on the Canterbury Plains for distinguishing between alpine river recharge and rainfall-based recharge. However, they recommended using a suite of tracers to draw comprehensive conclusions regarding groundwater recharge sources and flow paths (Hanson and Abraham 2009). Stewart (2012) examined $\delta^{18}\text{O}$ ratios, age tracers and major ions to determine groundwater sources and flow paths in the Christchurch Aquifer System. Groundwater seepage seems to be a main source of new nutrients to the lagoon, but very limited data sets are available (Larned and Schallenberg 2006). This study builds on the literature by conducting an in-depth investigation into groundwater sources and their implications in nutrient transport at a site where these processes have been minimally investigated.

Sampling and analysis

Forty water samples were collected in November–December 2020 from various locations around Te Waihora and consisted of four main sample types: lagoon surface water, porewater on the lagoon margins, groundwater wells and springs (Fig. 1). Lagoon surface samples ($n=5$) were taken in five locations spatially distributed across the lagoon on a moderately windy day (mean wind speed = 10.2 m/s). Porewater samples ($n=14$) were taken with a stainless-steel drive-point 2-m long mini-piezometer screened in the bottom 30 cm (design similar to Coluccio (2018)). The piezometers were installed as close to the edge of the lagoon as possible (max distance from margin = ~750 m) so that shallow groundwater could be sampled (max depth = 0.75 m). Existing groundwater wells at a variety of depths and locations were sampled ($n=19$), including two multi-level wells. Wells screened in the unconfined surface aquifer to the third confined aquifer were targeted (screened between 0.5 and 90.5 m below ground). Two springs were sampled: a spring-fed agricultural drain and a spring that emerges in the mudflats on the north margin of the lagoon that has artesian flow at many times of the year, though at the time of sampling, it did not appear to have significant artesian flow.

Most samples were pumped with either peristaltic or submersible pumps. Several groundwater wells were sampled through existing taps, and for one of the springs (SPR1), a bottle was filled directly. All but three samples (GW1, GW8, SPR1) were pumped through a flow cell so that water quality measurements were not exposed to the air. Water quality parameters (dissolved oxygen, specific conductivity, temperature, pH, oxidation–reduction potential (ORP)) were measured while the samples were pumped using a YSI Pro Plus Multiparameter Meter (YSI Incorporated, Yellow Springs, OH). All groundwater samples were taken once water quality parameters stabilised. Wells were purged in excess of three well volumes (Daughney et al. 2006), except for four wells that are continuously pumped (GW4, GW10) or were too deep to practically pump three well volumes (GW6, GW15). Sample colour and smell were noted at time of collection, and samples were refrigerated immediately after collection.

Samples were analysed for major ions, nutrients, stable isotopes and trace metals. Samples for major cation analysis were filtered with 0.45 μm Millipore® mixed cellulose ester filters, preserved with ultra-pure nitric acid and stored at 4°C until analysis. These samples were analysed for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe and Mn on an ICP-OES (Inductively coupled plasma—optical emission spectrometry) at Lincoln University (Lincoln, New Zealand). Major anion analysis (Cl^- , SO_4^{2-} , NO_3^-) was carried out using ion chromatography at University of Canterbury (Christchurch, New Zealand) with refrigerated (4°C) filtered (0.2 μm Millipore®

samples. We used a Metrohm Eco IC (Metrohm AG, Herisau, Switzerland) with a Metrosep A Supp 17–150/4.0 column, 5 mmol/L Na_2CO_3 0.3 mmol/L NaHCO_3 eluent and a flow rate of 0.600 mL/min. Samples were diluted when necessary using deionised water (purified to 0.67 $\mu\text{S}/\text{cm}$). Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions were determined by measuring total alkalinity by titrating to pH 4 with 1.600 N sulfuric acid using a HACH digital titrator (HACH, Loveland, CO). Samples were analysed for a suite of nutrients at an accredited lab (Hill Laboratories, Hamilton, NZ). Nitrate–N (NO_3^- -N) and nitrite–N (NO_2^- -N) were determined using automated cadmium reduction and automated colorimetry. Total Kjeldahl nitrogen (TKN) and ammoniacal nitrogen (NH_4^+ -N) were analysed by phenol/hypochlorite colorimetry. Total nitrogen (TN) was calculated ($\text{TKN} + \text{NO}_3^-$ -N + NO_2^- -N). Dissolved reactive phosphorus (DRP) was determined using molybdenum blue colorimetry, and total phosphorus (TP) was analysed by ascorbic acid colorimetry. Stable isotope analysis ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) was carried out on 38 refrigerated and filtered (0.45 μm Millipore®) samples at the GNS Science Stable Isotope Laboratory (Wellington, NZ) (note: samples SW2 and SW5 were not analysed). Samples were analysed on an Isoprime mass spectrometer for $\delta^{18}\text{O}$ by water equilibration at 25°C using an Aquaprep device, and for $\delta^2\text{H}$ by reduction at 1100°C using a Eurovector Chrome HD elemental analyser with analytical precisions of 0.2‰ for $\delta^{18}\text{O}$ and 2.0‰ for $\delta^2\text{H}$. All stable isotope results are reported in terms of deviation from Vienna Standard Mean Ocean Water 2 (VSMOW2) and normalised to internal GNS laboratory standards. Where results were below detection limits, half the detection limit was used to calculate statistics such as averages, standard deviations and medians.

Results

Field parameters

The mean values and standard deviations for the parameters measured revealed different sample groups (Table 1). Water temperature ranged from 11.3 to 21.6°C (median = 13.7°C). Electrical conductivity (measured as specific conductivity) ranged from 110.3 to 34,858 $\mu\text{S}/\text{cm}$ (median = 390.6 $\mu\text{S}/\text{cm}$). We recorded dissolved oxygen levels between 0.9 and 102.7% saturation (median = 43.6% saturation). The pH of samples ranged from 6.1 to 8.9 (median = 6.9). ORP values were between -136.0 to 256.3 mV (median = 147.6 mV). During the 5-week sampling period, the ambient air temperature and wind speed ranged from 8 to 25°C and 0 to 19 m/s, respectively, and there was 50.5 mm of rainfall (Environment Canterbury 2020). The lagoon was on average 0.8 m above mean sea level during the sampling campaign and had

Table 1 Summary mean and standard deviation of field parameters, major ions, trace metals, nutrients and stable isotopes measured in samples collected in and around Te Waihora

Parameter (unit)	Inland Groundwater (n=14)	Inland Porewater (n=6)	Barrier Groundwater (n=5)	Barrier Porewater (n=8)	Springs (n=2)	Lagoon (n=5)
Temperature (°C)	13.5±0.7	12.4±1.1	14.7±1.2	13.3±1.5	17.6±5.6	18.5±0.2
Electrical conductivity (µS/cm)	194.6±87.3	295.1±63.1	1461.3±1422.1	6432±12,025	2843.5±3308.5	16,335±603
pH (-)	7.52±0.49	6.68±0.25	6.91±0.14	6.25±0.15	7.09±0.23	8.65±0.15
Dissolved oxygen (% sat)	56.9±34.1	32.3±30.4	36.2±30.6	15.5±13.8	75.3±0.9	98.0±1.6
Redox potential (mV)	188.7±61.0	62.1±52.4	-12.1±128.3	60.3±63.4	250.5±8.2	234.7±12.8
Ca ²⁺ (meq/L)	1.04±0.45	1.35±0.38	1.67±1.96	2.49±3.65	2.57±0.47	5.92±0.36
K ⁺ (meq/L)	0.03±0.01	0.06±0.04	0.41±0.29	1.43±2.30	0.94±1.23	6.37±0.43
Mg ²⁺ (meq/L)	0.42±0.25	0.77±0.15	2.00±1.74	2.45±1.91	2.92±2.67	6.56±0.10
Na ⁺ (meq/L)	0.42±0.28	1.06±0.57	13.00±14.11	67.43±130.46	30.04±38.73	189.97±35.09
HCO ₃ ⁻ + CO ₃ ²⁻ (meq/L)	1.10±0.28	1.67±0.54	0.88±0.20	2.08±1.93	1.99±0.64	2.10±0.05
Cl ⁻ (meq/L)	0.35±0.24	0.78±0.35	13.25±14.58	70.09±140.04	25.96±34.65	174.56±7.54
SO ₄ ²⁻ (meq/L)	0.27±0.39	0.34±0.19	1.08±1.16	5.32±9.95	2.69±2.25	14.99±0.68
Fe (µM)	0.45±1.18 ^a	16.44±29.64 ^a	18.82±22.05 ^a	71.06±85.35	0.14±0.16 ^a	<0.05 ^b
Mn (µM)	0.29±0.87 ^a	2.53±2.37	1.58±1.75 ^a	10.45±15.09	1.57±1.47	0.02±0.04 ^a
δ ¹⁸ O (‰)	-8.78±0.24	-8.56±0.15	-7.46±0.50	-6.60±0.81	-7.42±0.81	-2.30±0.31 ^c
δ ² H (‰)	-59.32±1.93	-57.92±0.78	-50.58±3.52	-45.41±4.13	-51.08±3.68	-18.84±2.25 ^c
Dissolved reactive phosphorus (mg/L)	0.010±0.004 ^a	0.012±0.012 ^a	0.017±0.028	0.092±0.204 ^a	0.006±0.005 ^a	<0.010 ^b
Total P (mg/L)	0.014±0.013 ^a	0.166±0.332	0.077±0.065	0.233±0.319	0.037±0.035	0.186±0.013
Nitrate-N (mg/L)	2.144±3.117	0.068±0.076	0.687±0.700	0.062±0.127 ^a	0.060±0.084 ^a	<0.01 ^b
Nitrite-N (mg/L)	<0.002 ^b	0.006±0.006 ^a	0.005±0.008 ^a	0.007±0.009 ^a	0.003±0.003 ^a	<0.01 ^b
Ammoniacal-N (mg/L)	0.008±0.013 ^a	0.047±0.059 ^a	0.064±0.066 ^a	0.106±0.253 ^a	0.019±0.020 ^a	0.03±0.01 ^a
Total N (mg/L)	2.17±3.10 ^a	0.91±1.25 ^a	0.85±0.71	0.601±0.817	0.48±0.45	3.1±1.6

^aWhere results fell below the detection limit, half the detection limit was used to calculate the average values reported here

^bThe detection limit is reported for these samples where all results were below detection

^cOnly three lagoon samples were analysed for δ¹⁸O and δ²H

last been opened to the sea in mid-August 2020 (Environment Canterbury 2020).

Major ions

The average concentrations and standard deviations of major ions are reported in Table 1. Of the 40 samples, 92% (n=37) had an ion balance percent difference less than 10% (Fig. 2). Of the remaining three samples, two had ion balance percent differences of 11 and 13%, while one sample had a 22% difference. These ion balance results are similar to another ion chemistry study in a coastal lagoon (Santos et al. 2008), indicating an overall acceptable level of accuracy for these results. The dominant cations were Ca²⁺ or Na⁺ + K⁺ (Fig. 3). The dominant anions were HCO₃⁻ or Cl⁻, with a small number of samples composed of a mix between the two. As for overall major ion composition, nearly all samples

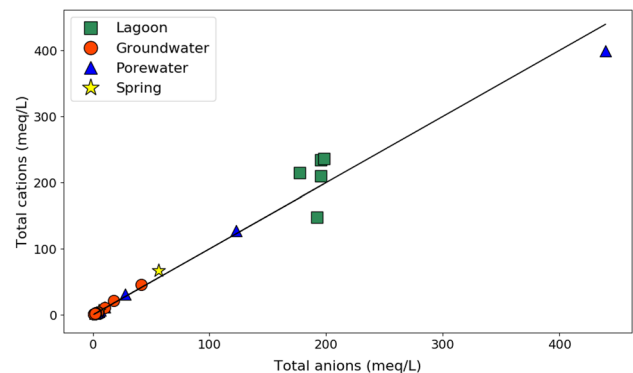


Fig. 2 Scatter plot of the sum of the anions versus the sum of the cations in the 40 samples taken in and around Te Waihora plotted against a 1:1 line

were either $MgHCO_3$ or $NaCl$ types, with a small number ($n=3$) consisting of a mixture between the two (though closer to $MgHCO_3$ type).

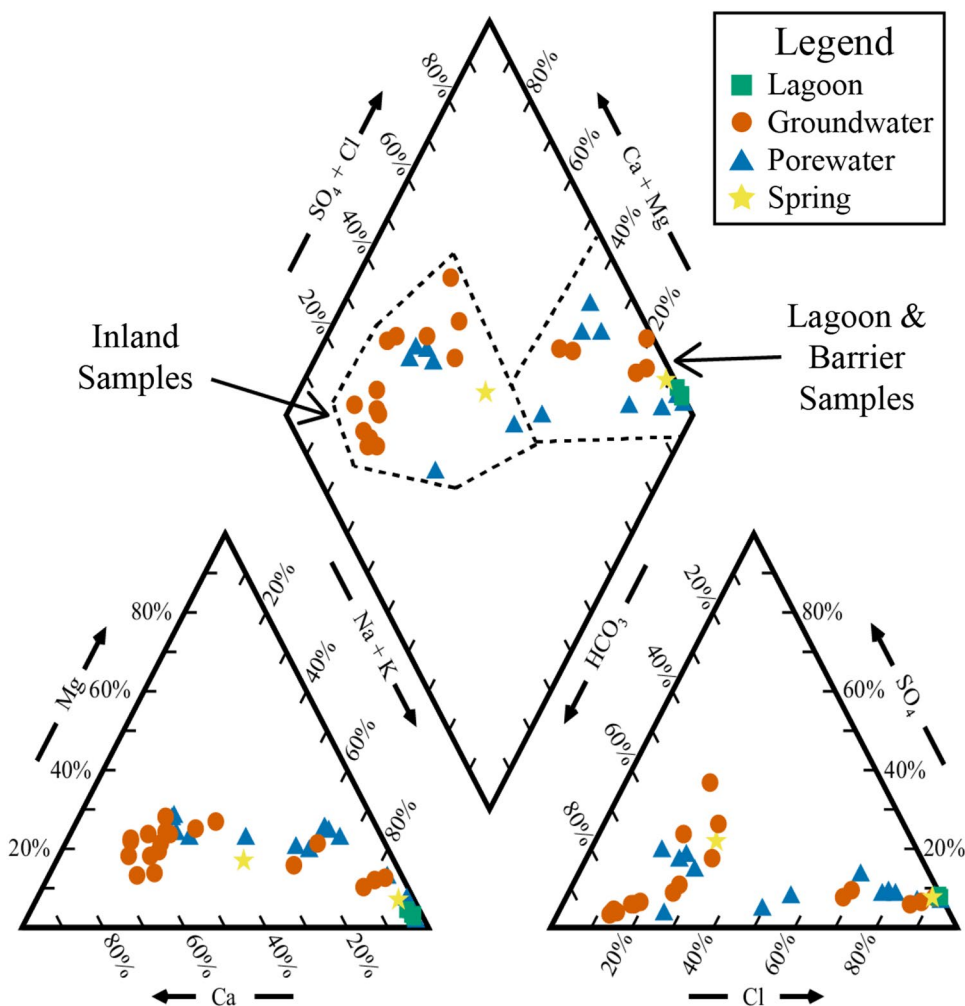
Trace metals

Trace Fe and Mn were above analytical detection limits in 20 and 29 samples, respectively (Table 1). Dissolved Fe concentrations ranged from <0.05 to $236.03 \mu M$. Dissolved Mn concentrations ranged from <0.004 to $44.96 \mu M$. Fe and Mn were overall highest in groundwater wells on the barrier and porewater samples. Mean Fe concentrations were $18.82 \pm 22.05 \mu M$, $16.44 \pm 29.64 \mu M$ and $71.06 \pm 85.35 \mu M$ in barrier groundwater, inland porewater and barrier porewater, respectively. Mean Mn concentrations were $1.58 \pm 1.75 \mu M$, $2.53 \pm 2.37 \mu M$ and $10.45 \pm 15.09 \mu M$, respectively.

Nutrients

TN was on average highest in the inland groundwater samples ($2.17 \pm 3.10 \text{ mg/L}$), but the lagoon had the highest median at 2.3 mg/L (Table 1). Nitrate-N (also referred to here as nitrate) was highest in the inland groundwater wells ($2.14 \pm 3.11 \text{ mg/L}$) with the remainder of sample types on average between 0.06 and 0.69 mg/L and all lagoon samples below detection. Nitrite-N (also referred to here as nitrite) was below detection in inland groundwater and the lagoon and was most often measured above detection in porewater samples. Porewater and groundwater wells on the barrier had the highest NH_4^+ concentrations while the inland groundwater was the lowest. TP was highest in porewater samples on the barrier with slightly lower TP concentrations in the lagoon and in barrier groundwater, while all inland samples were much lower. Overall, inland groundwater samples had the highest median DRP concentration (0.011 mg/L), while the barrier porewater had several high readings, including one sample as high

Fig. 3 Piper diagram showing dominant cations and anions and overall major ion composition in 40 surface and groundwater samples in the study area



as 0.59 mg/L. All lagoon samples were below detection for DRP.

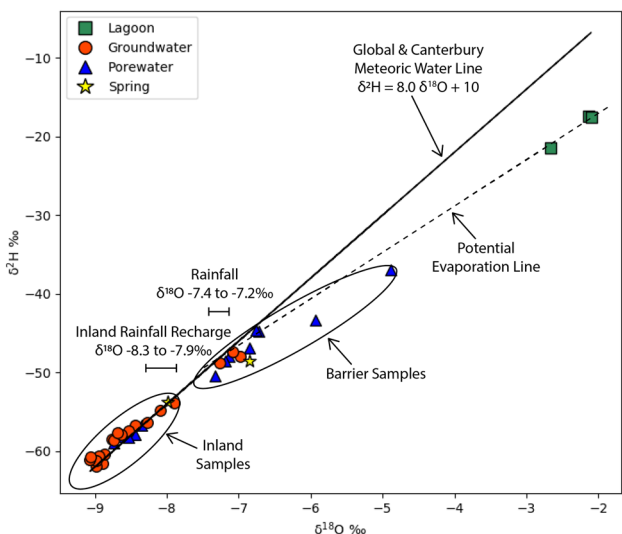


Fig. 4 $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ values for 38 samples in and around Te Waihora. The Global and Local meteoric water line is plotted (Stewart and Morgenstern 2001), as well as a potential evaporation line. Inland rainfall recharge isotope ratios are from Hanson and Abraham (2009). Rainfall isotope ratios are from Stewart (2012)

Stable Isotopes

$\delta^{18}\text{O}$ ranged from -9.07 to -2.10‰ (median = -8.31‰) (Table 1), and $\delta^2\text{H}$ ranged from -61.9 to -17.4‰ (median = -56.5‰) (Fig. 4). Samples from inland groundwater wells had the most negative $\delta^{18}\text{O}$ ratios (most between -8.4 to -9.0‰). Samples from groundwater wells on the barrier had less negative $\delta^{18}\text{O}$ ratios ($\sim 7.0\text{‰}$). Inland porewater samples had $\delta^{18}\text{O}$ values between -8.74 and -8.35‰ , while barrier porewater samples were less negative (between -7.33 and -4.89‰). This compares to lagoon $\delta^{18}\text{O}$ ratios that were significantly less negative than all other samples (-2.1 to -2.7‰).

Discussion

Groundwater sources to the lagoon

The major ion chemistry revealed relatively clear distinction of water types based on sample locations. Groundwater from both inland wells and on the barrier had more defined hydro-chemical facies, while porewater samples showed more mixed signatures. The lagoon samples had a strong NaCl signature, as did all porewater and groundwater samples taken on the barrier (Figs. 3, 5). This is likely due to the influence of seawater, particularly in the lagoon samples affected by mixing via the ocean outlet, wave overtopping and salt spray (Spigel 2009). Similar Na^+ and Cl^- dominance

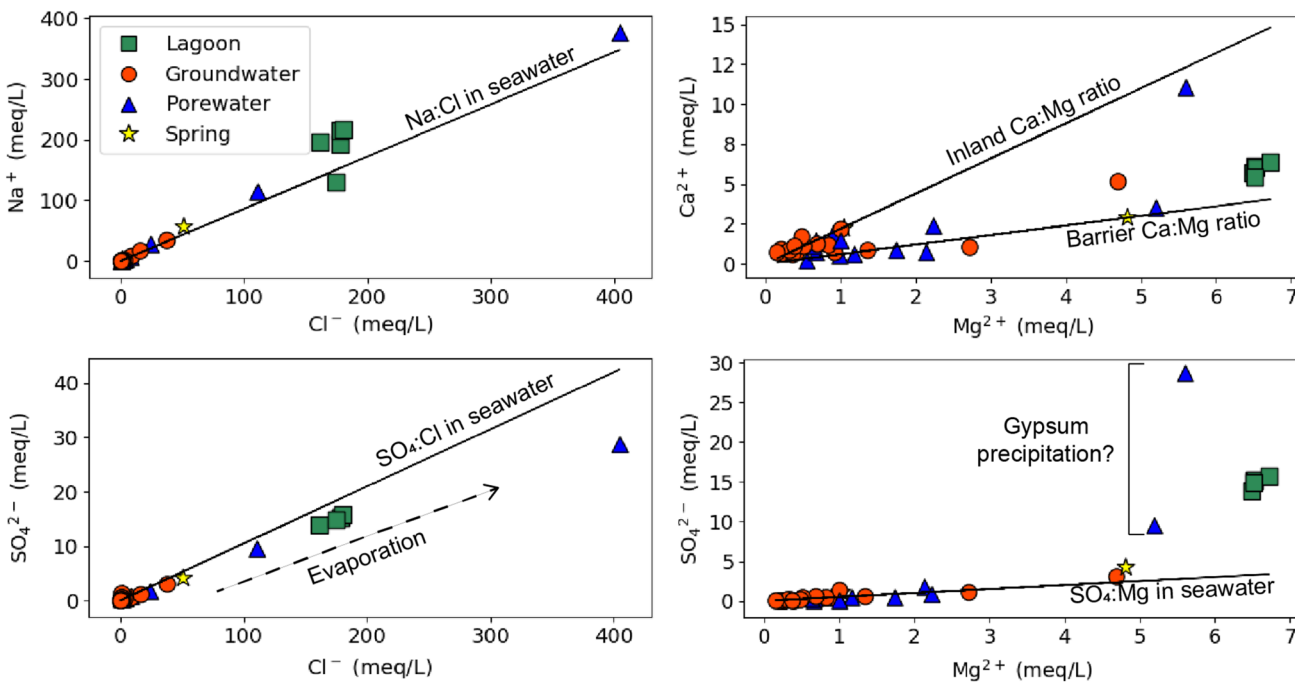


Fig. 5 Plots of key major ion ratios sampled at Te Waihora with seawater dilution lines and slopes representing major groups of samples

has been found in other coastal lagoons in Spain and Turkey where mixing of fresh and sea water is a significant driver of lagoon ion chemistry (Menció et al. 2017; Stumpp et al. 2014). Te Waihora surface water is strongly dominated by Na^+ and Cl^- , and the Na:Cl ratios of the lagoon samples plot close to the seawater dilution line with a Na:Cl ratio of 0.86 (Møller 1990) (Fig. 5), indicating that the Na^+ and Cl^- are sourced from seawater as opposed to weathering (Rosen 2001). In contrast, previous investigations in Germany and Brazil have found more evidence of geological drivers influencing ion chemistry in lagoon and barrier samples, such as carbonate mineral dissolution resulting in higher HCO_3^- , Ca^{2+} and Mg^{2+} compositions (Röper et al. 2012; Santos et al. 2008; Seibert et al. 2018).

In general, groundwater wells on the barrier also had high Cl^- , Na^+ and K^+ ; low HCO_3^- and Ca^{2+} ; and less negative $\delta^{18}\text{O}$. This reflects stronger influence from coastal rainfall with salt spray influence, representing a lens of locally recharged groundwater, as well as seepage from the lagoon (Hanson and Abraham 2009). Both lagoon samples and groundwater from the barrier had higher SO_4^{2-} concentrations, which also correlated with higher Cl^- concentrations (Fig. 5). The sulfate is therefore most likely sourced from seawater, with little additional input from other sources, such as geological minerals (e.g., pyrite, gypsum or anhydrite) (Rosen 2001), or fertiliser applications (Hem 1985). The lagoon samples and two porewater samples on the barrier had reduced SO_4^{2-} when compared to the SO_4 :Cl seawater concentration dilution line (Fig. 5), which may be explained by gypsum precipitation as a result of evaporation (Menció et al. 2017). This group of samples plots above the SO_4 :Mg seawater concentration dilution line (Fig. 5), implying gypsum precipitation (Rosen 2001).

In contrast to the lagoon, inland samples were MgHCO_3 type and largely dominated by Ca^{2+} and HCO_3^- ions (Fig. 3). The MgHCO_3 signature corresponds with data from groundwater sampled elsewhere from the greywacke-derived alluvial gravel aquifers of the Canterbury Plains, which have mostly HCO_3^- -type groundwater (Hayward 2002; Vincent 2005). Most HCO_3^- in this location is sourced from interactions between dissolved atmospheric CO_2 and organic matter in soil that results in HCO_3^- ions dissolved in groundwater (Rosen 2001). Most groundwater in New Zealand is relatively young and rarely evolves past the HCO_3^- phase in the Cheboratev sequence (Freeze and Cherry 1979) because of a lack of soluble minerals (Rosen 2001). The Ca^{2+} sources in Canterbury are mainly from carbonate cement, pebbles and shells, which are common in the coastal aquifer system (Hayward 2002; Rosen 2001). The chemistry of the inland samples in this study suggests an inland source, in contrast to the lagoon and barrier samples, which showed evidence of seawater influence (Rosen 2001). Hayward (2002) noted that even as groundwater approaches the coast in this area,

HCO_3^- remains the dominant anion except where there is obvious saltwater influence.

In general, the inland samples had lower Ca^{2+} , K^+ , Mg^{2+} , SO_4^{2-} , and significantly lower Na^+ and Cl^- compared to the lagoon and barrier samples, aligning with results from Hanson and Abraham (2009). Most ion concentrations reduced with depth, reflecting a greater influence of low-ion alpine river recharge and more rainfall recharge at shallower depths (Hanson and Abraham 2009; Hayward 2002). Previous studies have shown Ca:Mg ratios to be higher in alpine river-sourced groundwater on the Canterbury Plains, whereas rainfall-recharged groundwater had lower Ca:Mg ratios (Hanson and Abraham 2009). Local river water and rainfall have low Mg^{2+} concentrations, and Mg^{2+} has a proportionally greater increase than Ca^{2+} when groundwater reacts with soil and aquifer sediments (Hanson and Abraham 2009). This is evident in the inland samples from the current study, which had a higher Ca:Mg ratio (median ratio = 2.2, max ratio = 4.9) than the barrier samples (median ratio = 0.6) (Fig. 5), indicating an influence of alpine river recharge in inland groundwater. However, it is worth noting that the inland Ca:Mg ratios found here are on the low end of the range compared to those in Hanson and Abraham (2009) who found that the Ca:Mg ratio was a more useful tracer closest to the recharge source and may be less helpful for groundwater near the coast.

Overall, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distinguished water sources as demonstrated in previous studies in China, Europe and Brazil (e.g., Luo et al. 2018; Rapaglia et al. 2010; Schmidt et al. 2011) and specifically on the Canterbury Plains (e.g., Blackstock 2011; Dench and Morgan 2020; Stewart 2012; Vincent 2005). Similar to the major ions, the $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ ratios fit into clear groups based on sample locations and types (Fig. 4). Samples from inland groundwater wells had the most negative $\delta^{18}\text{O}$ ratios, reaching -9.1‰ . This is in line with Blackstock (2011) and Stewart (2012) who found alpine river recharge to have $\delta^{18}\text{O}$ ratios below -8.8‰ . Shallower inland wells had less negative $\delta^{18}\text{O}$ ratios and may reflect a mix of alpine river recharge and rainfall recharge (Stewart 2012). It is worth noting that there may be some potential masking of stable isotope recharge sources because alpine-sourced water is used for irrigation on the Canterbury Plains (Close et al. 1995; Dench and Morgan 2020).

On the opposite end of the local meteoric water line (Fig. 4) were the lagoon samples, which were significantly more positive than all other samples ($\sim 2\text{‰}$). The lagoon $\delta^{18}\text{O}$ ratios deviate strongly from the meteoric water line plotted in Fig. 4, indicating that the heavier oxygen isotopes have been enriched due to evaporation from the large open surface of the lagoon (Schwartz and Zhang 2003). Röper et al. (2012), Cartwright et al. (2019) and Lopez et al. (2020) also found isotope ratios strongly influenced by evaporation of surface waters in barrier islands, rivers

and estuaries in Germany, Australia and the U.S., respectively. The evaporation effect in the current study may have also been enhanced due to sampling in summer (i.e., temperature effects) and because of strong winds at the site (Craig and Gordon 1965; Stewart and Morgenstern 2001).

Water sampled on the barrier was in between the lagoon and inland groundwater samples in terms of $\delta^2\text{H}:\delta^{18}\text{O}$ ratios (Fig. 4). Samples from groundwater wells in general had the most negative $\delta^{18}\text{O}$ ratios ($\sim -7.0\text{‰}$) amongst the barrier samples, while porewater samples ranged more widely from (-7.33 to -4.89‰). All of the barrier $\delta^{18}\text{O}$ ratios were more positive than the range of ratios (~ -8.3 to 7.9‰) previously found in rainfall-recharged groundwater on the Canterbury Plains (Hanson and Abraham 2009), suggesting locally specific hydrological processes on the barrier. Barrier groundwater had similar $\delta^{18}\text{O}$ ratios to local rainfall samples reported in Stewart (2012), which were -7.4 to -7.2‰ . As the range of barrier samples becomes more positive in terms of $\delta^{18}\text{O}$, they plot increasingly below the local meteoric water line (Fig. 4) indicating isotopic enrichment from evaporation (Mazor 1991).

In this study, we use the porewater samples at the lagoon margins as proxies for groundwater seepage into the lagoon. The chemistry of the porewater samples separates out two groups: the samples on the north and west margins of the lagoon (referred to here as “inland porewater”) and the samples on the barrier (referred to here as “barrier porewater”). Overall, the inland porewater was more chemically similar to inland groundwater samples, and on the barrier, porewater was chemically similar to barrier groundwater. These distinct groups are visible in the Piper plot (Fig. 3) and $\delta^2\text{H}:\delta^{18}\text{O}$ plot (Fig. 4). Previous studies also distinguished groups of samples in other coastal lagoons and lakes using similar hydro-chemical and stable isotopic tracers (Menció et al. 2017; Sánchez-Martos et al. 2014; Santos et al. 2008; Young et al. 2008).

Combining $\delta^{18}\text{O}$ and Cl^- may provide further insight into recharge sources for porewater samples (Fig. 6) (Duque et al. 2019; Han et al. 2019; Luo et al. 2018). Inland $\delta^{18}\text{O}$ ratios suggest that the deeper groundwater wells are likely sourced primarily from alpine recharge, whereas shallow inland groundwater is likely sourced from rainfall recharge on the plains (Stewart 2012). This is also reflected in the increased Cl^- concentrations (10–100 mg/L) in the shallower groundwater and porewater, which corresponds to typical ranges in inland rainfall-derived recharge (Hayward 2002). In contrast, the barrier samples plotted closer to the coastal rainfall recharge $\delta^{18}\text{O}$ signature (Fig. 6), indicating a different water source than the inland samples. This aligns with Schmidt et al. (2011) who found groundwater on the barrier of a Brazilian lagoon to be mostly recharged from precipitation rather than lagoon infiltration.

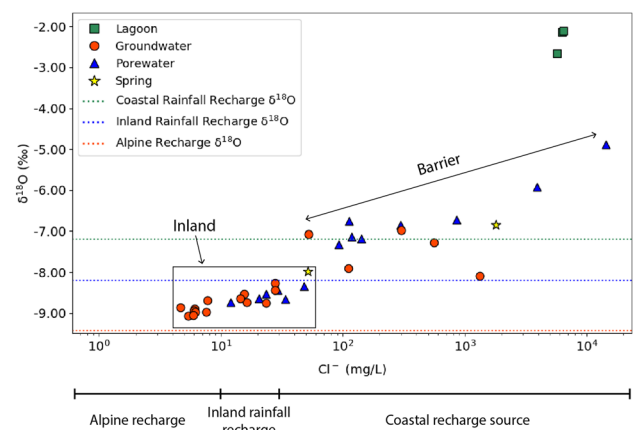


Fig. 6 Chloride vs. $\delta^{18}\text{O}$ for the four sample types. $\delta^{18}\text{O}$ ratios from the literature are plotted as horizontal lines for coastal rainfall recharge (Stewart 2012), inland rainfall recharge (Stewart 2012) and alpine recharge (Stewart et al. 1983)

Despite a previous study showing freshwater inputs along the lagoon side of the barrier that may have been groundwater discharge (Coluccio et al. 2020), the major ion and stable isotope composition of the barrier porewater most likely reflects a combination of seepage from the lagoon and rainfall-recharged groundwater on the barrier (Hanson and Abraham 2009). Barrier groundwater and porewater samples were chemically more similar to the lagoon than inland groundwater (Blackstock 2011; Vincent 2005). This provides supportive evidence that the general direction of shallow groundwater flow underneath the barrier is from the lagoon towards the sea. During sampling in November–December 2020, the lagoon was on average 0.8 m above mean sea level, which would have resulted in seepage through the barrier from the lagoon towards the sea (Horrell 1992).

Implications of groundwater sources for nutrient transport

Te Waihora is a hypertrophic lagoon with significant water quality issues. Analysing groundwater-derived nutrient inputs is a key part of gaining a holistic understanding of drivers of water quality (Schallenberg et al. 2010). Inland groundwater wells had the highest NO_3^- -N concentrations (4.9–9.3 mg/L), similar to other sites on the Canterbury Plains (Hanson and Abraham 2009; Hayward 2002). In contrast, both inland and barrier porewater samples had low NO_3^- -N concentrations (mean = 0.06 mg/L), demonstrating a trend of decreasing NO_3^- -N concentrations near the lagoon (Hanson & Abraham 2009; Rutter and Rutter 2019). Porewater observations imply denitrifying conditions around the lagoon margins with increased Fe, Mn, NO_2^- -N and NH_4^+ (Fig. 7) (Close et al. 2001; Dahiru et al. 2020),

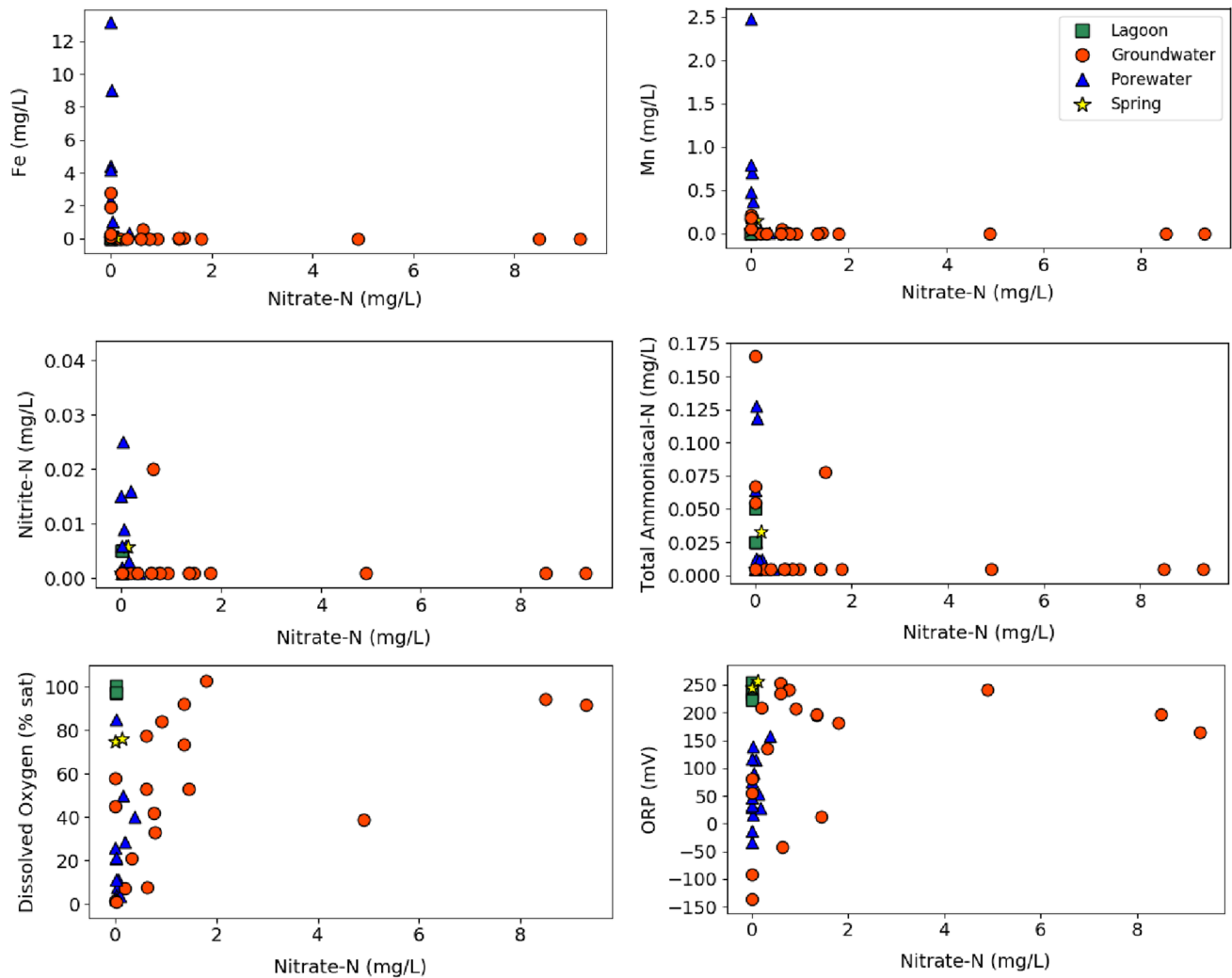


Fig. 7 Plots of Fe, Mn, nitrite, ammonia, dissolved oxygen and oxidation reduction potential (ORP) vs. nitrate concentrations in lagoon margin porewater. Note, one (high concentration) outlier was excluded from the ammonia plot to improve plot display

and denitrification has been confirmed in the lagoon bed sediments (Crawshaw et al. 2019). Organic matter deposition causing anoxic conditions on the margins of lagoons and other coastal waterbodies can provide the ideal setting for denitrification (Burgin and Hamilton 2007). Bratton et al. (2009) highlights that denitrification of groundwater in nearshore sediments before it discharges offshore is not often accounted for in models or nutrient budgets. Yet, it may serve as an important natural bioremediation pathway for nitrogen-rich SGD (Bratton et al. 2009). The results here align with a recent global review that found the main N species in SGD to be ammonium and dissolved organic nitrogen (Santos et al. 2021).

Reactive phosphorus results did not display trends as clear as the nitrogen. Overall, inland groundwater wells had the highest median DRP (0.011 mg/L). These values are similar to those in Hayward (2002), who reviewed ~ 15 years of

groundwater monitoring data in the neighbouring Christchurch-West Melton catchment. However, the DRP results from the groundwater wells in the current study are higher than the median found in Hanson and Abraham (2009) of 0.004 mg/L in the Te Waihora catchment. While inland groundwater had higher median DRP, samples from porewater and groundwater wells on the barrier in the current study had the highest maximum DRP concentrations (0.590 and 0.066 mg/L, respectively). Given anoxic conditions in nearshore sediments (i.e., low dissolved oxygen and higher dissolved Fe, Mn, NH_4^+ and NO_2^- -N concentrations), it is possible that phosphorus is being released to groundwater at the lagoon margins during dissolution of sedimentary iron oxides (to which the phosphate is adsorbed). It has been well established in the literature that phosphorus mobilisation is enhanced in low-oxygen conditions (Kazmierczak et al. 2020). Mobilisation of phosphorus may also be

enhanced in more saline anoxic barrier porewater where higher SO_4^{2-} concentrations were observed (Hartzell & Jordan 2012). The sulfides may combine with Fe in the sediments, forming FeS and FeS_2 , making Fe less able to bind to phosphate (PO_4^{3-}), and thereby making phosphorus more bioavailable (Hartzell and Jordan 2012).

Examining the ratios of nitrogen to phosphorus can be useful for shedding light on nutrient limitations for phytoplankton production in receiving water bodies (Ptacnik et al. 2010). When TN:TP ratios from samples in this study are plotted against the 16:1 Redfield N:P ratio (Redfield 1934, 1958), it appears that most samples are phosphorus limited (Fig. 8). This corresponds to analysis of long-term regional groundwater monitoring data that also found most groundwater to be phosphorus limited (Hayward 2002). The main exception in the current study was four porewater samples, three of which were from the barrier. Santos et al. (2021) found that most groundwater discharging on the coast has higher concentrations of nitrogen relative to phosphorus. In Te Waihora, both TN and TP concentrations are relatively high compared to other coastal lakes in the region and put the lagoon into the hypertrophic Trophic Lake Index category (Hayward and Ward 2009).

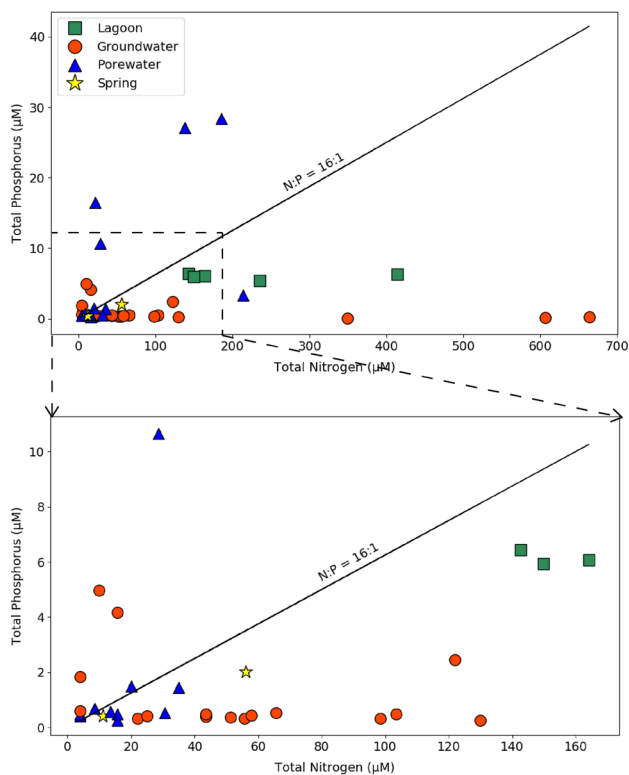


Fig. 8 Total nitrogen vs. total phosphorus ratios in porewater, groundwater well, lagoon and spring samples at Te Waihora. The plots include the 16:1 N:P Redfield ratio. Top panel: Full dataset. Bottom panel: Zoomed inset

High nitrogen concentrations appear to drive algal growth in Te Waihora, as algal blooms have been linked to sudden increased N fluxes from rivers (Schallenberg and Crawshaw 2017). Measurement of denitrification rates in the lagoon have shown that nitrate is quickly processed by phytoplankton (Crawshaw et al. 2019). There is also evidence of phosphorus production in the lagoon via the release of phosphorus bound to sediments under anoxic conditions (Schallenberg and Crawshaw 2017). As a result, the measured N:P ratios in the lagoon (between 22 and 65) (Fig. 8) were relatively low compared to N:P ratios in SGD across 169 studies (mean = 259, range 1–12,100) (Santos et al. 2021). Light availability, which is a function of sediment suspension, also plays an important role in controlling phytoplankton and biomass growth (Larned and Schallenberg 2006). Visual clarity in the shallow, wind-affected lagoon has decreased in recent decades largely due to the removal of macrophytes in a large storm in the late 1960s (Hayward and Ward 2009).

The nutrient observations shed light on nitrogen and phosphorus loads to the lagoon (Fig. 9). In some cases where groundwater inflow was a small proportion of water budgets, the nutrient and ion load contribution from groundwater has been significant due to the lack of other sources and high concentrations in groundwater (Luo et al. 2018; Santos et al. 2008). In some cases, nutrient inputs to coastal lagoons have been underestimated because groundwater was not considered (Schallenberg et al. 2010). Here, we use the mean DIN (dissolved inorganic nitrogen, i.e., $\text{NO}_3^- - \text{N} + \text{NO}_2^- - \text{N} + \text{NH}_4^+$) and DRP concentrations in the inland porewater samples (0.121 mg/L and 0.012 mg/L, respectively) to represent nutrient concentrations in

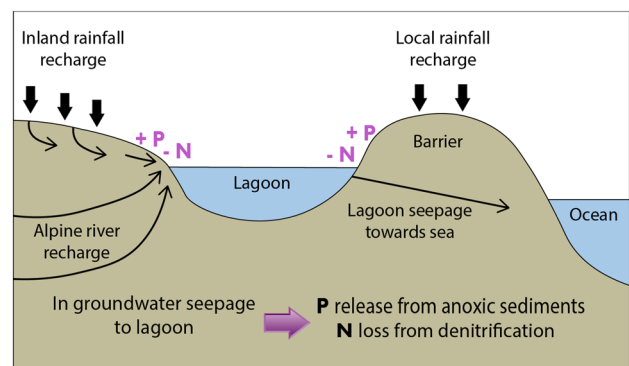


Fig. 9 Conceptual diagram illustrating groundwater sources and nutrient processes in seepage to Te Waihora. Results of this study indicate inland porewater is sourced from alpine river recharge and inland rainfall recharge. Porewater on the barrier appears to be sourced from local rainfall recharge on the barrier and mixing from lagoon surface water. Porewater on the lagoon margins had low nitrate concentrations and showed evidence of potential denitrifying conditions, while porewater had elevated levels of phosphorus possibly due to release from anoxic nearshore sediments

groundwater seepage to the lagoon. For DIN in particular, using this value (as opposed to the higher average DIN in inland groundwater wells) takes into account possible nutrient processing on the margins before groundwater enters the lagoon. This approach prevents an over-estimation of nitrogen loads (Robinson et al. 2018; Rocha et al. 2016). Using groundwater discharge estimates from the radon mass balances in Coluccio et al. (2021), this results in an average annual DIN load of 28.6 T (tonnes) and DRP load of 2.8 T.

When compared to estimated nutrient loads from tributaries (Larned and Schallenberg 2006), groundwater inputs comprise approximately 3% of DIN and 30% of DRP. This highlights that groundwater seepage may be an important contributor of phosphorus to Te Waihora, while the nitrogen contribution may be relatively small. A ~30% phosphorus contribution from groundwater discharge (as a proportion of river DRP load) is much higher than estimates in previous studies (Hayward and Ward 2009; Larned and Schallenberg 2006). Notably, previous studies relied on a limited number of groundwater samples, which did not target shallow groundwater on the lagoon margins, as well as earlier seepage estimates that were lower than those in Coluccio et al. (2021). Given the affinity of phosphorus to bind with sediment, it is possible that this phosphorus load is an over-estimate. Also, while the groundwater discharge rate in Coluccio et al. (2021) used to calculate the nutrient loads includes both winter and summer estimates, we have only used nutrient concentrations from one sampling campaign (late spring), so it is possible that our flux estimates vary as a result of seasonal changes in concentrations in the groundwater endmember. Assuming the low DIN concentrations in porewater are representative of direct groundwater seepage into the lagoon, this highlights the importance of managing surface water inputs of nutrients to Te Waihora. Also, the potential denitrifying capacity of wetlands around the lagoon margins provides support for current efforts to restore and construct wetlands around the lagoon. Wetland restoration will need to be carried out by maintaining a balance between enhancing denitrifying conditions while preventing phosphorus release from sediments.

Conclusion

There has been increasing interest in recent years in delineating the source waters of groundwater seepage to coastal lagoons. Hydrochemistry and stable isotope analysis revealed two distinct water types in groundwater around the lagoon. Inland groundwater was dominated by Ca^{2+} and HCO_3^- , and had lower ion concentrations and more negative $\delta^2\text{H}:\delta^{18}\text{O}$ ratios, reflecting a combination of alpine river recharge and rainfall recharge from

the plains. Groundwater on the barrier, which was NaCl type and had high ion concentrations and more positive $\delta^2\text{H}:\delta^{18}\text{O}$ ratios, is a mix of seepage from lagoon surface water and locally recharged rainfall. The general flow direction of shallow groundwater underlying the barrier is towards the sea. Nutrient analysis implied potential denitrification occurring in the nearshore sediments around the lagoon due to low NO_3^- -N concentrations and the presence of dissolved Fe, Mn, NO_2^- -N and NH_4^+ associated with P release in anoxic sediments. Groundwater seepage to the lagoon seems to be a minor contributor of inorganic nitrogen compared to rivers, but groundwater may play an important role in phosphorus transport. This study contributes to the literature on identifying the sources of groundwater discharge to waterbodies that are in the mixing zones between terrestrial water sources and seawater. The findings also highlight the importance of understanding how groundwater contributes to nutrient transport to coastal waterbodies in catchments with intensive agriculture.

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Author contributions KC designed the study methodology and carried out the data collection, curation and analysis. KC wrote the original manuscript and all authors assisted with manuscript revisions. LM and KC procured funding for this study. LM and IS provided supervisory support.

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Code availability Not applicable.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

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