Land-use change and managed aquifer recharge effects on the hydrogeochemistry of two contrasting atoll island aquifers, Roi-Namur Island, Republic of the Marshall Islands

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Abstract: Freshwater resources on low-lying atoll islands are highly vulnerable to climate change and sea-level rise. In addition to rainwater catchment, groundwater in the freshwater lens is a critically important water resource on many atoll islands, especially during drought. Although many atolls have high annual rainfall rates, dense natural vegetation and high evapotranspiration rates can limit recharge to the freshwater lens. Here we evaluate the effects of land-use/land-cover change and managed aquifer recharge on the hydrogeochemistry and supply of groundwater on Roi-Namur Island, Republic of the Marshall Islands. Roi-Namur is an artificially conjoined island that has similar hydrogeology on the Roi and Namur lobes, but has contrasting land-use/land-cover and managed aquifer recharge only on Roi. Vegetation removal and managed aquifer recharge operations have resulted in an estimated $8.6 \times 10^5 \text{ m}^3$ of potable groundwater in the freshwater lens on Roi, compared to only $1.6 \times 10^4 \text{ m}^3$ on Namur. We use groundwater samples from a suite of 33 vertically nested monitoring wells, statistical testing, and geochemical modeling using PHREEQC to show that the differences in land-use/land-cover and managed aquifer recharge on Roi and Namur have a statistically significant effect on several groundwater-quality parameters and the controlling geochemical processes. Results also indicate a seven-fold reduction in the dissolution of carbonate rock in the freshwater lens and overlying vadose zone of Roi compared to Namur. Mixing of seawater and the freshwater lens is a more dominant hydrogeochemical process on Roi because of the greater recharge and flushing of the aquifer with freshwater as compared to Namur. In contrast, equilibrium processes and dissolution-precipitation non-equilibrium reactions are more dominant on Namur because of the longer residence times relative to the rate of geochemical reactions. Findings from Roi-Namur Island support selective land-use/land-cover change and managed aquifer recharge as a promising management approach for communities on other low-lying

atoll islands to increase the resilience of their groundwater supplies and help them adapt to future climate change related stresses.

1. Introduction

Low-lying atolls are generally <3 m above mean sea level and particularly vulnerable to climate change induced inundation from sea-level rise (SLR) and storm waves (Dickinson, 2009; Storlazzi et al., 2015). The estimated SLR by the end of the 21st century ranges from 0.26–1.6 m to as much as 2.0 m above 2000 levels (Jevrejeva et al., 2010; Pachauri et al., 2014; Storlazzi et al., 2015). Inundation poses a serious threat to communities, natural resources, and ecosystems on atoll islands, and thus many of the >400 atolls worldwide may be uninhabitable by the end of the 21st century (Bailey et al., 2013). In addition to the SLR-induced inundation, climatic and population pressures are threatening the sustainability of the limited freshwater resources on most atoll islands (Karnauskas et al., 2016). In some cases, the lack of freshwater, including groundwater resources, may be a limiting factor for habitability of atolls even before loss of land due to SLR-induced inundation (Gurdak et al., 2015; Treidel et al., 2012). In addition to SLR, incremental seawater encroachment, more frequent storm over-wash events, and droughts related to El Niño/Southern Oscillation (ENSO) variability will reduce land cover and threaten groundwater supplies, forcing inhabitants to adapt or relocate (White et al., 2007). Because groundwater is an important source of freshwater supply on low lying atolls, especially during droughts, any adaptation measures to climate stressors and SLR must include an appropriate management plan that accounts for both groundwater quantity and quality.

Freshwater in atoll aquifers floats on top of saline water, is roughly lenticular in shape, and is referred to as the 'freshwater lens' (FWL). Here we define the FWL as <1.3% seawater, based on U.S. EPA secondary drinking water standard for chloride (250 mg L⁻¹) (USEPA, 2016). Calls to increase the resilience of groundwater resources on atolls and other islands have focused on groundwater management plans that minimize pollution from land derived sources and seawater intrusion from over-pumping of the FWL (Nath et al., 2010). However, the resilience of the FWL and

groundwater supply can also be increased if management strategies are implemented that favor recharge over evapotranspiration (ET). Tree cover, vegetation, and rainfall variability can have a substantial effect on rates of ET and subsequent recharge to the FWL. Empirical relationships show that recharge increases on some atolls with increasing mean annual precipitation and decreasing vegetated cover. For example, a study on Enewetak Atoll reported that with average annual rainfall of 1,040 mm and 0%, 40%, or 80% tree cover, only a corresponding 18%, 11%, or 4% of precipitation becomes recharge, respectively (Buddemeier and Oberdorfer, 1997). In comparison, greater average annual rainfall of 1,878 mm with the same percentages of tree cover (0%, 40%, or 80%), corresponds to relatively larger percentages of precipitation that becomes recharge (46%, 27%, or 25%, respectively).

Increasing recharge to groundwater supplies could also be accomplished using managed aquifer recharge (MAR). MAR usually involves collecting surface water during wet periods and taking advantage of seasonal over-supply to replenish an aquifer. In recent years, the use of MAR has greatly increased, particularly in coastal aquifers to minimize seawater intrusion (Vandenbohede et al., 2009) and increase local groundwater supplies (Racz et al., 2012; Russo et al., 2015; Schmidt et al., 2011). However, the use of MAR on atolls or similarly small islands is not widely reported. One exception is Roi-Namur, a small atoll island leased to the U.S. by the Republic of the Marshall Islands, which has implemented an MAR system and removed most of the native vegetation for a military base. As a result, the groundwater supply has increased significantly. However, it is unknown how these changes to the land-use/land-cover (LULC) and use of MAR have altered natural hydrogeochemical reactions that control the quality of groundwater and hydrogeologic properties of the aquifer.

A few previous studies have characterized the groundwater geochemistry of inhabited atolls and carbonate islands across a range of landscape alteration, rainfall and recharge rates, and sizes and locations (Anthony et al., 1989; Buddemeier and Oberdorfer, 1986; Plummer et al., 1976; Tribble, 1997). However, no study to date has systematically evaluated the link between LULC change and artificially increasing recharge and the combined effects on the hydrogeochemistry of the FWL. Roi-Namur Island presents a unique setting because a managed aquifer (with altered vegetation

and MAR) on Roi, the western lobe of the island, is co-located and directly adjacent to a naturally recharged aquifer (with natural vegetation and no MAR) on Namur, the eastern lobe (Figure 1). The aquifer on Roi is estimated to have $8.6 \times 10^5 \text{ m}^3$ of (potable) freshwater compared to $1.6 \times 10^4 \text{ m}^3$ on Namur (Gingerich, 1996). The order of magnitude difference in total estimated volume of freshwater between Roi and Namur has largely been previously attributed to differences in ET as a result of less vegetation on Roi (Gingerich, 1996). The same geographic location and similar sizes and hydrogeology of the contrasting Roi-Namur Island aquifers provides an ideal system to study how LULC change and MAR influence hydrogeochemical processes and groundwater quantity and quality on atoll islands.

A better understanding of LULC and MAR on the hydrogeochemical processes and groundwater supply on Roi-Namur Island will help provide a framework for best water resource management practices on other low-lying and carbonate islands in the context of climate change. Using geochemical parameters sampled from a groundwater monitoring network and results of geochemical modeling, this study addresses three main research questions about the Roi-Namur Island: (1) Does the altered LULC and MAR practices result in statistically significant differences in groundwater quality on the two lobes of the island? (2) Do changes in the recharge quantity and quality caused by the altered LULC and MAR practices affect the aqueous and solid carbonate system with respect to dissolution rates and natural hydrogeochemical processes? and (3) Is the practice of clearing native vegetation and MAR a suitable adaptation approach toward groundwater sustainability on atolls under future climate stressors?

2. Materials and Methods

2.1 Site Description

Kwajalein Atoll, Republic of the Marshall Islands, is located in the western Pacific at approximately latitude 9°N and longitude 167°E (Figure 1). The atoll covers an area of $2,850 \text{ km}^2$ and contains the world's largest enclosed lagoon. The subaerial ring-shaped coral reef that surrounds the lagoon has a total land area of 16.4 km^2 . Roi-Namur Island is positioned at the northern-most point of Kwajalein Atoll and is

made up of two reef islets (Roi and Namur), which were artificially conjoined by dredge fill during Japanese occupation prior to World War II. Currently, the island is leased to the U.S. military for use as a missile defense site.

Both Roi and Namur house some of the military infrastructure; however, Roi has been mostly cleared of natural vegetation to accommodate a 1,370-m-long runway, golf course, and living quarters for military and civilian personnel (Figure 1). Only thin grasses and relatively few coconut palms remain for aesthetics. Water supply on Roi-Namur is limited to surface catchment and storage during the rainy season and pumping of the FWL during the dry season and at times of drought. Two concrete-lined rainwater catchment basins on Roi are used to collect rainwater that is subsequently pumped into two 2,840 m³ storage tanks (C.J. Golby-Saunders, 2015, personal communication). When the tanks reach capacity, the rainwater is pumped to the western side of the runway and poured over a grassy field to recharge the aquifer. At times of drought and low surface-water supply, groundwater is pumped from the FWL using a 1,000-m-long horizontal lens well that parallels the western side of the runway (Figure 1). There are several pumps spaced across the horizontal lens well that skim water from the top of the water table. This type of well pumping system prevents up-coning of deeper, saline waters during groundwater withdrawal.

Adjacent to Roi on the windward reef, Namur contains heavy vegetative cover, including coconut palm trees, banana trees, pandanus, and other thick jungle-like scrub vegetation that has been minimally altered (Gingerich, 1992) (Figure 1). A few buildings are located on the northern and central part of this lobe, but the difference in LULC between the Roi and Namur lobes is substantial. The groundwater on Namur is naturally recharged, but the volume of the FWL is limited by higher ET rates compared to Roi. The FWL dynamics on Namur are more indicative of natural atoll island settings where human impact has been minimal, yet a relatively thin, viable FWL exists. A horizontal lens well is located on Namur, but it is not being actively pumped for water supply (not shown here). In this study we identify Roi as the human-modified lobe and Namur as the natural, vegetated lobe.

2.2 Roi-Namur Hydrogeochemistry

Observations of atoll island geology have identified two distinct stratigraphic layers that influence the depth of the FWL and tidal propagation (Ayers and Vacher, 1986; Hunt and Peterson, 1980) (Figure 2). The bottom layer is a highly permeable Pleistocene limestone layer that overlies basaltic basement rock and can be as thick as 3,000 m on some islands (Raitt and Perkins, 1954). The high permeability is due to subaerial diagenesis and the karstification of limestone during low sea-level stands. The upper layer is significantly less permeable and consists of unconsolidated fine-grained Holocene carbonate sediments that are typically <30 m thick, with larger, leeward islands accumulating the thickest deposits. An unconformity delineates the Holocene and Pleistocene stratigraphic layers, which is termed the “Thurber Discontinuity” and represents a hiatus in carbonate deposition and subsequent diagenesis between approximately 125 ka and 8 ka during low glacio-eustatic sea-levels (Thurber et al., 1965). Studies on Enewetak Atoll (Wardlaw and Quinn, 1991) and Deke Atoll (Ayers and Vacher, 1986) have used drilling cores and seismic interpretation to identify the Thurber Discontinuity.

Drilling records from Roi-Namur indicate that consolidated limestone, presumed to be the lower Pleistocene limestone, is located between 7 and 14 m below land surface (bls) (Gingerich, 1992) (Figure 2). The depth of the Thurber Discontinuity and bottom layer is consistent with observations from nearby atolls of Enewetak, Bikini, and Majuro (Anthony et al., 1989; Buddemeier and Oberdorfer, 1997; Emery et al., 1954). Using the groundwater model SUTRA (Voss, 1984), the estimated hydraulic conductivity (K) of the Holocene sediments is 10-50 m day⁻¹ (Underwood et al., 1992) and the Pleistocene limestone is 1,000 m day⁻¹ (Oberdorfer et al., 1990) (Figure 2).

In general, the FWL on atoll islands is a function of average annual rainfall, recharge, K of the unconsolidated Holocene deposits, island width, depth to the Thurber Discontinuity, and in some cases the reef flat plate, which is a relatively thin and shallow, lagoon-ward sloping limestone layer on the ocean side (Bailey et al., 2010). Other factors such as the position of the island relative to wind direction,

cross-island grain size differences, and tidal lag also affect the FWL dynamics (Hunt and Peterson, 1980). Larger islands tend to form on the leeward side of atolls and have thicker Holocene deposits and finer sediments because they are not exposed to the large swells and higher energy environment of windward islands (Spennemann, 2006). Numerical model simulations have indicated that the relatively less permeable Holocene deposits on the leeward islands results in K values of about 50 m day⁻¹, while the Holocene sediments on windward islands result in K values as high as 400 m day⁻¹ (Bailey et al., 2009). The relatively lower K of the leeward islands results in less tidal propagation and mixing of seawater with the FWL. Thus, the lower-energy environment on leeward islands tends to promote a thicker FWL than windward islands. This is evident on Kwajalein Atoll and the thinner FWL on the smaller windward island of Roi-Namur (Gingerich, 1996) as compared to the thicker FWL on the larger, southern leeward Kwajalein Island (Hunt and Peterson, 1980).

In addition to difference in hydrogeology between leeward and windward islands, the cross-island lithology of an atoll island can contribute to differences in FWL thickness. The lagoon side of a typical atoll island is a relatively low-energy depositional environment protected from big ocean waves where fine Holocene sands are deposited (Figure 2). In contrast, the ocean facing section of an atoll island is a higher-energy depositional environment where coral fragments and pebble to cobble size sediments have been deposited in the Holocene. In general, sediment size in the unconsolidated Holocene deposits decrease in size from ocean to lagoon, as observed by Anthony (1989). It has been demonstrated on Kwajalein Island that variations in cross-island lithology affect the rate and extent of tidal propagation, thus affecting the FWL geometry (Hunt and Peterson, 1980). The higher permeability and hydraulic conductivity found on the ocean side promotes faster tidal propagation and increased mixing, and explains the asymmetrical shape of the FWL on atoll islands (Figure 2). A relatively thick saline transition zone (sometimes thicker than the FWL) can form on the ocean side because of dispersive tidal mixing (Figure 2). For these reasons, atoll islands generally have a thicker FWL on the lagoon side compared to the ocean side (Figure 2).

2.3. Field Methods and Groundwater Sampling

Between April 30 and May 7, 2015, groundwater samples were collected from a total of 33 existing U.S. Geological Survey (USGS) monitoring wells from nine separate well clusters located on Roi-Namur (Figure 1 and Supplementary Material, Table S1). Not all of the original USGS monitoring wells on Roi-Namur (Gingerich, 1996, 1992) were sampled because of time and resource constraints. Therefore, well selection was prioritized so that lagoon and ocean side wells on both lobes of the island are represented and several cross-island transects (Figure 1) could be compared.

The nine well clusters include six on Roi and three on Namur (Figure 1); each cluster represents a single location where a group of wells were drilled to discrete depths so that groundwater samples could be obtained along the depth profile of the vertical salinity gradient in the FWL and transition zone to the deeper saline groundwater. A total of 21 discrete well depths on Roi and 12 discrete well depths on Namur were sampled. All wells are identified with the letter 'R' followed by a number that denotes the well cluster and approximate depth below mean sea level of the screen mid-point for each well within each cluster (e.g. R1-1, R1-7, etc.) (Table S1), which is consistent with the original USGS well identification (Gingerich, 1996, 1992). The monitoring wells are constructed of 5.1-cm-diameter poly-vinyl-chloride (PVC) flush-threaded pipe. A 0.61 m section of each pipe is screened 0.15-m from the bottom to allow groundwater to flow into the well only from the desired depths.

All groundwater wells were sampled using protocols of the USGS National Field Manual for the collection of water-quality data (U.S. Geological Survey, variously dated). Using an electrical submersible pump, three wet-casing volumes were purged prior to sample collection. A peristaltic pump and nylon tubing was used to lift groundwater to the surface, where it was run through a 0.45 μm filter to remove particulates before being gravity drained into sample bottles. Prior to sample collection at each well, the inside of the nylon tubing was rinsed with well water equivalent to at least two sample volumes to ensure only representative samples from that location and depth were being collected. Chemical preservatives were not used for any collected samples. Sampling procedures were identical for all sample

constituents, but sample volume varied from 20 ml vials to 1.0 L bottles depending on the constituent of concern. Samples were placed in a field cooler and transported to a refrigerator for preservation and storage.

A calibrated YSI 556 multi-probe handheld multi-parameter field meter was used to measure field water-quality parameters, including pH, temperature, oxidation-reduction potential (ORP), dissolved oxygen (DO), electrical conductivity, and salinity. Total alkalinity was determined for each sample at the end of each field day using the inflection point method by performing multipoint titration with 1.6M H₂SO₄.

2.4. Laboratory Methods

Groundwater samples were analyzed at various laboratories. Major ions and trace elements (except for chloride, bromide, fluoride, and sulfate) were analyzed at the University of Southern Mississippi Center for Trace Analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The chloride, bromide, fluoride, and sulfate were analyzed using an ion chromatograph (IC), and dissolved inorganic carbon (DIC) and $\delta^{13}\text{C}$ -DIC were analyzed via continuous flow cavity ring-down spectroscopy following wet chemical oxidation at the USGS in Menlo Park, CA. The nutrient analysis was performed at Woods Hole Oceanographic Institution (WHOI), in Woods Hole, MA using a SEAL AA3 four-channel segmented flow analyzer. The dissolved organic carbon and $\delta^{13}\text{C}$ -DOC were analyzed using high temperature catalytic con-version DOC analyzer, a GD-100 CO₂ trap and a continuous flow IRMS at WHOI's National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS).

2.5. Statistical Analysis

To evaluate if water-quality parameters and geochemical processes on Roi and Namur are statistically different at the 95% confidence level, median concentrations of selected constituents are compared using a Wilcoxon rank-sum test. All statistical analyses were performed using the software package JMP version 12.1.0 (SAS

Institute, Cary, NC). We used a Wilcoxon rank-sum test on the distribution of residuals to evaluate whether the median concentrations on Roi and Namur differ:

$$H_0: C_r = C_n; \quad H_a: C_r \neq C_n; \quad \alpha = 0.05 \quad \text{equation 1}$$

where C_r is the median concentration on Roi and C_n is the median concentration on Namur, α is the significance level required to reject the null hypothesis (H_0), and H_a is the alternative hypothesis. The constituents are generally selected based on the mechanistic hypothesis that the decay of vegetation in the soil and root zone will lead to more microbial oxidation and increased carbonate dissolution through the following reactions:

equation 2

equation 3

The differences in vegetation cover between Roi and Namur may alter the geochemical reactions in equations 2 and 3, which would be observed in the geochemical signal of each lobe of Roi-Namur. The specific mechanisms and subsequent geochemical processes tested in the statistical analyses are described next.

A geochemical study on Kwajalein Island by Tribble (1997) showed that microbial oxidation in the root zone plays an important role in carbonate dissolution on atoll islands. Increasing vegetative cover would likely result in greater organic matter input to the soil, and thereby produce greater inorganic carbon through microbial oxidation (equation 2). We also use results of the Wilcoxon rank-sum test to evaluate if the removal of natural vegetation on Roi has significantly reduced CO_2 flux in the groundwater and overlying vadose zone, thus reducing dissolution of the carbonate rocks (equation 3).

The inorganic carbon formed by these reactions can either be from microbial oxidation of organic matter (equation 2) or carbonate mineral dissolution (equation 3). To distinguish whether microbial oxidation or carbonate dissolution is a greater source of dissolved inorganic carbon (DIC) on each lobe, $^{13}\text{C}/^{12}\text{C}$ for DIC ($\delta^{13}\text{C}\text{-DIC}$) was

evaluated. Plants preferentially take up the lighter stable isotope of carbon-12 for photosynthesis and are more depleted in the heavier carbon-13 isotope. Conversely, carbonate minerals are less depleted in carbon-13 and dissolution reactions produce inorganic carbon with an isotopic signature reflective of the Vienna Pee Dee Belemnite (VPDB) reference standard. Dissolved organic carbon (DOC) in groundwater results from microbial breakdown of leaf litter and other decaying organic matter or from hydrocarbon contamination. Therefore, we expect to find that groundwater on Namur has higher concentrations of DOC due to the larger input of organic litter in the soil zone as compared to Roi.

Carbonate dissolution-precipitation reactions can affect calcium (Ca^{2+}), magnesium (Mg^{2+}), and bicarbonate (HCO_3^-) ion concentrations in groundwater of carbonate aquifers (Plummer et al., 1976). Therefore, we also tested for statistically significant difference in Ca^{2+} , Mg^{2+} , and HCO_3^- concentration in groundwater on Roi as compared to Namur. If the mechanism for dissolution is related to DIC input, we expect to observe higher Ca^{2+} , Mg^{2+} , and HCO_3^- concentrations in groundwater related to the dissolution of carbonate minerals (equation 3).

Nutrient cycling also plays an important role in geochemical processes. Decaying organic matter in the soil is a source of macronutrients, such as nitrogen (N) and sulfur (S). Biological decomposition of organic matter in the soil produces the mineralized form of these nutrients, which are subsequently taken up by plants and/or leached into the groundwater. Under anaerobic conditions, denitrification and sulfate reduction may reduce N and S to their gaseous form (i.e. NO_3^- to N_2 and SO_4^{2-} to H_2S) where they become unavailable for plant uptake and are released to the atmosphere (Korom, 1992). More vegetative input and microbial oxidation may lead to additional leaching of nutrients in the groundwater, thus we tested for statistically significant difference in nitrate (NO_3^-), ammonium (NH_4^+), total dissolved nitrogen (TDN), and sulfur (S) concentrations in groundwater on Roi as compared to Namur. Similarly, decomposition of organic matter and oxidation reactions influences the pH and oxidation-reduction potential (ORP) of the aqueous system, and thus we also tested for statistically significant differences in pH and ORP on Roi and Namur.

Prior to geochemical reactions with carbonate rocks, groundwater chemistry is a function of the percent seawater that is mixed with recharge from precipitation or other freshwater sources. Therefore, the groundwater sample concentrations must be normalized by seawater to account for mixing before they can be compared. The mixing of recharge water with seawater in the transition zone results in groundwater chemistry that is a result of conservative and non-conservative reactions. Chloride (Cl^-) does not react readily compared to other major ions, and variations in concentrations of Cl^- in natural waters is primarily due to physical processes (Hem, 1985). Thus, the percent seawater that is mixed with recharge in each groundwater sample can be determined using Cl^- concentration and the assumption that all the Cl^- in the groundwater sample originates from seawater. Normalizing the groundwater samples is done by plotting constituent concentrations with respect to percent seawater for both lobes and calculating a least squares regression line from the combined data set. The residuals for each lobe are then calculated from the regression line and the differences in residuals become statistically comparable.

2.6. Geochemical Modeling

Solution concentrations from each groundwater sample were input into the geochemical modeling program PHREEQC (Parkhurst and Appelo, 2013) to obtain charge balance, saturation indices (SI), and pCO_2 values. The WATEQ4 reference thermodynamic database (Ball and Nordstrom, 1991) was used for all PHREEQC simulations. The end-member chemistry used in the geochemical modeling was derived from proportions of seawater and rainwater based on the conservative Cl^- concentrations in each sample. The difference in chemistry between rain and artificial recharge from the MAR system is assumed to be negligible. The geochemical modeling was also used to identify reactions such as dissolution of the carbonate minerals in the groundwater that deviate from conservative freshwater-seawater mixing processes. In the vadose zone and aquifer of carbonate islands, groundwater ion concentrations are affected by the dissolution of calcite and aragonite minerals, which is controlled predominantly by the pCO_2 , pH, and alkalinity. Differences between observed groundwater sample concentrations and theoretical speciation

values may indicate a system that has additional chemical inputs from diagenesis or non-equilibrium dissolution-precipitation reactions.

Geochemical modeling was also used to estimate dissolution rates of carbonate minerals in the FWL of Roi and Namur, and evaluate the effects of recharge, inorganic carbon input, and residence times on the rates of the carbonate-diagenetic reactions. Aragonite and magnesian-calcite are precipitated on atoll reefs and have been shown to be more soluble than pure calcite (Morse and Mackenzie, 1990). Based on core samples and thin sections on Majuro Atoll, the predominant dissolution of aragonite skeletal material followed by minor amounts of calcite and low-magnesian-calcite, indicates a system favoring aragonite dissolution (Anthony et al., 1989). Water flux through the subsurface dissolves source rock, increases secondary porosity, and ultimately results in a net flux of sediment out of the system. Studies have measured dissolution for small carbonate islands and found that water in the FWL and transition zone increases permeability because of diagenetic reactions (Anthony et al., 1989; Plummer et al., 1976). The important driver in this reaction is CO_2 input, which in solution, dissolves carbonate rock (equation 3).

To estimate the dissolution rates of carbonate minerals in the FWL, source rock contributions from carbonate dissolution were determined by measuring excess Ca^{2+} , Mg^{2+} , and HCO_3^- in the aquifer system. Given that the only source of these ions is from dissolution of carbonate minerals or seawater, the concentrations in solution that are outside what is expected from conservative rainwater-seawater mixing represent the dissolution of carbonate rock. Therefore, the molar ratios of $\text{Ca}^{2+}:\text{Cl}^-$, $\text{Mg}^{2+}:\text{Cl}^-$, and $\text{HCO}_3^-:\text{Cl}^-$ in local seawater were used to determine the theoretical concentration in each groundwater sample under conservative reactions, and the sum of the excess concentrations of Ca^{2+} , Mg^{2+} , and HCO_3^- represent the mass contribution from dissolution of source rock. Only one sample on Namur (R6-1, Table S1) was within the FWL (<1.3% seawater), so only the excess concentrations for this well were used to calculate dissolution rates and increases in secondary porosity on Namur. Roi has a larger FWL and five samples were collected (R1-1, R2-1, R3-1, R4-1, and R10-2) that represent FWL concentrations. The average of excess concentrations from the five samples was used to calculate dissolution rate and increases in secondary porosity.

Estimated recharge rates are also needed to estimate the dissolution rates on Roi and Namur. Using numerical simulations, Gingerich (1992) estimated 84% less recharge on Namur due to the greater vegetative cover and ET rates compared to Roi. However, other empirical studies have reported less of an effect of ET on recharge to atoll aquifers. Buddemeier and Oberdorfer (1997) estimated that given 1,878 mm of average annual rainfall, recharge will be 46% and 25% of rainfall for an atoll with 0% and 80% tree cover, respectively. Because of the similar average annual rainfall on Roi-Namur (1,927 mm yr⁻¹, 1980-1991 (Gingerich, 1992)) as the Buddemeier and Oberdorfer (1997) study, we used the more conservative recharge estimates from the empirical study to calculate the dissolution rates.

The annual volume of rainwater from the concrete-lined catchment basin that artificially recharges Roi has not been reported. Therefore, the calculated net recharge on Roi that we use here does not account for the percentage of the approximately 30,000 m³ of average annual rainwater that is collected in the concrete-lined catchment basin and artificially recharged (Gingerich, 1992). However, the absolute contribution of artificial recharge on the net recharge is minimal because the 30,000 m³ in the catchment basin represents <10% of the estimated annual recharge volume on Roi (Gingerich, 1992). Although there is typically a net withdraw of water from the FWL each year, some percentage of the water collected in the catchment during the wettest months is used for artificial recharge and increases the volume of water that percolates through the vadose zone overlying the FWL. Therefore, the freshwater flushing rate is somewhat underestimated in this analysis.

Solution parameters are used to calculate SI with respect to aragonite using PHREEQC, to determine the favorable thermodynamic direction of the dissolution-precipitation reaction:

The primary driver of this dissolution reaction (equation 4) is the availability of CO₂ (equations 2 and 3), which produces weak acids:

equation 6

equation 7

Therefore, the pCO_2 in the infiltration and recharge is an important factor in the subsequent geochemical processes of the aqueous and solid carbonate system. Rainwater in equilibrium with the atmosphere will have a pCO_2 of approximately $10^{-3.4}$ or 0.04% Vol CO_2 (400 ppm). In groundwater systems, pCO_2 values of $10^{-2.5}$ to $10^{-1.0}$ have been observed (Hem, 1985), which are one to three orders of magnitude greater than rain. Plummer and others (1976) found similarly elevated pCO_2 in soil pore water samples. The elevated pCO_2 in soil pore water is driven by plant decay and microbial respiration in the top soil, which is especially prevalent in tropical climates with dense vegetation. Studies have shown there is a moderate trend of increased dissolution of carbonate minerals with increasing pCO_2 (Anthony et al., 1989; Plummer et al., 1976). Respiration and aerobic decay has been shown to increase pCO_2 (equation 2), which in turn reduces the pH (equations 5-7) and reduces saturation and carbonate concentrations of water (Drever, 1988). On Kwajalein Island, Tribble (1997) showed that the predominant reaction in the system was the dissolution of calcium carbonate driven by CO_2 from microbial respiration. If residence time is sufficient during water flux in the vadose zone, carbonate dissolution proceeds and Ca^{2+} , Mg^{2+} , and HCO_3^- is transported to the groundwater where thermodynamically favored reactions continue.

3. Results and Discussion

3.1. Freshwater Lens Asymmetry

Results of the groundwater sampling were used to estimate the shape of the FWL on Roi and Namur (Figure 3). Most atoll islands generally have an asymmetrically shaped FWL, with a relative thicker FWL on the lagoon side and thinner FWL on the ocean side (Ayers and Vacher, 1986; Hunt and Peterson, 1980). The asymmetry of the FWL on atoll islands is generally attributed to greater hydraulic conductivity on the ocean side that increases tidal efficiency and the dispersion of saline waters through

the upper aquifer. As a result, the transition zone is thicker on the ocean side, and the FWL is truncated at shallower depths compared to the lagoon side. However, the shape of the FWL on Roi is not consistent with most atoll islands because a substantially thicker FWL and transition zone is observed on the ocean side (Figure 3a-b). Namur exhibits the more classic asymmetric shape, with a slightly thicker FWL on the lagoon side (Figure 3c). The observation of a relatively thicker FWL on the ocean side of Roi compared to natural atoll aquifers, such as Namur, is likely the result of the influx of additional diffuse recharge from the reduced ET and MAR on Roi, as discussed below.

In general, the FWL thickness and shape is function of recharge, K of the unconsolidated Holocene sediments, and depth to the Thurber Discontinuity (Bailey et al., 2010). For example, Bailey et al. (2008) used numerical models to show that although the FWL thickness increases with increasing recharge rates and the FWL could be truncated if the bottom extends to the depth of the Thurber Discontinuity, the geometry and shape of the FWL did not significantly change. Drilling records on Roi-Namur indicate there is a hard consolidated layer located 7-14 m bIs (Gingerich, 1992), which likely represents the Thurber Discontinuity. However, the FWL on Roi is only 3 m and 5 m thick on the lagoon and ocean side, respectively (Figure 3a-b), and thus is not likely truncated by the Thurber Discontinuity. Although the depth of the Thurber Discontinuity may vary from ocean to lagoon side, it is unlikely to result in a thicker FWL on the ocean side because the geology of most atolls have thicker Holocene deposits on the lower-energy lagoon side, as observed on Enewetak Atoll (Buddemeier, 1981) and Majuro Atoll (Anthony et al., 1989).

Focused recharge from the MAR is a more likely cause of the FWL shape on Roi. If recharge was equally distributed across Roi, the previously discussed hydrogeologic controls on the lagoon side would likely limit seawater mixing, forming a thicker FWL. Groundwater level contours developed by Gingerich (1996) shows that the highest hydraulic head on Roi is located in the eastern part of the lobe approximately half-way between the ocean and lagoon side under the concrete-lined catchment basin (Figure 1). The concrete-lined catchment covers a large area of the eastern section and lagoon side of Roi, and effectively eliminates direct recharge beneath the

catchment. Although recharge is limited, the hydraulic head (Gingerich, 1996) is highest and the FWL is relatively thick beneath the concrete-lined catchment (Figure 3a). This is likely due to the relatively low hydraulic conductivity on the lagoon side that limits tidal mixing and freshwater drainage. The general groundwater flow direction in the FWL on Roi radiates from the highest head near the concrete-lined catchment outward in all directions (Gingerich, 1996). The MAR system on Roi reroutes rain that would normally infiltrate beneath the concrete-catchment and artificially recharges that water on the grassy area adjacent to the runway and near well clusters R1 and R2 (Figure 1). This focused artificial recharge has created the thickest part of the FWL under well cluster R1, even though it is on the ocean side (Figure 3a). The groundwater level contours (Gingerich, 1996) indicates that the artificial recharge adjacent to the runway will flow downgradient towards the ocean side of the island, with the strongest gradients favoring flow towards well clusters R4 and R10 and producing a thick FWL (Figure 3b). The result of the concrete-lined catchment and MAR is that the rainfall that would have been recharged on the lagoon side has been diverted and recharged on the ocean side and in an area that favors groundwater flow towards the ocean, which helps explain the unexpected asymmetry of the FWL. It is likely that without the LULC modifications and MAR on Roi, the FWL geometry would reflect a more typical atoll aquifer, similar to what is observed on Namur.

3.2. Statistical Differences in Groundwater Quality on Roi and Namur

Results of the Wilcoxon rank-sum test indicate that pH, ORP, Ca^{2+} , NH_4^+ , TDN, and $\delta^{13}\text{C}$ -DIC in groundwater of Roi and Namur are statistically different at the significance level of 5% ($\alpha = 0.05$) (Figure 4). Alkalinity, DO, S, HCO_3^- , Mg^{2+} , NO_3^- , DIC, and DOC in groundwater of Roi and Namur are not statistically different at $\alpha = 0.05$. Statistically lower pH values and higher Ca^{2+} concentrations are observed on Namur (Figure 4a,b), indicating relatively more acidic groundwater and greater dissolution of carbonate minerals than on Roi. Groundwater on Namur is depleted in $\delta^{13}\text{C}$ -DIC relative to groundwater on Roi (Figure 4c). Although the DIC concentrations are not statistically different on Roi and Namur, the statistical differences in $\delta^{13}\text{C}$ -DIC

between Roi and Namur indicates that microbial oxidation of organic matter is a more important source of DIC than dissolution reactions on Namur compared to Roi. Considering that Roi and Namur have statistically similar DIC concentrations and that Namur has a higher calculated carbonate dissolution rate in the FWL than Roi, as discussed below, there are likely important processes other than decaying vegetation on Roi that contribute to DIC. Comparison of groundwater quality from the well clusters on Roi (Table S1), reveals that well clusters R3 and R4 have elevated concentrations of DIC (Figure 5a) and corresponding elevated $p\text{CO}_2$ and nutrients (Figure 5b-e), as compared to other clusters. As discussed next, the elevated nutrients are likely an indication of fecal contamination, which could represent an important process on Roi that contributes to DIC.

Given the relatively greater vegetation density on Namur, we expected the organic matter and microbial respiration and consumption of oxygen in the soil would result in more reduced (lower ORP) groundwater on Namur than Roi. However, the results of the statistical tests indicate significantly more reduced groundwater on Roi than Namur (Figure 4d), which may be related to the elevated concentrations of NH_4^+ and other nutrients in groundwater on Roi (Figure 5c-e). Because the landscape on Roi is not fertilized, point-source contamination associated with human activity is the likely source of elevated nutrients in the groundwater on Roi. NH_4^+ can derive from human and animal waste and is often found at elevated concentrations in groundwater near septic systems and leaky sewage pipes. There are three actively used septic tanks and leach fields on Roi-Namur; one is located on the dredge-filled, conjoined section of the island that is adjacent to well cluster R3, and two are located on Namur (Thomas Hutchinson, Roi Operations Manager, 2015, personal communication).

The elevated concentrations of TDN, NO_3^- , and NH_4^+ (Table S1), generally occur in the well clusters R3 on the lagoon side and R4 on the ocean side of Roi (Figure 5). Of the R3 cluster, NO_3^- concentrations are highest in well R3-1, but are not detected at deeper depths where NH_4^+ concentrations are elevated (Figures 5d,e). Similarly at the R4 cluster, the shallow wells at (R4-1, R4-4, R4-7) have the highest NO_3^- concentrations and NH_4^+ increases with depth, but to a lesser extent than the deep

well at R3 (Figure 5e). The observation of increasing NH_4^+ and decreasing NO_3^- with depth likely indicates that dissimilatory nitrate reduction to ammonium (DNRA) may be occurring in the more anoxic conditions in the deeper parts of the aquifer (Korom, 1992). At well cluster R4, the rate of increase in NH_4^+ with depth is less what is observed at R3 (Figures 5e). These differences R3 and R4 can be attributed to the location of R4 further from the leach field and closer to the ocean side of Roi. The closer proximity of R4 to the ocean side will likely result in relatively greater water flux, mixing of freshwater and seawater, and lower residence time of freshwater in the FWL compared to R3, which would have the cumulative effects of increasing NO_3^- transport with depth and limiting DNRA at R4.

3.3. Carbonate Dissolution

The calculated average source rock contributions (SRC) from the FWL and overlying vadose zone (6.10 and 9.81 mmol L⁻¹ for Roi and Namur, respectively) indicate that relatively more dissolution is occurring on Namur than Roi (Table 1a). However, with a larger FWL and overlying vadose zone area (0.46 and 0.14 km² for Roi and Namur) and greater flushing (4.08x10⁸ and 6.74x10⁷ L yr⁻¹ for Roi and Namur), the rate of sediment volume dissolved is 72 m³ yr⁻¹ on Roi compared to 20 m³ yr⁻¹ on Namur (Table 1b). Using the estimated recharge for each lobe (886 and 482 mm yr⁻¹ for Roi and Namur), the area underlain by a FWL, the volume of the FWL, a rock density of 2.5 kg/m³, and assuming an effective porosity of 0.3, the estimated annual increase in porosity is 0.002% on Roi and 0.014% on Namur (Table 1b). Therefore, the annual increase in porosity in the FWL and overlying vadose zone on Namur is approximately seven times greater than Roi, which indicates that the dissolution of carbonate rock (increase in annual porosity) has been reduced on Roi relative to Namur as a result of LULC change (loss of vegetative cover) and use of MAR.

Using a similar method as the FWL calculations, we calculated the average SRC calculations at deeper depths in the aquifer to estimate changes in excess ion concentrations with depth and increasing salinity. The SRC for three different vertical zones and associated seawater percentages were calculated: FWL, ≤1.3%; transition zone, 1.3-50%; and deep aquifer, >50% (Table 3a). As previously discussed, the

greatest average SRC and dissolution rates occur on Namur in the FWL ($\leq 1.3\%$ seawater) and overlying vadose zone sediments. The relatively lower dissolution rates in the FWL and overlying vadose zone on Roi are likely a result of relatively greater flushing due to the relative increase in recharge from the lower ET rates and MAR. On Namur, the transition zone from 1.3-50% has a smaller average SRC (8.00 mmol L^{-1}) than in the FWL. However, the opposite pattern is observed on Roi where the transition zone (8.00 mmol L^{-1}) has greater average SRC than in the FWL (6.10 mmol L^{-1}) (Table 1a). In both lobes, the lowest average SRC occurs in deep aquifer ($>50\%$ seawater), either as a result of tidal flushing and removal of dissolved sediment and/or non-equilibrium reactions as a result of mixing.

Estimating the changes in dissolution rate and porosity in deeper, more saline parts of the aquifer is challenging because dissolved minerals can be transported from shallower depths and precipitate at deeper depths if the saturation conditions change. However, we find that the SI values on Roi and Namur (Table S1) are consistent with the SRC calculations (Table 1). The groundwater at low ($\leq 1.3\%$ seawater) and intermediate (1.3-70% seawater) salinities in Roi are generally undersaturated with respect to aragonite and become supersaturated at the most saline depths ($>70\%$ seawater), with only one exceptions at 40% seawater (Figure 6). This is consistent with the interpretation that undersaturated water is being transported from the FWL on Roi to deeper transition zone where dissolution persists until the most saline depths ($>70\%$ seawater) where the groundwater is supersaturated with respect to aragonite. Most groundwater samples on Namur stay close to saturation ($\text{SI} = 0 \pm 0.2$) throughout the profile (Figure 6). Groundwater reaches equilibrium conditions in the FWL before being transported deeper in the aquifer, and the vertical gradients in the geochemical processes are explored using the results from the geochemical modeling, as discussed in the next section.

3.4. Equilibrium/Non-equilibrium Reactions

The equilibrium/non-equilibrium dissolution-precipitation reactions in carbonate aquifers are described in this study using the SI with respect to aragonite and pCO_2 of groundwater. Changes in the SI of groundwater in carbonate aquifers can

be generally attributed to five possible factors: variability in soil $p\text{CO}_2$, evasion of CO_2 through the soil zone, CO_2 flux in the phreatic zone, dissolution-precipitation non-equilibrium reactions of carbonate minerals, and seawater mixing (Plummer, 1975). To investigate how geochemical processes have been altered on Roi due to the LULC changes and MAR operation, we analyze these five factors and compare to processes on Namur using geochemical modeling.

Soil $p\text{CO}_2$ and CO_2 Evasion: For this study, we assume a closed system exists once water enters the phreatic zone, and CO_2 flux is only caused by dissolution or mixing process that transport groundwater to sea. There is sufficient soil cover to limit CO_2 evasion and there are no direct sources of additional CO_2 input in the groundwater, such as from marshes or other natural sources. These are reasonable assumptions because it was observed on Kwajalein Island that most of the production of CO_2 by microbial oxidation occurs in the vadose zone or near the top of the water table (Tribble, 1997).

Groundwater CO_2 Flux: The only FWL sample collected on Namur is from well R6-1, and it has the greatest log $p\text{CO}_2$ (-1.51) of either lobe (Figure 7). The log $p\text{CO}_2$ of the FWL samples on Roi range from -2.52 to -1.53 (Figure 7 and Table S1). The linear regressions (Figure 7) indicate that there is relatively more CO_2 in the FWL and transition zone of the aquifer on Namur compared to Roi. The $p\text{CO}_2$ values in the most saline groundwater on Namur tend to be higher than Roi (Figure 7). On Roi, the lowest $p\text{CO}_2$ concentrations occur in the most saline groundwater (>80% seawater) (Figure 7) and at the shallowest well at site R3-1 (Figure 5b).

Although the overall DIC concentrations in groundwater on Roi and Namur are not statistically different, there are important differences in the vertical DIC profiles of the two lobes (Figure 8). On Namur, the FWL and shallowest sections of the aquifer have the greatest DIC and concentrations generally decrease with depth (Figure 8c). In contrast on Roi, the FWL and shallowest sections of the aquifer generally have some of the lowest DIC concentrations (5.00-5.99 mg C/L) and concentrations with depth (<6.00) in many parts of the transition zone and deep aquifer (Figure 8ab). These results indicate an apparent shift to greater DIC concentrations deeper in the profile on Roi compared to Namur. The apparent differences in vertical DIC profiles (Figure 8)

may be attributed to the lower residence times and more rapid flushing rates of groundwater on Roi than Namur, which promotes more dissolution deeper in the profile on Roi.

The well cluster specific anomalies in $p\text{CO}_2$ and DIC may be attributed to the previously discussed point-source contamination. The low $p\text{CO}_2$ at well R3-1 may be related to the elevated NO_3^- concentrations from the nearby leach field. It is likely that NO_3^- predominates in the shallowest well where sufficient oxygen is present ($\text{DO} = 3.40 \text{ mg L}^{-1}$, Table S1). The next deepest well (R3-4) has elevated NH_4^+ , a spike in TDN, and an increase in DOC, DIC, and $p\text{CO}_2$ relative to R3-1 (Figure 5), which is attributed to the lower DO concentration and greater mass of nutrients at this lower depth in the aquifer. Wells R4-1, R4-4, and R4-7 also have elevated NO_3^- , TDN, DOC, DIC, and $p\text{CO}_2$, but NH_4^+ concentrations are low or not detected (Figure 5). The source of nutrients at this location is unknown since well R4 is not located near any septic systems, but the lack of NH_4^+ may indicate a non-organic source of N, leaky sewage pipes, or possibly a lack of mineralization due to low residence times as a result of a large recharge flux.

Non-equilibrium Reactions: The FWL on Roi is generally undersaturated with respect to aragonite (Figure 6), which indicates that the residence time of the groundwater in the FWL is shorter than the rate of equilibrium reactions with the carbonate aquifer. These non-equilibrium conditions are likely the result of more recharge and greater water flux through the groundwater system, which allows for discharge of freshwater out of the system at a relatively faster rate. By contrast, the FWL and transition zone on Namur is saturated or supersaturated with respect to aragonite (Figure 6), indicating a longer groundwater residence times on Namur that contributes to more dissolution and the relatively greater average SRC as compared to Roi.

Seawater Mixing: The resulting SI of seawater mixes with carbonate groundwater is a function of the $p\text{CO}_2$ and SI of the original FWL groundwater (Matthews, 1971). For example, observations of mixing supersaturated and/or saturated waters can produce undersaturated water (Thraillkill, 1968; Wigley and Plummer, 1976), and the mixture of two undersaturated waters can produce

supersaturated water (Runnells, 1969). Here, we used PHREEQC to calculate a theoretical mixing line for seawater and carbonate groundwater for Roi and Namur to predict and compare the groundwater chemistry assuming mixing only to the calculated SI values from the field samples (Figure 9). The SI values of field samples from Roi follow the non-linear theoretical mixing line reasonably well (polynomial best fit R^2 value = 0.43) (Figure 9a). Similar to the theoretical mixing line, groundwater on Roi skews towards undersaturated waters at lower seawater percentage and supersaturated water at mixtures containing predominantly seawater (>75%) (Figure. 9a) These results indicate that seawater-groundwater mixing is a dominant geochemical process on Roi. Conversely, SI values of field samples from Namur do not correspond with the theoretical mixing line, but generally remain close to equilibrium ($SI = 0 \pm 0.2$) (Figure 9b). Although seawater-groundwater mixing occurs on Namur, it is apparently less of an important process than on Roi.

The groundwater samples from Roi have a strong inverse relation ($R^2 = 0.714$) between SI and pCO_2 while the samples from Namur have a weaker relation ($R^2 = 0.106$) of decreasing SI with increasing pCO_2 (Figure 10). The supersaturated conditions and low pCO_2 from deep parts of the aquifer on Roi resemble seawater ($SI = 0.68$, $\log pCO_2 = -3.45$) (Figure 10). Conversely, most of the groundwater samples from Namur are relatively close to saturation with respect to aragonite ($SI = 0 \pm 0.2$), and deep wells have relatively higher pCO_2 . These trends in SI and pCO_2 are consistent with a larger flux of water through the aquifer and observations of undersaturated water in the FWL, which indicate shorter residence times of groundwater on Roi. Mixing of seawater and carbonate groundwater is greater on Roi compared to Namur as a result of the increased recharge and flux through the system, and consequently, residence time in the aquifer on Roi is reduced. Relatively lower recharge rates on Namur corresponds to less flushing and slower mixing processes that increases residence time in the FWL, as indicated by waters that are closer to saturation with respect to aragonite (Figure 10). The higher pCO_2 and saturated or slightly undersaturated conditions in deep wells on Namur indicates processes other than mixing are dominant. The apparent CO_2 transport out of the system on Namur is occurring at a significantly slower rate and the kinetics of equilibrium and non-equilibrium

dissolution-precipitation reactions is a more dominant geochemical process than on Roi.

4.0 Summary and conclusions

LULC change and MAR on Roi have altered natural recharge patterns and hydrogeochemical processes in the FWL. Greater tidal efficiency on the ocean side of atoll islands typically limits the FWL volume relative to the lagoon side. However, the influx of water from the relatively lower ET and MAR operations on Roi has increased recharge and the volume and thickness of the FWL on the ocean side. These findings indicate that the ocean side of an atoll aquifer has the capacity for additional storage of fresh groundwater. LULC change and MAR have also resulted in a thicker FWL on the lagoon side, which is naturally more efficient in storing freshwater because it has less tidal mixing and relatively slower drainage compared to the ocean side. On Roi-Namur, the area directly beneath the concrete-lined catchment basin may have the greatest capacity to store fresh groundwater due to its central location, reduced ET, and suitable hydrogeology.

LULC change and MAR have also contributed to statistical differences in pH, ORP, Ca^{2+} , NH_4^+ , TDN, and $\delta^{13}\text{C}$ -DIC and related hydrogeochemical processes in groundwater of Roi and Namur. Depleted $\delta^{13}\text{C}$ -DIC, lower pH, and higher Ca^{2+} indicate decay of vegetation and increased microbial respiration is responsible for the higher dissolution rate on Namur compared to Roi. The annual increase in porosity in the FWL and overlying vadose zone is 0.002% on Roi and 0.014% on Namur. The greater dissolution of aragonite and magnesian-calcite should theoretically produce more Mg^{2+} and inorganic carbon species, and consequently differences in alkalinity and HCO_3^- . However, statistically significant differences were not observed for these parameters. These unexpected findings are likely related to contamination from human activities on the island, chemically altered recharge water from the MAR system, and increased groundwater flux and reduced residence time. Observations of individual well concentrations provide more insight into the responsible geochemical processes. High DIC concentrations at wells R3 and R4 correlate with elevated pCO_2 and nutrient concentrations. Therefore, changes in groundwater-quality parameters due to LULC

change can be masked by geochemical processes related to contamination from human activity.

There is considerable evidence that residence time is reduced on Roi due to the large influx of water and strong flow gradient toward the more permeable ocean side. Dissolution rates are higher in the FWL on Namur and the water is saturated with respect to aragonite. In contrast, most shallow wells on Roi have groundwater that is undersaturated with respect to aragonite, which indicates that the residence time is slow relative to the reaction rate for carbonate dissolution. Undersaturated waters are transported and persist deeper in Roi compared to Namur, and SRC calculations indicate some dissolution has been shifted to the intermediate transition zone. In the deepest wells on Roi, the SI values indicate supersaturation with respect to aragonite and have other geochemical similarities to seawater. These observations and low $p\text{CO}_2$ at deeper depths support a mixing-dominated signal in Roi groundwater. In contrast, longer residence times on Namur allow equilibrium reactions to take place over a longer period time, while less mixing reduces CO_2 transport out of the system. This interpretation is further supported by higher $p\text{CO}_2$ in general and groundwater on Namur that is close to saturation with respect to aragonite at most depths.

The reduction in natural vegetation and the implementation of an MAR system on Roi has increased potable groundwater supply in the FWL. The LULC change has also altered natural geochemical reactions and reduced dissolution rates in the FWL without detrimental effects to the overall groundwater quality. Aside from seawater intrusion of the FWL, contamination from human activities poses the greatest threat to groundwater quality, but this can be mitigated by a groundwater management plan that emphasizes oversight of this limited and vulnerable resource. Findings from Roi-Namur Island support selective LULC change and MAR as a promising management approach for communities on other low-lying atoll islands to increase the resilience of their groundwater supplies and help them adapt to future climate change related stresses.

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Table 1. (a) Calculated source rock contribution (SRC) on Roi and Namur for the freshwater lens (FWL) ($\leq 1.3\%$ seawater), transition zone ($1.3\text{-}50\%$ seawater), and deep aquifer ($>50\%$ seawater); and (b) the calculated dissolution rates for the FWL ($\leq 1.3\%$ seawater) and overlying sediments on Roi and Namur.

(a) Calculated Source Rock Contribution (SRC)				
	Ca ²⁺ (mmol L ⁻¹)	Mg ²⁺ (mmol L ⁻¹)	HCO ₃ ⁻ (mmol L ⁻¹)	Average SRC (mmol L ⁻¹)
$\leq 1.3\%$ seawater				
Roi	1.63	0.80	3.68	6.10
Namur	2.28	1.16	6.37	9.81
$1.3\text{-}50\%$ seawater				
Roi	1.91	1.21	4.89	8.00
Namur	2.29	0.59	5.18	8.06
$>50\%$ seawater				
Roi	1.05	0.99	2.16	4.21

Namur	1.13	0.80	1.89	3.82
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(b) Calculated Dissolution Rates		
Parameters	Roi	Namur
rainfall (mm yr ⁻¹)	1,927	1,927
recharge (mm yr ⁻¹)	886	482
area underlain by FWL (km ²)	0.46	0.14
flushing (L yr ⁻¹)	4.08E+08	6.74E+07
source rock contribution (kg L ⁻¹)	3.09E-04	5.08E-04
source rock flushed (kg yr ⁻¹)	1.26E+05	3.43E+04
volume dissolved (m ³ yr ⁻¹)	72	20
annual increase in porosity (%)	0.002	0.014

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Figure 1. Roi-Namur Island is located on the northern most point of Kwajalein Atoll, Republic of the Marshall Islands. Location of the well clusters, transects, and horizontal lens well on Roi-Namur Island are shown.

Figure 2. Generalized hydrogeology and tidal mixing conceptual model of a typical atoll aquifer. The hydraulic conductivity (K) values and approximate depth of the Thurber Discontinuity have been reported previously for Roi-Namur Island (Oberdorfer et al., 1990; Gingerich, 1992; Underwood et al., 1992).

Figure 3. Salinity profiles for cross-sections (a) A-A' and (b) B-B' on Roi and (c) C-C' on Namur.

Figure 4. Distribution of residuals of water quality constituents (a–f: pH, Ca^{2+} , $\delta^{13}\text{C-DIC}$, ORP, TDN, NH_4^+) in groundwater of Roi and Namur that are significantly different at the significance level of 5% (p-values from the Wilcoxon-rank sum test are shown). Residuals are calculated from a least squares regression line of the combined data from Roi and Namur.

Figure 5. Vertical profiles of (a) DIC, (b) pCO₂, (c) TDN, (d) NO₃⁻, and (e) NH₄⁺ from well clusters R3 (white circle) and R4 (black circle) on Roi plotted as function of percent seawater (%). The R3 wells include R3-1, R3-4, R3-7, R3-11, and R3-16; and the R4 wells include R4-1, R4-4, R4-7, R4-11, and R4-16 (Table 1).

Figure 6. Saturation indices with respect to aragonite plotted as a function of percent seawater for groundwater samples from Roi and Namur. Linear regressions and corresponding r-square values are shown for Roi (solid line) and Namur (dashed line). The seawater sample is shown for comparison.

Figure 7. pCO_2 plotted as a function of percent seawater for groundwater samples from Roi and Namur. Linear regressions and corresponding r-square values are shown for Roi (solid line) and Namur (dashed line). The seawater sample is shown for comparison.

Figure 8. Dissolved inorganic carbon (DIC) profiles interpolated from groundwater samples along cross-sections (a) A–A' and (b) B–B' on Roi and (c) C–C' on Namur.

Figure 9. Saturation indices with respect to aragonite plotted as a function of percent seawater for groundwater samples from (a) Roi and (b) Namur compared to the theoretical mixing model (solid line) for groundwater saturated with carbonate and seawater. Polynomial regression (dotted line) and corresponding r-square values are shown.

Figure 10. Saturation indices with respect to aragonite plotted as a function of pCO₂ for groundwater samples from Roi and Namur. Linear regressions and corresponding r-square values are shown for Roi (solid line) and Namur (dashed line). The seawater sample is shown for comparison.