NUTRIENT AND PESTICIDE TRANSPORT AND FLUXES IN A SMALL ISLAND WATERSHED

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ABSTRACT

Water quality issues are prevalent in many populated South Pacific island nations and territories. It is increasingly recognized that groundwater plays an important role in pollutant transport. Specifically, submarine groundwater discharge (SGD), the subsurface flow of freshwater across the land-ocean interface, is a major source of contaminants in many coastal ecosystems. This study explores the distribution and transport of nutrients and selected pesticides in the Faga`alu aquifer, on the island of Tutuila in American Samoa, which has been deemed a federally designated priority watershed by the U.S. Coral Reef Task Force. We seek to demonstrate the importance of groundwater relative to the total water and contaminant budget in a small island watershed. Field measurements were taken in August 2016, including a seepage run of the Faga`alu Stream to determine gaining and losing stretches, to help better understand surface-groundwater interactions in the watershed. Groundwater samples from stream banks, coastal springs, and a well were analyzed for pesticide and nutrient concentrations to assess their spatial distribution. Pesticides tested include glyphosate (GLY), DDT, imidacloprid, and azoxystrobin, while nutrients include total dissolved nitrogen (TDN), dissolved inorganic nitrogen (DIN), phosphate (PO_4), and silicate (SiO_4). Hydrogeological flow and transport models of the aquifer were built to simulate groundwater flow and to provide estimates of contaminant fluxes from groundwater-derived stream baseflow and SGD to Faga`alu Bay. GLY and DIN were specifically used in the contaminant transport model. Scenarios were run to determine the relative contribution of each land-use zone (agriculture, urban) or point-source (cesspool, piggery) to total groundwater pesticide and nutrient fluxes. Pesticides were found in 90% of tested groundwater samples, specifically glyphosate and DDT, with GLY distribution following land-use patterns and DDT not showing any obvious distribution trends. The flow model estimated that stream baseflow in the upper reach of the stream delivers 63% of its flow, and the lower reach contributes 37%. Of the total SGD entering Faga`alu Bay, 69% was found to be entering via the central bay near the stream mouth, while the northern and southern coastlines contributed 18% and 13%, respectively. In total, SGD provided 41% and stream baseflow 59% of the total water budget flow into the bay. Pesticide and nutrients fluxes were then modeled to illustrate their transport in the aquifer via groundwater pathways. Fluxes of GLY and DIN into the bay were heavily correlated to hydrology and land-use. The transport model predicted that domestic small-scale applications contribute more GLY than agricultural plots to the nearby stream, while estimating that on-site disposal systems contribute 90% of total groundwater DIN. Groundwater transport of nutrients and pesticides via stream baseflow and SGD proved to be significant source of pollutant loading into Faga`alu Bay during low flow conditions.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PREFACE

Some of the foundation for this work was performed as part of my undergraduate (B.S.) research project and was included in my senior thesis submitted to the Global Environmental Science (GES) program of SOEST at the University of Hawai‘i at Mānoa in May of 2018. The work that was included in the B.S. thesis includes field measurements of stream discharge, stream and groundwater sample collection, water analysis for radon, and pesticides. The thesis also included an initial hydrological model constructed in MODFLOW. The model was only partially calibrated against a limited number of groundwater level observations available at the time and did not fully capture all aspects of groundwater flow properly, especially stream baseflow. This M.S. Plan B project uses the field observations and laboratory analysis results published in the B.S. thesis, along with more groundwater level and stream baseflow observations to improve the hydrological model (MODFLOW) and to build a transport model (MT3DMS) to help determine source contributions. Additionally, both models are validated against published rates of observed stream baseflow and submarine groundwater discharge in the watershed. Finally, nutrient concentrations not included in the scope of the B.S. project were analyzed, their distributions interpreted, and sources speculated in this M.S. project.

While there are clearly defined and different contributions from the B.S. thesis and M.S. project, the M.S. project builds heavily upon results from the former. Therefore, for a more comprehensive description of the work, this report includes results from both studies.

1. Introduction

There is mounting evidence that populated Pacific islands struggle with water quality problems that affect human as well as ecosystem health (Mosley and Aalbersberg, 2003; Bolabola, 2007; Cawdrey, 2018). Typically, population density is high along coastlines, where centralized sanitary systems serve only a small fraction of population, and decentralized agriculture leaves room for unregulated practices resulting in nutrient, pathogen, and pesticide pollution. While issues related to rising human population have been recognized for decades, such as stream and coastal pollution, erosion, changing reef cover, and ecosystem health decline, the contributions from individual sources and pathways of pollutants are diverse and still, at best, under investigation (Mosley and Aalbersberg, 2003; Craig et al., 2005). For example, in the U.S. territory of American Samoa, anthropogenic contaminants from point and non-point sources such as onsite sewage disposal systems (OSDS), piggeries, and agriculture, have been a widespread problem. Boil water notices have been prevalent since 2009, impacting much of Tutuila, the largest island in the American territory (Tuitele et al., 2014; Shuler et al., 2017). As 90% of the municipal water on the heavily populated island is sourced from groundwater, the concern over polluted drinking water resources has become a serious issue (Shuler et al., 2017). The urgency of the problem is exacerbated by the fact that drinking water quality is not the only concern, but pollution from groundwater propagates to streams and coastal ecosystems as well (Shuler et al., 2019).

Coral reefs support a high amount of biodiversity and, if unaffected by human pollution, they can be quite resilient to natural stresses such as hurricanes and elevated temperatures (Nyström, 2000). However, anthropogenic pollution from the land, along with a multitude of other manmade stresses has been increasingly endangering this ecosystem (Craig et al., 2005). Nutrient loading and contamination from terrestrial sources not only damages the reefs, but also make them more susceptible to diseases and reduces their ability to recover from diseases as well (Bruno et al., 2003). Although surface water discharge collects and distributes large amounts of dissolved and suspended particulate-associated

pollutants to the coastal region (Polidoro et al., 2017), the contributions by submarine groundwater discharge (SGD) on the coastal contaminant budget is becoming more widely accepted as important, if not dominant (Johannes and Hearn, 1985; Dulai et al., 2016). Submarine groundwater discharge refers to the flow of groundwater across the land-ocean interface, which can carry dissolved compounds and often serves as an important pathway of nutrients and contaminants from coastal aquifers into the ocean (Rodellas et al., 2015). Coastal reef habitats in American Samoa are facing increased degradation due to anthropogenic contaminant transport via runoff and SGD, tracing back to sources of human and animal waste, along with agricultural chemicals applied on cultivated and residential properties (Craig et al., 2005; Polidoro et al., 2017).

Nutrients have been a focus of many studies because they are widely known to leach into the water table and undergo groundwater transport (Amato et al., 2016; Shuler et al., 2017; Richardson et al., 2017). Pesticides also commonly leach and undergo transport via groundwater (i.e. Schicho, 1993), although their overall mobility in the aquifer is often contested (Davidson, 1995). In addition to hydrological factors, chemical and physical properties of both nutrients and pesticides, and their rate of application ultimately determine the potential contamination of groundwater supplies as they leach through the vadose zone. Such a potential is driven by a number of factors, such as solubility, soil adsorption, degradation, and volatilization (Chin and Weber, 1988; Davidson, 1995; Gardner, n.d.). Many studies have described pesticide movement in groundwater (Zhang et al., 2009; Rendón-von Osten and Dzul-Caamal, 2017), including presence of the ubiquitous pesticide glyphosate (Magga et al., 2008) but few have documented their transport to the coastal ocean through SGD (but see Gallagher et al., 1996; Almasri, 2008). A study in coastal Virginia by Gallagher et al. (1996) took an integrated approach of nutrients and pesticides (alachlor, atrazine, cyanazine, and metolachlor), and linked them to nearby agricultural plots while documenting their presence in groundwater, but did not explore glyphosate.

Glyphosate (GLY) has become the most heavily used herbicide in the world since its introduction in 1974 by the Monsanto Company (https://monsanto.com/) as a key ingredient in the popular Roundup formula (Benbrook, 2016). Its heavy use in both agricultural plots and roadside-to-backyard domestic

settings makes it an ideal tracer for groundwater mobility, and was thus used to model transport of pesticides. Other pesticides surveyed in this study based on available information regarding current and past pesticide application on island include the insecticide dichlorodiphenyl-trichloroethane (DDT) along with its breakdown product dichlorodiphenyl-dichloroethylene (DDE) (from here on both collectively referred to as "DDT"), the insecticide imidacloprid, and the fungicide azoxystrobin. DDT has not been legally sprayed in American Samoa since 1972, after the U.S. EPA officially banned the compound due to its adverse effects on wildlife and potential threat to human health (Lallanilla, 2019). The insecticide, however, was sprayed heavily across the island in the mid-20th century by airplane with no relation to any specific land-use region and is still persistent thanks to its long residence time in the environment (NPIC & Oregon State University, 1999). Dissolved inorganic nitrogen (DIN) was chosen as the tracer for nutrient fluxes in the transport model, as it is a representative N-species for anthropogenic sources such human and livestock waste to fertilizer application (Waters, 2015; Shuler et al., 2019). Other nutrients assessed for overall flux, but not transport, include phosphate (PO_4^{3-}), nitrate plus nitrite (N+N), ammonia (NH_3), and silicate (SiO_4).

The groundwater transport of the representative pesticide and nutrient, respectively GLY and DIN, were sampled and modeled in this study to investigate pollutant distribution. The goal of the model simulation was to describe the multiple GLY and DIN groundwater pathways and their sources, including OSDS and piggery contamination from individual households as well as urban and agricultural non-point source contamination. Field sampling data is integrated with hydrogeological modeling to characterize groundwater pathways and fluxes of selected pesticides and nutrients in the Faga`alu aquifer on the island of Tutuila, in American Samoa. Modeling utilized the modular 3-dimensional MODFLOW model (Harbaugh et al., 2000) to estimate SGD and baseflow contribution and the multi-species transport model MT3DMS (Zheng and Wang, 1999) to model contaminant transport. This watershed was chosen as an ideal location for groundwater contaminant research as it is a priority remediation watershed according to the U.S. Coral Reef Task Force (Messina and Biggs, 2016). The objectives of this study are:

1. Field-based assessment of the distribution of nutrients and pesticides in the groundwater across the Faga`alu watershed.
2. Field-based assessment of the location and quantity of groundwater contribution to stream baseflow and SGD.
3. Building and calibration of a hydrological model and a contaminant transport model of Faga`alu using field observations and current land-use data.
4. Assessment of the contribution of subsurface water flow (via SGD and stream baseflow) to the overall water and contaminant budget of the stream and coastal area.
5. Evaluation of scenarios of varied land-use and corresponding contribution of nutrients and pesticides to assess potential remediation actions towards developing better land-use management practices.

2. Study Area

2.1 American Samoa

The island of Tutuila (14.3258° S, 170.7325° W), hosts the capital city of Pago Pago, which is the center of government and business for the territory of American Samoa (Crossett et al., 2008). Tutuila lies within the South Pacific Convergence Zone (SPCZ) and experiences seasonal fluctuations in rainfall and cloud cover. Rainfall varies geographically across the island, ranging from 3000 to 6000 mm/yr, heavier in the orographic zone over the interior mountains than in the drier southern and eastern sides of the island (Shuler et al., 2017; Izuka et al., 2007). The wet season takes place between October and May, while the shorter and cooler dry season commonly lasts from June through September (Craig et al., 2005). Geologically, Tutuila rose from the ocean approximately 1.5 Mya as a mid-ocean volcanic hotspot (Craig et al., 2005). The island is comprised of igneous formations with alkalic rocks overlying the dense cores, derived from ancient lava flows and pyroclastic deposits. Alluvial valleys have been carved over time from erosion and are spaced regularly along the island coastline (Izuka et al., 2007).

Agriculture, which represents one of the major nutrient and pesticide sources, is widespread in American Samoa. A significant portion of the food consumed is grown locally in a self-supporting manner, and a quarter of the arable land is currently under cultivation ("Agricultural Land," 2014). In Faga`alu specifically, much of the agriculture is agroforestry, which is based more on tree crops (such as bananas and coconuts) than on cultivated crops (Marshall, 2012). Piggeries are the most prevalent form of livestock raised in American Samoa, as they represent an important part of the Samoan culture. The waste produced at these sites used to be largely uncontrolled, with urine and fecal waste runoff contaminating streams, coastal waters, and drinking water sources, but the American Samoa EPA (Environmental Protection Agency) recently introduced regulations to better manage runoff (Zennaro, 2007). OSDS units, which are the prime method of human wastewater management, used in over 5500 homes in American Samoa, contribute a significant amount of excess nitrogen into the water table (NOAA/EPA, 2003; Shuler et al., 2017). Small island watersheds with high precipitation rates, relatively high population density, and varied urban and agricultural land-use, such as Faga`alu, are of high concern in the transportation of contaminants to the coastal marine ecosystem. As Faga`alu has been documented to have excess nutrient loads in the SGD (Shuler et al., 2019) with the reef health severely in decline (McCormick, 2017; Vargas-Angel and Schumacher, 2018), it was chosen as an ideal location for this study. In addition, this site is typical in that there is very little information available about the hydrogeology of the watershed and there is no ongoing stream and groundwater level monitoring, which makes it extremely difficult to build hydrogeological models.

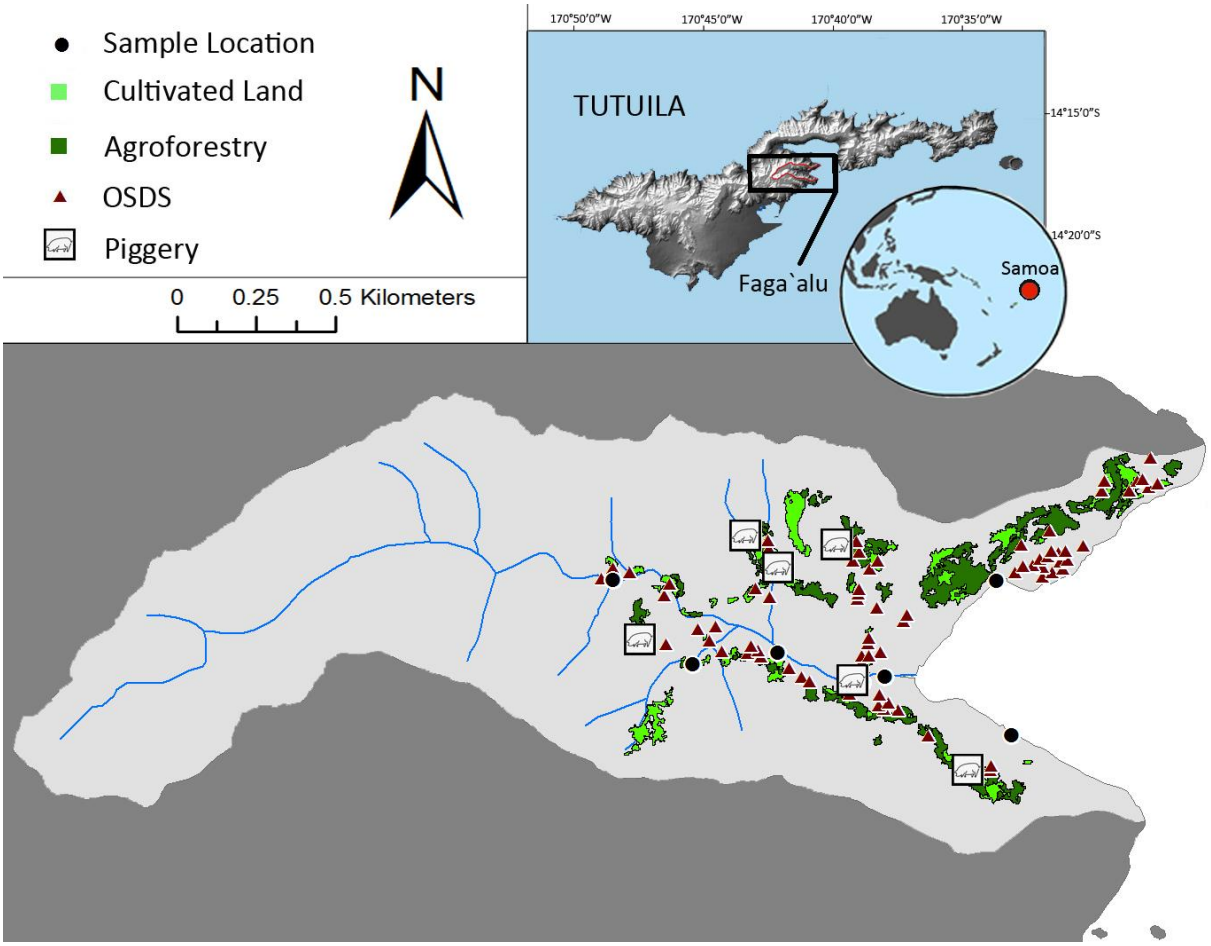

Figure 1: The Faga`alu watershed is located in the central-south sector of Tutuila. The Faga`alu Stream, stream bank pore water and groundwater sample locations, and selected land-use units relevant to this study are depicted.

2.2 Faga`alu Watershed

Faga`alu watershed (**Figure 1**) has been designated by the U.S. Coral Reef Task Force as a federal priority watershed and reef for conservation and remediation. The 1.78 $km^2$ watershed contains the winding Faga`alu Stream (3 km), with headwaters on the slopes of Matafao Mountain running down an alluvial valley, and emptying into Faga`alu Bay of the outer Pago Harbor (Messina and Biggs, 2016). The undisturbed upper watershed is steeply sloped and heavily forested, while the Faga`alu village lies on the lower alluvial plain. This lower portion of the stream is thus heavily disturbed by human activities. The Pago volcanic series contributes dense rocks to the sloped regions of the valley while silty and sandy clay loams comprise the alluvial plain where human development is highest (Messina and Biggs, 2016).

One groundwater well, regulated by the American Samoa Power Authority (ASPA) is used as a municipal water source, and is located about halfway up the developed area, adjacent to a tributary off the main stream. A fringing coral reef exists at the shoreline and extends 50-400 m offshore in Faga'alu Bay. Water quality of the bay is currently of major concern, due to turbid, nutrient-enriched waters from the high-sediment stream runoff and anthropogenic activities of the lower reach of the stream (Messina and Biggs, 2016). The benthic ecosystem in Faga`alu Bay is classified as one of the most impacted on Tutuila (Houk et al., 2005). As a consequence of this concern, the U.S. Coral Reef Task Force has begun a remediation program in the watershed.

3. Methods

3.1 Sample collection and analysis

Groundwater samples were taken from six sites (three from stream bank, two from coastal springs, and one from the well) (**Figure 2**) in August 2016 during the dry season, and were used for calibrating the groundwater flow and transport model. Surface samples were also taken at seven stream sites for analyzing surface contaminant distribution. Surface sites, however, played no part in developing the MODFLOW and MT3DMS models for this study. The collected samples represent a snapshot during baseflow conditions, so should not be taken as long-term representatives. Water from the well site was collected from a wellhead collection port while stream bank groundwater and spring sites were sampled using a Push Point pore water sampler (MHE Products) and peristaltic pump. Nutrient samples were filtered on-site with a 0.45-µm capsule filter and collected in high density polyethylene (HDPE) bottles. Pesticides were collected in 40 mL glass amber vials to prevent photodegradation. Once collected, all samples were chilled on site, and then refrigerated for short-term storage. Nutrients were analyzed within one month of collection, while pesticide storage varied from six to ten months before analysis. A YSI multiparameter sonde (6600 V2-2 model) was used to measure temperature, salinity, and dissolved oxygen in situ for each sample.

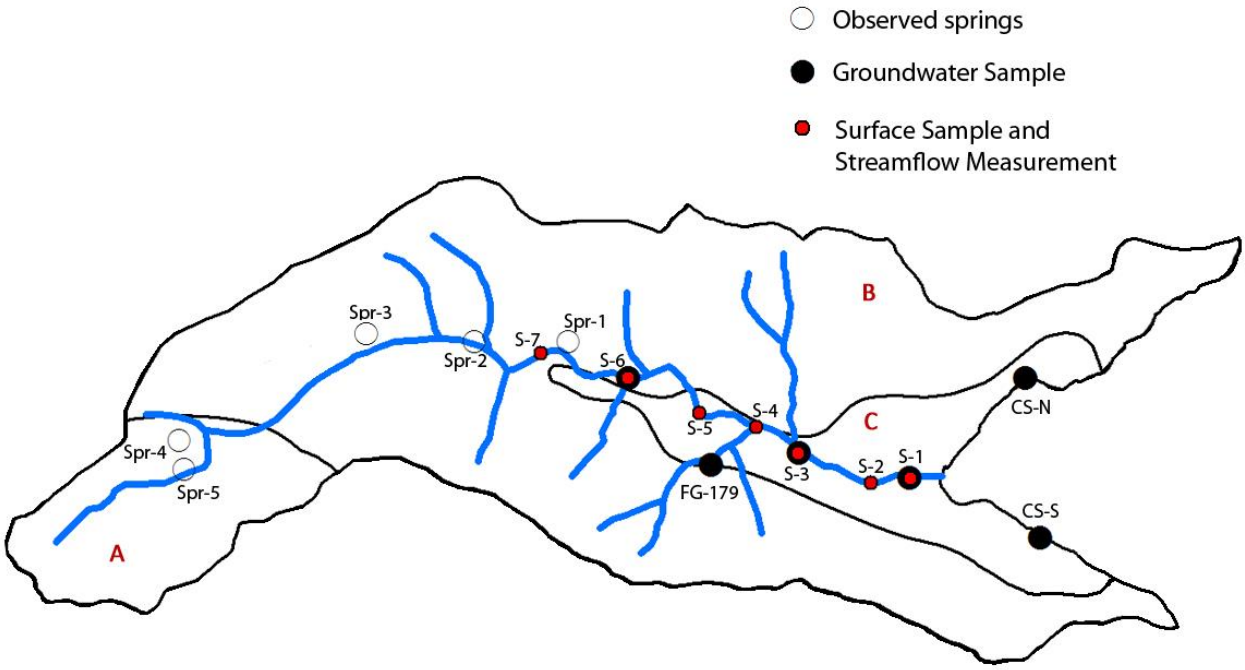

Figure 2: The Faga`alu watershed divided into primary geologic units: (A) Pago Volcanic Series, intra-caldera, trachyte plugs and dikes, (B) Pago Volcanic Series, intra-caldera, (C) Beach sand and silty/clay alluvium ("Geologic Map of A. Samoa" 2008). Groundwater* and surface sampling sites (also as locations of the seepage runs and ^{222}Rn measurements) are marked by appropriate symbols according to the legend, and mountain springs used as observation points for calibration are indicated by hollow circles. (*groundwater samples- FG-179 represents a deep groundwater well sample, the other five represent shallow stream bank pore water samples and coastal springs collected using push point samplers (0.8m below ground surface)).

Seepage runs were performed under baseflow conditions on the same day and same locations as water sample collection (August 10, 2016). Available data from the stream gauge on Faga`alu Stream (monitored by the University of Hawai`i and ASPA) showed that the average annual discharge was 20,135 m^3/d between 2016 and 2018, with 1,737 and 413,024 m^3/d as minimum and maximum, respectively. Average discharge in August over 2016-2018 was 6,116 m^3/d, and the day of sampling had a total flow of 3,914 m^3/d. In addition, baseflow separation confirmed that during our date of sampling, baseflow contribution was 96% of total stream discharge. Streamflow was measured at seven stations

along the main channel between 0 and 1300 m distance from the estuary in the Faga`alu Stream using a SonTek FlowTracker Handheld Acoustic Doppler Velocimeter (**Fig.2**). Samples were also taken to analyze for radon (^{222}Rn) concentration at each site to identify groundwater contribution and hyporheic exchange, thus identifying gaining and losing sections of the stream. Higher stream ^{222}Rn concentrations correlate with groundwater addition to the stream, as in the absence of groundwater inputs, surface waters do not contain detectable amounts of the noble gas and lower pore water concentrations indicate stream water infiltration (Burnett and Dulaiova, 2003; Dulaiova et al., 2006).

Water samples were analyzed for their nutrient concentrations of total dissolved nitrogen (TDN), phosphate (PO_4^{3-}), nitrate plus nitrite (N+N), ammonia (NH_3), and silicate (SiO_4) at the University of Hawai‘i SOEST Laboratory for Analytical Biogeochemistry. The dissolved inorganic nitrogen (DIN) concentrations are the sum of the measured N+N and NH_3 values. Pesticides tested included glyphosate, DDT, imidacloprid, and azoxystrobin. An enzyme linked immunosorbent assay (ELISA) (Abraxis LLC) analysis was performed for the four chosen pesticides. This process varies for each pesticide, but generally involved: 1) filling an antibody-coated 96-well microtiter plate with standards, controls and samples, followed by 2) pipetting of antibody solution, 3) enzyme conjugate, 4) rinsing with buffer solution, 5) adding color solution, 6) then stop solution, and finally 7) analyzing in a spectrophotometric microplate reader (Abraxis PN 475010, Microplate format, 96 well, Model 4303) at a wavelength of 450 nm to obtain concentration values. Incubation periods between each step also varied per test. DDT and azoxystrobin additionally required a 10% sample dilution with methanol before the procedure. Imidacloprid and azoxystrobin were below detection level in all Faga`alu sites, thus were not included in this report. The minimum detection limits for glyphosate, DDT, imidacloprid, and azoxystrobin were 50 ng/L, 370 ng/L, 6 ng/L, and 9 ng/L, respectively (www.abraxiskits.com; “DDE/DDT (Microtiter Plate);” “Glyphosate (Microtiter Plate)”).

3.2 Modeling Approaches

Water flow and contaminant transport were evaluated using the models MODFLOW (Harbaugh et al., 2000) and MT3DMS (Zheng and Wang, 1999), respectively. MODFLOW was used to predict groundwater levels and water fluxes necessary for transport modeling via MT3DMS. The Groundwater Modeling System (GMS) software (https://www.aquaveo.com) served as a graphical interface in building the conceptual model. The MODFLOW model was calibrated by using 1) stream baseflow from seepage runs taken during sample collection and 2) water table head levels obtained from the well and previously identified spring locations (Shuler, personal communication), utilizing elevation of observed mountain springs as water level based on the assumption that water is flowing under atmospheric (zero-gauged) pressure. It is also assumed that the water level reflects a true water table and not that of a perched layer, although information is not presently available to confirm this. A few meters of uncertainty in head may also be present at each site (which is less than 5% total head). Groundwater levels and baseflow fluxes were utilized through both iterative and automatic approaches in calibrating MODFLOW. The iterative approach was used initially to constrain hydraulic conductivity, while the automatic approach via the PEST code (Doherty and Hunt, 2010) was used to refine the conductivity estimates. MT3DMS modeled contaminant transport in the aquifer through various physical and chemical processes, specifically convection, dispersion, adsorption and decay. MT3DMS was calibrated next through an iterative approach to match observed against modeled GLY and DIN concentrations. A flow chart relating the models and their respective inputs and outputs can be found in **Figure A1** of the Appendix.

3.3 Hydrogeological model

The MODFLOW-2000 model, which uses a finite-difference method to simulate three-dimensional groundwater movement through porous media (McDonald and Harbaugh, 1988), was used to build the hydrogeological model of the Faga`alu aquifer. With only six observation points for head level compared to the multiple input parameters, the model was highly parameterized, and thus the regularizing inverse PEST method was used to obtain a fit with minimal error variance. The zonal parameter

estimation method via PEST software ("MODFLOW-PEST Pilot Points," 2016) was used under steady-state conditions for an unconfined aquifer. Conductivity-calibrated zones were set based on known geological units (**Fig.2**). The model was comprised of 4221 active cells (each measured 38 m x 30 m in width and length) across two vertical layers. The top layer covered the vertical zone between mean sea level (MSL) and the terrain elevation above, while the lower layer covered the zone between MSL and 500 m below MSL. The zone below 500 m was not included in the model, assuming that the region below this depth to be considered insignificant to the overall flow (El-Kadi, personal communication).

A recharge coverage was estimated, representing precipitation rates, based on a Soil and Water Assessment Tool (SWAT) model created by O. Leta (2018), with daily recharge ranging from 0.0018 – 0.0035 m/d across the watershed. Other coverages added in the model as GIS shapefiles include a stream, a source/sink (representing the well), the hydraulic conductivity (based off geologic units described by the American Samoa National Park Service), specified head (using the watershed boundary), and water table observation points. The one well in Faga`alu was considered a sink in the model, with a pumping rate of -163.53 m^3/d based on data provided by ASPA of current pumping rates.

The automated PEST software was used to calibrate the model. PEST uses the inverse method to estimate the values of system inputs (hydraulic conductivity in this case) based on outputs (observed head and discharge), as opposed to manually calibrating such parameters to obtain the best match between estimated and observed values (Kennedy, 2012). Manual calibration, however, was initially used to constrain hydraulic conductivity values to reasonable ranges in each zone before utilizing the PEST method to obtain optimal calibration. Head calibration utilized five documented head values from mountain springs (Shuler and ASPA, personal communication) representing elevations where the water table intersects the land surface, and the records of water depth in the one existing well in Faga`alu (FG-179) (**Fig.2**). As there are only a total of six head observations, and these values come from multiple sources, we acknowledge a large uncertainty in the water table used for model calibration. However, calibration also used stream discharge rates, which were obtained from seepage run measurements at seven sites on August 10, 2016. Streambed conductance was assigned to stream arcs, ranging from

values of 0.001 to 100.0 m^2/d/m, while only hydraulic conductivity was calibrated via the automated PEST method. The model was considered successfully calibrated when residuals for head and discharge were minimized to reasonable error less than 10% of maximum observed values.

3.4 Pesticide and nutrient fluxes in baseflow and SGD

To capture baseflow from high level and coastal aquifer portions of the watershed in the model, the stream arcs were divided into upper and lower reaches (boundary set just below S-5 in **Fig.2**). The lower reach extends all the way to the coastline, which includes the estuary at the mouth of the stream. To obtain the respective mass flux rate, pesticide and nutrient concentrations from stream bank groundwater samples were multiplied by the modeled groundwater flow rate from each segment (average of S-1 and S-3 for lower reach, and S-6 for upper reach). In the case of DDT, where below detectable limits were found in groundwater at S-6, an average of groundwater samples in the upper portion of two adjacent watersheds (Vaipito and Vaitele, collected during the same time period) were used to substitute as a representative concentration (Welch, 2018), based on the assumption of uniform widespread spraying (Travis et al., 1946).

SGD fluxes at the land-ocean interface were determined by summing up flow through coastal grid cells in three sections of the model: 1) the northern coastline, 2) the central coastline, and 3) the southern coastline (later shown in **Fig.7**). The only grid cell excluded from the SGD analysis was the cell in the central coastal segment representing the region from the stream mouth to S-1, which was assumed to be part of the stream, including the estuary. Pesticide and nutrient concentrations at the northern and southern coastal springs were used to represent their respective segment of the coast, while the stream bank pore water sample concentrations from stream station S-1 (100 m upstream from the bay) was used for the central coastal segment. To estimate the flux rates, the pollutant concentrations were multiplied by the estimated SGD flow of the corresponding coastal segment. The combined SGD of all three coastal segments thus represents the entire estimated SGD mass flux across the land-ocean interface into Faga`alu Bay.

3.5 Contaminant transport model

An MT3DMS transport model was developed to simulate the transport of contaminants through the aquifer. Processes simulated include advection, dispersion, and simplified chemical reactions. Various coverages, such as calibrated hydraulic conductivity and simulated flow field, were carried over from the MODFLOW model as inputs into the transport model. Other parameters were incorporated in calibrating the transport model, including porosity, longitudinal dispersivity, porosity, dispersivity-anisotropy ratios, and DIN and GLY attenuation coefficients. In the absence of information about the variability of these parameters across the watershed, they were set as equal across all coverages and grid-cells within the model (**Table 1**). A sensitivity analysis test was run to determine which parameters most affected the calibration, as shown in **Figure 3**. Adjustments were made to find the optimal match between the modeled to observed values before the model was considered sufficiently calibrated. Following the sensitivity analysis, longitudinal dispersivity was set to 46 m, the lower bounds estimate made by Glenn et al. (2003) in a study on Maui, Hawai`i, which has similar alluvial type. Porosity was calibrated to 0.2, as porosity can have a wide range (0 – 0.5) of values in volcanic rocks (Earle, 2016). Several studies have addressed typical anisotropic values (Lan et al., 2015; Majumder and Bhattacharjya, 2017; Shuler et al., 2017), that were adapted in this study. Ultimately, each parameter was adjusted to match model outputs to observations (**Tab.1**), and was kept within a range of previously published accepted values. Simulation-time was run to a length of 20,000 days to obtain steady-state conditions at each sample site for each contaminant analyzed.

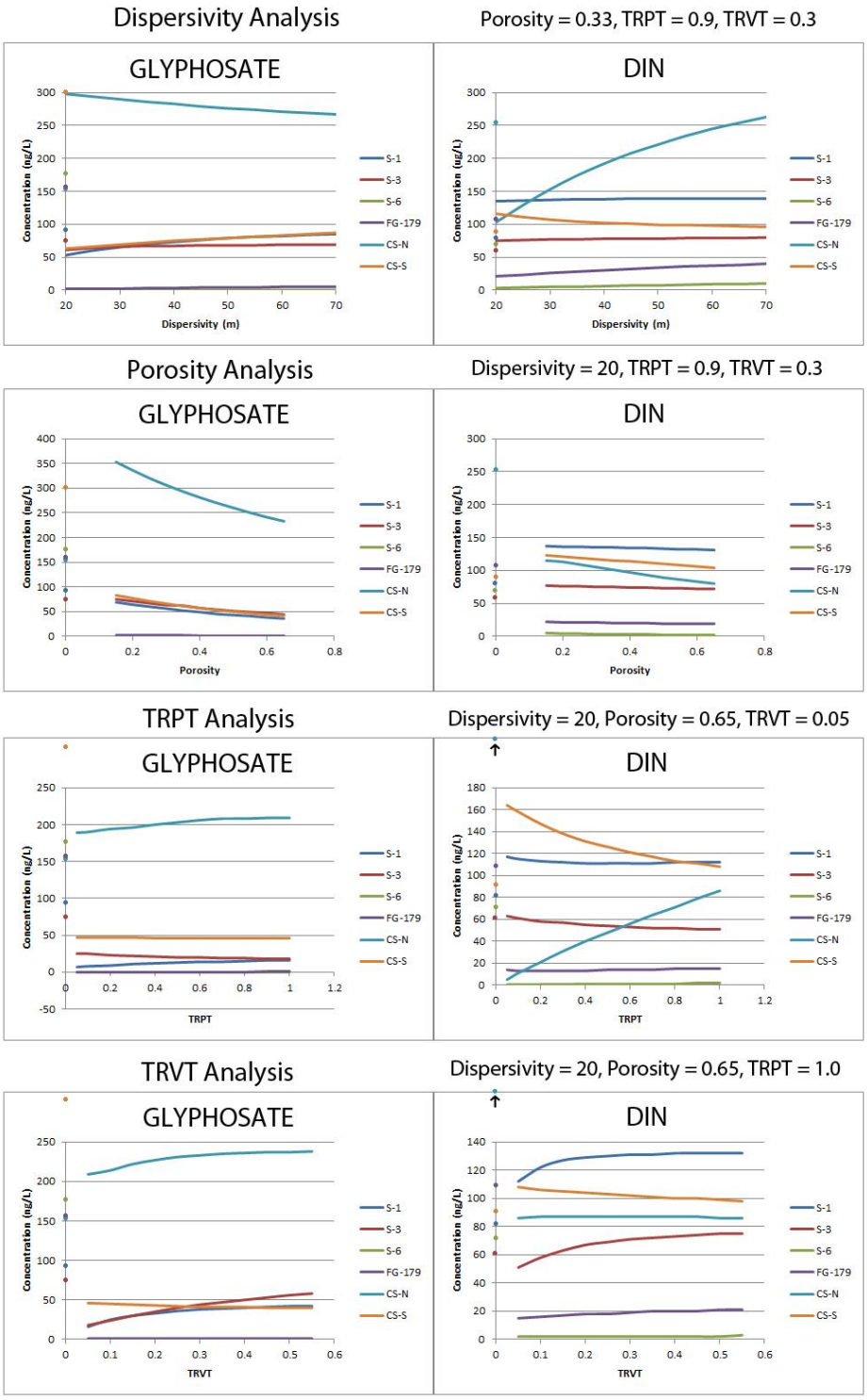

Figure 3: A sensitivity analysis was run for four parameters within the transport model. Observed values are marked with colored points on the y-axis* correlated to the modeled lines representing the analysis. (*Observed values that were beyond the values marked on the axis, were placed approximately where they should be if it were to extend further up for glyphosate (CS-S), and with an arrow, indicating it is too distant to mark for DIN (CS-N).)

Table 1: MT3DMS parameter inputs for this study

Parameter	Value
Longitudinal Dispersivity	46 m*
Porosity	0.2**
Ratio of horizontal transverse dispersivity to longitudinal dispersivity (TRPT)	1.0
Ratio of vertical transverse dispersivity to longitudinal dispersivity (TRVT)	0.05
Simulation-Time Length	20,000 days (54.8 yr)

*lower limit in Glenn et al. (2003), **based on previously published range for volcanic rock (Earle, 2016)

Glyphosate served as the representative pesticide to trace movement through the groundwater. GLY concentrations were added in the model based on annual applied concentration derived from literature values, which were added to the recharge coverage. Initial concentration for agricultural application was 84 mg/L observed in a controlled study by Newton et al. (1984) and attenuation was originally set to 75% removal efficiency, similar to rates found by Imfeld et al. (2012), but later adjusted to 50% (**Table 2**) to obtain better agreement between modeled and observed concentrations. GLY, however, is not only used for agriculture, but also sprayed along roadsides and in residential yards for weed control ("What Is Glyphosate?," n.d.). Half the concentration applied for agricultural plots was applied to urban coverages in the model to represent a small-scale domestic application of this herbicide. Literature-based sorption coefficients (1.64×10^{-5}) as well as decay rate constants (based on half-lives ranging from 91 to 197 days) were used in the model to represent natural degradation of GLY (Henderson et al., 2010; Schuette, 1998). Considering ranges of input of dissolved compounds based on literature values, we ran a scenario where ten times the amount of each contaminant from all sources was present, along with a scenario where one-tenth of each contaminant from all sources was present. These were run in order to assess flux uncertainty in the model.

For N-loading, DIN was estimated for each endmember (OSDS, piggeries, and agriculture) with attenuation rates specific to each source, 45 ± 7% for OSDS-N, 86 ± 4% for piggery-N, and 64 ± 17% for agriculture-N, estimated in a prior study by Shuler et al. (2017). The OSDS and piggery coverage was treated as a source of mass loading, attenuated by 45% and 86% respectively. Fluxes for OSDS point-

sources at 21 g/d/unit and piggery point-sources at 38.1 g/d/unit were also adapted from the nearby Tafuna study by Shuler et al. (2017). As agricultural N is a non-point source, applied periodically, it was treated similarly to the GLY input, and was included as part of the recharge coverage where average concentrations were applied annually. A study of groundwater nutrient concentrations by Schilling and Streeter (2018) were used, where 2.85 kg/ha fertilizer was sprayed and produced concentrations in groundwater of 2.43 mg/L, along with annual agricultural fertilizer application rates for nearby Western Samoa (4.64 kg/ha/yr; World Bank Group 2016). Using this information, the annual fertilizer-derived DIN input was determined to be 3.96 mg/L/yr, and was applied to the polygonal agricultural coverages in the model. These values were attenuated by 64% (Shuler et al., 2017) and served as a representative annual rate for the irrigation plots in Faga`alu. A fixed background level of N was added to all non-agricultural cells of the recharge coverage at 6 µg/L, also identical to the Shuler et al. (2017) to account for natural levels of N in the environment (**Table 2)**. After calibration of the transport model, fluxes for the stream and coastal grid cells were evaluated for DIN and GLY and compared to results from the hydrogeological model and measured values.

Table 2: Summarization of DIN and GLY inputs, and attenuation in the MT3DMS model. Attenuation rate literature ranged are in parentheses, and the rate used in the model outside parentheses.

	Type	N-load (g/d)	Attenuation (%)
DIN	OSDS	21*	(38-52) 45*
	Piggeries	38.1*	(82-90) 86*
		Concentration (mg/L/yr)	**Attenuation**
	Agriculture	3.96**	(47-81) 64*
	Natural	0.006*^	-
GLY	Agriculture	84***	50†
	Urban	42***	50†

^ steady-state concentration, mg/L (not mg/L/yr) *numbers from Shuler et al. (2017) were used
**estimated annual concentration using World Bank data for W. Samoa and Schilling and Streeter (2018)
***using concentration determined in Newton et al. (1984) for agriculture, and ½ for urban
†calibrated rate to best fit observations in this study

3.6 Transport scenarios

The calibrated MT3DMS model was used to run several land-use scenarios for DIN and GLY sources through the watershed. Scenarios where each source of DIN (i.e.- piggeries, OSDS, fertilizers, natural) was individually simulated with others eliminated to determine relative source contributions of each source to the total N flux via baseflow and SGD, and thus signifying the level of importance each point or non-point source plays in the overall contaminant budget. A scenario where halving the rates of cesspool-DIN leakage into the groundwater was also run to simulate how nutrient fluxes may change if septic systems were improved to double the current cesspool efficiency. To determine how the rates of GLY being applied for agricultural or domestic zoning affect concentration at each site, scenarios where each source was simulated individually, while neglecting the other to determine the percent each zone contributes to GLY contamination in Faga`alu groundwater. In the final two scenarios, the application amount of GLY was halved first in the developed zones, then in all the application zones, to simulate the effect that would take place if half of the currently used herbicide was applied in the village area and entire watershed, respectively. These scenarios may give insight to what can be accomplished in the future to promote better land management in the valley.

4. Results

4.1 Water Quality Results

Overall, 100% of all samples in Faga`alu had detectable levels of GLY and 85% had DDT. Measured groundwater GLY concentrations ranged between 74 and 301 ng/L across the six sample sites in Faga`alu. Stream bank groundwater samples had a relatively higher value furthest upstream (176 ng/L), a lower value in the mid-stream site (74 ng/L), and a moderate value nearest to the stream mouth (91 ng/L). The well (FG-179) had a concentration of 156 ng/L and the northern and southern coastal springs were 154 and 301 ng/L, respectively (**Table 3**). Glyphosate levels in Faga`alu groundwater were orders of magnitude lower than the Maximum Contaminant Level (MCL) of 700,000 ng/L designated by the EPA (2009). Patterns in glyphosate concentration in groundwater generally reflected land-use patterns in

Faga`alu (**Fig.4)**. DDT was notably present in groundwater samples as well, ranging from 876 to 2,068 ng/L, although it expectedly did not follow land-use patterns, as it was indiscriminately sprayed in the mid-20$^{th}$ century. DDT groundwater concentrations in Faga`alu averaged 1,397 ng/L.

Table 3: Groundwater sample nutrient and pesticide concentrations. (< indicates below detection limits)

Sample Site	Type	Glyphosate (ng/L)	DDT/DDE (ng/L)	TDN (µg/L)	PO_4 (µg/L)	SiO_4 (µg/L)	N+N (µg/L)	NH_3 (µg/L)	DIN (µg/L)
S-1	Stream bank	91	1,219	69	161	16,617	14	67	81
S-3	Stream bank	74	1,313	84	176	15,631	44	17	61
S-6	Stream bank	176	<	109	96	16,385	69	2	71
FG-179	Well	156	876	163	253	20,199	88	20	108
CS-N	Coastal Spring	154	2,068	333	109	6,911	244	7	252
CS-S	Coastal Spring	301	1,509	141	51	1,944	85	6	91

Glyphosate from surface samples at the seven total stream sites ranged between 57 and 232 ng/L (**Table 4**). Higher concentrations existed in the upper four sites (S-4 to S-7), averaging 184 ng/L with S-5 having the highest concentration (232 ng/L). The lower three stream sites (S-1 to S-3) averaged 75 ng/L, with S-3 having the lowest concentration (57 ng/L). When comparing the concentrations at sites which had both surface and groundwater samples (S-1, S-3, S-6), the upper two sites had more GLY in surface water concentrations than in groundwater (S3- 91ng/L to 74 ng/L and S-6- 196 ng/L to 176 ng/L, respectively), while S-1 had more GLY in groundwater than in surface water (91 ng/L to 76 ng/L, respectively). DDT in surface water samples ranged from below detectable limits at S-5 to 2,026 ng/L at S-7 (**Tab.4**). Average DDT across Faga`alu surface samples was 1,515 ng/L. The other two pesticides surveyed, imidacloprid and azoxystrobin were not detected in any of the Faga`alu samples, and will not be discussed further in this study.

Table 4: Stream discharge measurements and surface sample nutrient and pesticide concentrations. (< indicates below detectable limits)

Sample Site	Type	Discharge (m^3/d)	Glyphosate (ng/L)	DDT/DDE (ng/L)	TDN (µg/L)	PO_4 (µg/L)	SiO_4 (µg/L)	N+N (µg/L)	NH_3 (µg/L)	DIN (µg/L)
S-1	Stream	3629	76	839	182	105	16,887	131	8	139
S-2	Stream	2894	57	1844	129	120	16,772	63	2	65
S-3	Stream	2290	91	1382	118	120	16,733	59	3	62
S-4	Stream	2367	142	839	118	109	15,999	64	4	68
S-5	Stream	1970	232	<	129	106	16,257	84	3	87
S-6	Stream	2532	196	1722	115	94	16,388	76	2	77
S-7	Stream	2385	164	2026	115	79	16,304	81	3	84

Dissolved inorganic nitrogen in Faga`alu groundwater was very low by EPA standards, ranging between 61 - 252 µg/L. DIN trends, like glyphosate, tended to follow land-use patterns (**Fig.5**), with a generally increasing concentration trend towards the coastal areas. The stream bank groundwater samples had lower DIN than the coastal springs and the well (**Table 3**). DIN does not actually have a set MCL, but its constituents, nitrite and nitrate have official drinking water MCLs set by the EPA of 1 and 10 mg/L (Appendix **Tab.A1**), respectively (EPA, 2009). Another component of DIN is ammonia, which does not have a set MCL by the EPA. Environmental limits have been placed on it ranging from 0.25 mg/L to 32.5 mg/L in the U.S. (Oregon Department of Human Services, 2000), which are much higher than any of the sites we sampled (ranging from 2 to 67 µg/L). Except for groundwater from the northern coastal spring, DIN in stream surface waters were comparable to groundwater concentrations across the watershed, with a range from 62 to 139 µg/L. The NH_3 component did show notable difference, as it averaged 3 µg/L in surface water sites compared to 20 µg/L in groundwater sites.

Phosphates had a range of 51 to 253 µg/L across the six groundwater sites, and a range from 79 to 120 µg/L across the seven surface sites. The 105 µg/L average of surface samples is only 74% the groundwater average of 141 µg/L. Silicates show a relatively even distribution across stream bank groundwater and stream surface samples, averaging 16,211 and 16,477 µg/L, respectively, but show much more diluted values at the northern and southern coastal springs (6,911 and 1,944 µg/L, respectively). The well, being sampled deep below the ground produced more elevated concentrations of 20,199 µg/L.

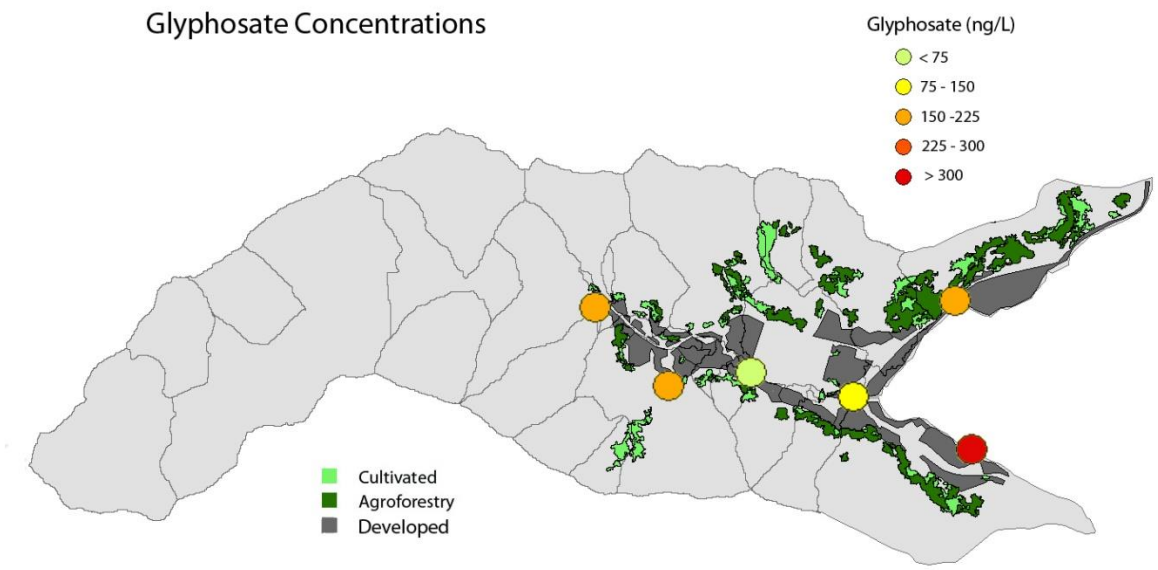

Figure 4: Glyphosate concentrations at the six groundwater sampling sites in Faga`alu, shown with related land-use areas, which may contribute to higher concentrations, such as cultivated (light green), agroforestry (dark green), and unpaved developed/residential land (dark gray).

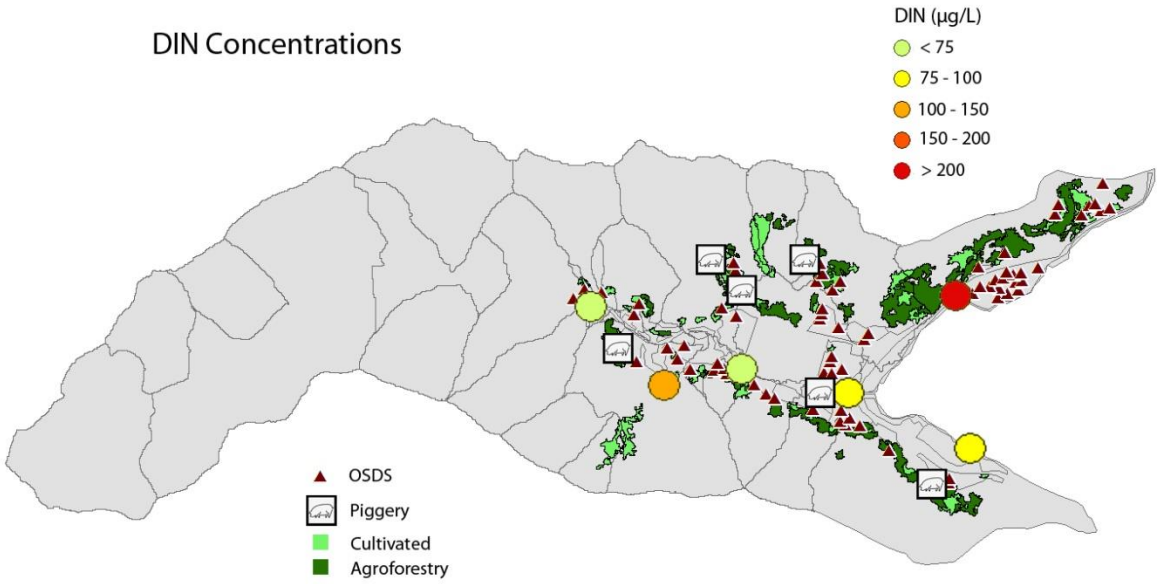

Figure 5

Figure 5: DIN concentrations at the six groundwater sampling sites in Faga`alu, shown with related point source and land-use contributors to higher concentrations, such as cultivated (light green polygons), agroforestry (dark green polygons), OSDS units (triangles), and piggeries (square icons).

4.2 Model results

Seepage runs taken during the time of sampling in August 2016 provided observed streamflow measurements from seven sites transecting the Faga`alu Stream, and ranged from 1970 m^3/d to 3629 m^3/d. Radon-222 measurements were taken at each site as well and its trends compared very well to measured discharge rates (**Figure 6**), validating assumptions about gaining and losing sections of the stream. Using the streamflow measurements at each site, the model was calibrated to best fit head level and stream discharge observations.

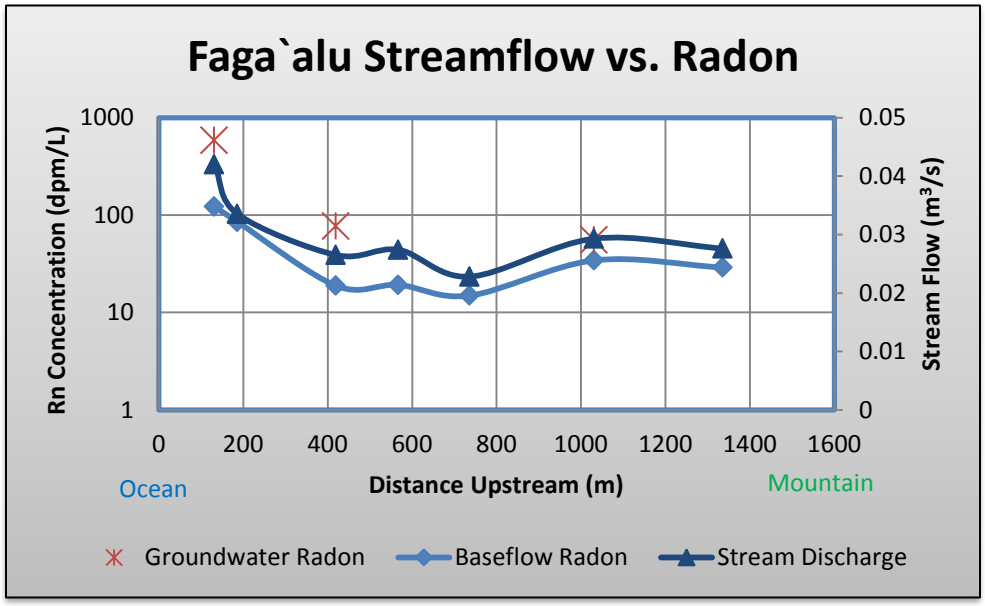

Figure 6: Comparing the values from the streamflow measurements (dark blue/right axis) to the ^{222}Rn values (light blue/left axis). The relative values seem to agree, indicating which segments of the stream tend to be losing or gaining water to and from the aquifer.

The final calibrated MODFLOW model had a root mean squared residual (RMSR) of 12.45 m for head and a RMSR of 256.25 m^3/d for discharge. The model was considered satisfactorily calibrated when the RMSR (head+flow) was 2.31 and the coefficients of determination (r^2) were 0.99 for head and 0.82 for flow. The modeled values are compared to observations in **Tables 5** and **6** for these two parameters. Although the relative error for the observed head level at the well (FG-179) was high, the difference in head was only 3 m, which although large by magnitude, is only 1% of the water table gradient across the entire aquifer (253 m at highest observed head). This is assuming that the upper watershed head

observations represent the water table of the main aquifer, and not from any perched or confined reservoirs.

Table 5: Observed vs. modeled head levels (rounded values) after calibrating MODFLOW model, with relative error.

Observation Point	Observed Head Level (m)	Modeled Head Level (m)	Relative Error (%)
Well FG-179	3	6	+156
Spring-1	42	69	+63
Spring-2	109	112	+3
Spring-3	160	162	+1
Spring-4	253	255	+1
Spring-5	250	264	+5
Root Mean Squared Residual		12 m	

Table 6: Observed streamflow for measured stretches of the stream under baseflow conditions, assuming no additional surface runoff contribution, in comparison to modeled baseflow results. Flow from tributaries was not specifically measured, assuming the associated flow contributions were reflected at downstream sites.

Stream Arc Station #	Observed Discharge (m^3/d)	Modeled Discharge (m^3/d)	Relative Error (%)
S-7	2,385	2,103	-12
S-6	2,532	2,367	-7
S-5	1,970	2,434	24
S-4	2,367	2,457	4
S-3	2,290	2,491	9
S-2	2,894	2,501	-14
S-1	3,629	3,235*	11
Root Mean Squared Residual		256 m^3/d	

*Not including stream mouth cell, as was added in later to baseflow. This is showing purely modeled stream arc values.

Once calibrated, SGD flow rates were estimated by summing the modeled flow rates in each coastal grid cell. The flow from the cell just below stream bank station S-1 was subtracted and included in the stream baseflow. The total SGD of the entire bay was estimated to be 2,680 m^3/d, while the modeled streamflow of 3,868 m^3/d was estimated by summing all of the stream arcs and adding the flow from the cell at the mouth of the stream. Nearly as much water is delivered to the bay via SGD (41%) than is from the stream (59%), making SGD a considerable fraction of the daily load. The high-level baseflow from the upper reach of the stream contributes 63% of the stream's total flow, while the lower reach contributes 37%, which reflects a gaining stretch upstream and near the coast, and a losing stretch in between, also

verified by the seepage runs. According to the model, most of the watershed's SGD comes from the central shoreline of the bay (69%) (**Figure 7**), which matches observations of maximum groundwater discharge focused in estuaries in literature (e.g. Buddemeier, 1996). The northern coast delivered slightly more SGD than the southern coast, contributing 18% to 13% of the total, respectively. These percentages match closely with the patterns found in a 2014 ^{222}Rn survey performed by Shuler et al. (2019). The modeled flow rates from the stream reaches and the three sections of the coastline are reported in **Table 7**, alongside measured values and estimated fluxes based on flows multiplied by concentrations. The modeled combined flow of water to Faga`alu Bay each day under baseflow conditions, delivered by the combination of stream baseflow and SGD is 6,547 m^3/d. Nutrient and pesticide fluxes are shown on **Table 7** for each section of the stream and bay, along with totals, and their comparison to measured fluxes.

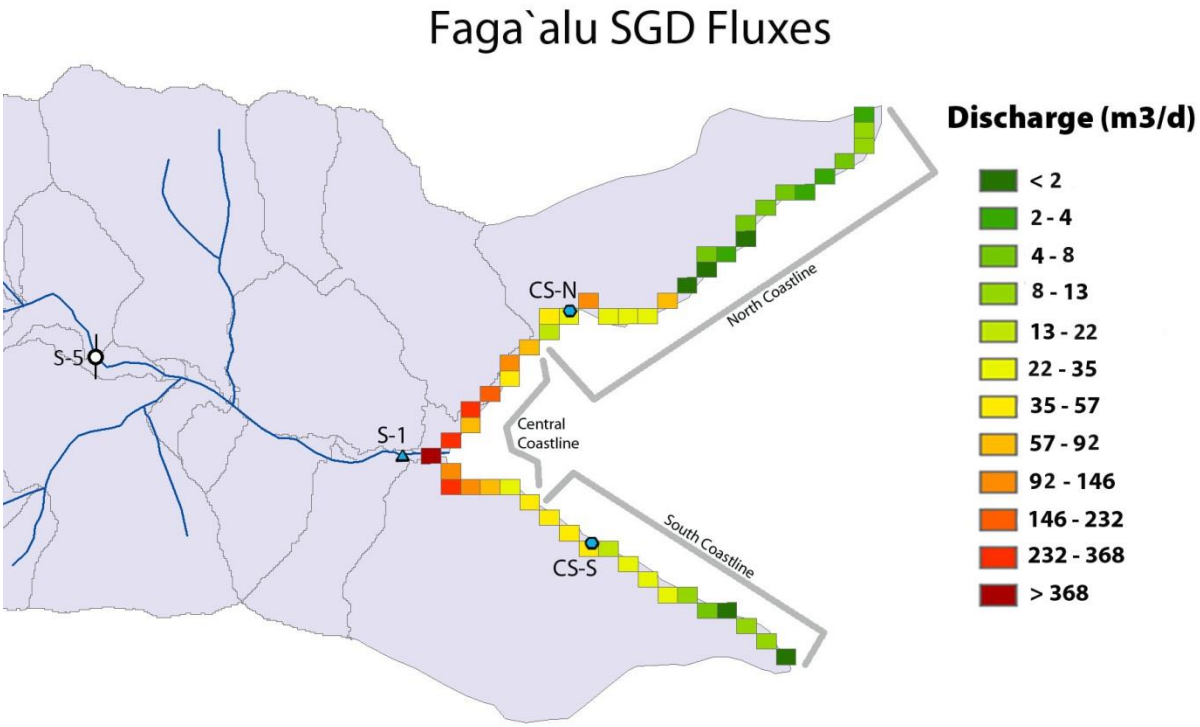

Figure 7: The modeled SGD fluxes show larger groundwater discharge to the central portion of the bay, with diminishing fluxes outward toward the northern and southern ends of the bay. Grid cells belonging to the northern, central, and southern sectors of the coastline as well as coastal springs (CS-N, S-1, and CS-S) are shown. Station S-5 delineates the boundary between the upper and lower reaches of the Faga`alu Stream, which was used in determining high level and basal aquifer baseflow fluxes.

Table 7: Modeled groundwater discharge rates via stream baseflow and SGD, and their associated pesticide and nutrient fluxes based on concentrations in each representative section of the watershed. Contributions from the lower and upper reaches of the stream are summed for total stream-derived fluxes into the bay while contributions from the north, central, and southern coastlines of the bay are summed for total SGD-derived fluxes. The measured stream discharge rate at station S-1 (nearest the bay) is given, with corresponding nutrient and pesticide fluxes based on water data collected at that station to compare to modeled values. The final column shows the total combined modeled flux for each contaminant derived from groundwater (baseflow+SGD).

	Modeled Stream			Measured Stream (2016)	Modeled Coastal SGD				Measured SGD (Shuler 2014)	Total Modeled GW Flux
	Upper Reach	Lower Reach	Stream Sum		North	Central	South	SGD Sum		
Discharge (m^3/d)	2,434	1,434	3,868	3,629	481	1,840	359	2,680	2,587	6,547
GLY (g/d)	0.43	0.12	0.55	0.33	0.07	0.17	0.11	0.35	0.47	0.90
DDT (g/d)	3.35	1.82	5.17	4.42	0.99	2.24	0.54	3.79	4.14	8.95
DIN (g/d)	172	102	274	296	121	150	33	304	366	578
TDN (g/d)	264	110	374	251	160	127	50	338	468	713
PO_4 (g/d)	233	242	474	585	52	296	18	367	277	842
SiO_4 (g/d)	39,878	23,119	62,997	60,300	3,321	30,579	697	34,597	21,965	97,594
N+N (g/d)	168	42	210	51	117	26	31	174	296	383
Ammonia (g/d)	4	61	65	244	4	124	2	130	70	195

4.3 Transport Model Results

Sensitivity analysis was performed until parameters reached an optimal setting to match observed solute distributions, while remaining within accepted literature ranges (**Fig.3**). Concentrations and attenuation rates of N-loading and GLY fluxes were also adjusted to refine the results. Shuler et al. (2017) noted that attenuation values had the greatest effect on model outputs in the neighboring Tafuna watershed. As their OSDS and piggery mass loading fluxes and attenuation rates were adapted as starting points for this Faga`alu model, these parameters did not need much adjustment. The estimated fertilizer N-input for cultivation, which was based on the World Bank dataset and Schilling and Streeter (2018), needed only minimal adjustment as well. Glyphosate however, continued to produce concentrations below observed levels at 75% attenuation (the minimum determined by Imfeld et al., 2013) from the determined initial input of 84 mg/L (Newton et al., 1984). Lowering the attenuation rate to 50% through calibration eventually produced results where modeled glyphosate concentrations were the same order of magnitude as the measured values (**Table 8**), although still having a high overall error. Since all attempts were made to match observations by adjusting the model parameters, the conclusion is that a better match could only be achieved by adjusting the mass loading.

The model results of the 20,000 day period are shown in **Table 8**, where calibration was attempted using GLY and DIN as tracers for agricultural, domestic and mass loading pathways within the watershed. In analyzing the DIN concentrations, the two upper sites (FG-179 and S-6) were highly underestimated in the model in comparison with the measured values, 75% and 91% in error, respectively. Site S-1 near the stream mouth also underestimated values by a large error of 67%. The southern coastal spring only had 23% error, and site S-3 and the northern coastal spring had the best fit modeled to observed values, with 9% and 1% error, respectively. Despite not capturing observations very accurately, the MT3DMS model was considered acceptable when the mean absolute error (MAE) of the total modeled vs. observed DIN values (38 mg/L) fell within 15% of the maximum observed DIN concentration 252 mg/L, and obtained an r^2 of 0.66. Modeled glyphosate levels had an MAE of 123 ng/L,

producing a wide margin of error and a low r^2 value (0.024), not agreeing well with observations. The two upper stations, similar to DIN, underestimated glyphosate concentrations (99% error) despite all calibration efforts (**Tab.8**). Therefore, glyphosate trends (and likely DIN as well) in upstream groundwater only matched an order of magnitude of observed concentrations. The two sites farthest downstream (S-1 and S-3), however, had moderate error compared to observed values (36% and 55% error, respectively). The coastal springs as well, did not fall near the regression line (CS-N 91% and CS-S 65% error), but produced estimates within an order of magnitude of the actual results. Despite the small number of observations that were taken during the single point in time and the uncertainty in the location and amount of actual application of the contaminants, the modeled GLY and DIN values could still be valuable in illustrating the importance of groundwater fluxes and that a non-trivial amount of at least 84 $g/m^3/yr$ of GLY and a daily 12 g/OSDS, 5 g/piggery, and a yearly 1.4 g/m^3 of N in fertilizer are added to the aquifer in this watershed. The modeled values can also be valuable in completing qualitative assessments and in comparing various scenarios. Certainly, additional data, especially in the underlying geology, are needed to better calibrate the model in the future.

Table 8: Modeled vs. observed concentrations of glyphosate and DIN after 20,000 days in the MT3DMS transport model, and the relative error of each point.

	Glyphosate (ng/L)			DIN (µg/L)		
Sample Site	Observed	Modeled	Relative Error (%)	Observed	Modeled	Relative Error (%)
S-1	91	58	36	82	137	-67
S-3	74	33	55	61	67	-9
S-6	176	0	100	71	7	91
FG-179	156	2	99	108	27	75
CS-N	154	294	-91	252	254	-1
CS-S	301	105	65	91	112	-23

Concentration values were derived from the transport model (MT3DMS) by selecting and analyzing grid cells intersecting the coastline and stream. These values are compared in **Table 9** against those estimated by using the hydrogeological model-derived flow (MODFLOW) multiplied by the

observed site-specific concentrations of solutes. Glyphosate fluxes in the transport model were underestimated in the stream's upper reach and overestimated the lower reach of the stream. The total baseflow-derived GLY estimate (0.356 g/d) fell between the MODFLOW results (0.55 g/d) and observed results (0.28 g/d). MT3DMS underestimated the total SGD (0.185 g/d) for glyphosate in comparison to the measured (0.47 g/d) and MODFLOW model (0.35 g/d) estimates. The total watershed flux, however, for the transport model was only slightly higher (0.88 g/d) than the measured values (0.75 g/d). For DIN, the transport model overestimated the lower steam baseflow flux (627 g/d) compared to the MODFLOW-estimated (102 g/d) rate. The total stream baseflow flux was thus high (861 g/d) in comparison to both the MODFLOW (274 g/d) and measured (506 g/d) fluxes. The northern coastline produced a high SGD flux according to the transport model (549 g/d) when compared to the MODFLOW estimate (121 g/d), producing an overestimate for total SGD as well by comparison to the other two methods (**Tab.9**). Similarly, looking at the DIN flux from the entire watershed, the transport model produced nearly double (1,634 g/d) the estimate of the measured (872 g/d), and three times the estimate of the MODFLOW results (578 g/d). Despite the error, all estimated fluxes no matter the method used, fell within the same order of magnitude.

Table 9: Comparison of the estimated glyphosate and DIN fluxes for the hydrogeological model (MODFLOW)-derived water discharge multiplied by observed concentrations, the transport model (MT3DMS) with modeled groundwater discharge and solute distribution, and the in situ measurements of groundwater discharge and associated solute concentrations for stream baseflow and SGD in the Faga`alu aquifer, using the 2016 survey data. *SGD totals are from 2014 ^{222}Rn survey data multiplied by 2016 solute concentrations, as the survey was not repeated in 2016.

		GLYPHOSATE			DISSOLVED INORGANIC NITROGEN		
		MODFLOW	**MT3DMS**	**Measured**	**MODFLOW**	**MT3DMS**	**Measured**
STREAM BASEFLOW	**Upper Reach (g/d)**	0.43	0.036		172	234	
	Lower Reach (g/d)	0.12	0.32		102	627	
	Total Stream (g/d)	**0.55**	**0.356**	**0.33**	**274**	**861**	**296**
SGD	**North Coast (g/d)**	0.07	0.088		121	549	
	Central Coast (g/d)	0.17	0.078		150	180	
	South Coast (g/d)	0.11	0.02		33	32	
	Total SGD (g/d)	**0.35**	**0.185**	**0.47 ***	**304**	**773**	**366 ***
BASEFLOW + SGD TOTAL (g/d)		**0.541**	**0.88**	**0.75**	**578**	**1634**	**872**

4.4 Land-use transport scenarios

Transport model scenarios were conducted to help determine what effects on groundwater would be obtained by reducing fluxes from certain pollutant sources or eliminating them altogether, and which are contributing the most relative to others. To begin, the model was run with ten times the concentration of glyphosate and DIN from each source term and also ten times less concentration per source, of each. It was found that the concentrations changed in a near-linear fashion proportional to the multiplication factor (i.e.- 10x more glyphosate at S-1 produced 1315 g/d compared to the original modeled value of 137 g/d). Likewise, dividing the initial concentrations and fluxes by ten, linearly decreased the observation point concentrations (i.e. 10x less glyphosate at S-1 produced 13 g/d). This scenario followed the same trend at all sites for both glyphosate and DIN. This means that, although there is absolutely no information on locations of and applied amounts of GLY and DIN in this watershed, the literature values produced estimates that agree within the order of magnitude with groundwater concentration observations. This also means that the model could be significantly improved by collecting data on the locations and amounts of applied GLY and DIN, rather than further fine tuning the other model parameters.

Scenarios were then run to determine the contribution of each point and non-point source of DIN into the total N-flux of the watershed. All but one N-source were eliminated per scenario in a step-wise manner to determine how much each (OSDS, piggery, agriculture, natural) contributes to the total concentration arriving by groundwater transport at each observation site. Resulting concentrations reflected the percentage of N that each source contributes to the total end-concentration in the modeled watershed. It was found that when excluding all DIN sources except piggeries from the model, 6.1% of the total DIN concentration was observed. If agriculture was the lone source, a very small percent (0.1%) of DIN made it to the observation sites, showing that agricultural N contributions via groundwater are nearly insignificant. The largest input came from only OSDS units leaching N, which indicated an 89.8% contribution of DIN to our observation points. Omitting the other inputs and leaving only natural N

contributions to each polygon, left 4% of the total concentration still making it to our observation sites. These percentages along with concentrations are shown in **Table 10**, and directly reflect the estimated contribution of each source to the total flux in the watershed. A scenario was then run when cesspools were improved (i.e. converted to septic systems) by doubling their efficiency to remove DIN, which was attained by adjusting the attenuation rate so that half the original concentration (5,807 mg/d) entered groundwater from each OSDS unit. It was found that using these rates, 46% less DIN made it to the observation points (**Tab.10**), significantly reducing the concentration of this anthropogenic pollutant.

Table 10: Several scenarios were run with DIN, each neglecting one of the key N-inputs. Using the resultant decrease in concentration, we can infer the contribution of each point or non-point source (Piggeries, Agriculture, OSDS) is the percent change that was attributed when taken out. Natural N was determined by the leftover residual. A scenario with improved septic systems was also run, setting the attenuation rate so as only half the contaminant was released from the sources, doubling their efficiency.

Sample Site	All N-sources **(µg/L)**	Only piggeries **(µg/L)**	Only Agriculture **(µg/L)**	Only OSDS **(µg/L)**	Only Natural N **(µg/L)**	Improved Cesspool Scenario **(µg/L)**
S-1	137	7	0.05	126	4	72
S-3	67	5	0.03	58	4	37
S-6	7	0.08	0	4	3	4
FG-179	27	3	0.02	21	3	16
CS-N	254	2	0.39	247	5	128
CS-S	112	20	0.19	86	6	68
Percent change (%)		6.1 %	0.1 %	89.8 %	4 %	-46%

Glyphosate was similarly compartmentalized between domestic and agricultural inputs. When the scenario was run with only agricultural inputs, 28.5% the total GLY arrived at the observation points. When domestic GLY input alone was considered, 71.5% of the total GLY arrived at the sites, indicating the importance of this source (**Table 11**). In our scenario, domestic application contributes over two times the amount of glyphosate than the agricultural application does at our specific sampling locations, which are focused on the lower alluvial plain in the watershed. The observation points are in the developed area, so may be biased toward individual household sources. At the same time, since the model used literature values and not actual watershed specific application rates, the model represents one possible scenario and these results should only be used to illustrate its applicability as a decision tool once actual field observations on application locations and amounts is obtained. The model still may be useful in that it

points out that relative GLY contributions from the village region may be primarily entering the stream via more direct groundwater pathways, while the agricultural inputs may get more dispersed before reaching the coastline. As domestic GLY applications deliver higher concentrations at stream and coastal observation points in our model than agricultural applications, a scenario was run where it was assumed that people used half of the glyphosate in the urban setting. The concentrations dropped by 37% in this scenario (**Tab.11**). If GLY were to additionally be cut by half in agricultural uses, the total concentrations entering our observation sites would drop an additional 13%, to total a 50% decrease.

Table 11: Glyphosate scenarios were performed using the transport model. A version was run without domestic inputs, and a version with no agricultural inputs. The percent change can help infer the percent contribution of each.

Glyphosate Scenarios					
Sample Site	**Modeled** (ng/L)	**Only Domestic** (ng/L)	**Only Agriculture** (ng/L)	**½ Domestic input** (ng/L)	**½ Domestic + ½ Agric input** (ng/L)
S-1	58	49	9	33	29
S-3	33	21	12	23	16
S-6	0	0	0	0	0
FG-179	2	2	0	1	1
CS-N	297	181	116	202	147
CS-S	105	101	4	55	53
	% change	-71.5%	-28.5%	-37%	-50%

5. Discussion

This study has demonstrated the significant contribution of groundwater discharge, as stream baseflow and SGD, to contaminant fluxes to the coastal reef ecosystem in the Faga`alu watershed. The respective discharges for SGD and baseflow into the bay are 41% and 59% of the total freshwater discharge during baseflow conditions. Although the stream baseflow contributes higher quantities of most of the studied contaminants, SGD was shown to contribute higher concentration levels of DIN to coastal marine ecosystems in Faga`alu. According to the transport model, most of these groundwater fluxes of DIN are related to the presence of OSDS units in the watershed, rather than piggeries and agricultural plots, which likely contribute more to surface water pollution (Shuler et al., 2017). The MODFLOW model, although reliant on few observation points in its calibration, agrees well with in situ stream

measurements from the same sampling period and a 2014 coastal ^{222}Rn survey (Shuler et al., 2019), where SGD was estimated via direct measurements. The MT3DMS transport model was less successful in calibrating to measured nutrient and pesticide concentrations, with only six sites used in its calibration. Although not acceptable for quantitative analysis, the modeled estimations were considered useful in determining relative transport properties, as the concentrations fell within a range of the same order of magnitude, as will be discussed later. The movement of pesticides through groundwater pathways was also of interest. GLY sources, as determined by the transport model, seem to be sourced relatively close to the sampling locations, showing proximity of application to be more important than the applied concentrations. This is likely due to glyphosate's relatively fast breakdown process compared to other contaminants studied. In regards to the offshore reef, and based on measured concentrations, the long residence time of DDT may pose a threat to the ecosystem along with excess N and P nutrient fluxes. GLY by itself may have some influence due to its chronic presence, but negative effects of chronic exposure at ng/L levels on coral reefs have not been demonstrated.

5.1 Contaminant concentrations and fluxes

5.1.1 Pesticides

As summarized in the results, no GLY concentrations approached the drinking water maximum contaminant level determined by the EPA. When comparing the maximum value of 301 ng/L found in the southern coastal spring to standards set by other organizations, the toxicity still remains well below their limits by orders of magnitude. Significantly lower limits have been set than the EPA's current guidelines (700,000 ng/L), such as a maximum acceptable concentration in drinking water of 280,000 ng/L in Canada (Health Canada, 1995), to an even lower standard with the Environmental Working Group's health guideline of 5,000 ng/L (EWG, 2014). Thus stream and groundwater GLY concentrations found in this study do not look to cause a drinking water threat.

Concentrations of GLY from stream bank samples showed a slight correlation with gaining and losing sections in the stream. The three push point samples from Faga`alu Stream lie in the developed

village area. According to the transport model, application on domestic properties has the potential to deliver more GLY to the stream sites than do the more distant agricultural inputs. Station S-1 (91 ng/L) in the lower village lies farthest from any significant agricultural plots, but lies within the central part of the village on a gaining section of the stream. Here, possible application sites include roadsides and yards in upstream homes where herbicides containing glyphosate may be used to control unwanted weeds. Station S-3 had the lowest concentration of all sites (74 ng/L), suggesting that domestic spraying may be lower at this mid-village location, but most importantly, the stream is losing water to the aquifer at this site, likely contributing to the depletion in glyphosate. Station S-6 (176 ng/L), although furthest upstream has a higher glyphosate concentration than the two downstream sites. This site marks the upper boundary of the village and there is a small plot of agriculture adjacent to it, with a quarry just upstream. Seepage runs show the stream to be gaining water from the underlying aquifer at this point as well, and the presence of GLY could indicate nearby herbicide application. The well and northern coastal spring (156 and 154 ng/L respectively) are both downslope of large plots of agriculture, possibly contributing to their higher glyphosate concentrations. The northern spring in particular lies on a thin stretch of grass separating the highway from the coast of Faga`alu Bay. Aside from the nearby agricultural plots, this stretch lies on the main road passing through town, and direct application of the herbicide may be applied to keep the roadway clear. The southern coastal spring has the highest concentration (301 ng/L) recorded in the watershed, and although it lies a further distance from cultivation than other spots, it is located directly on the coastal border of a large recreational park. It is also downstream of houses where GLY may be applied to regulate unwanted weeds.

Surface water GLY concentrations were higher in the upper reach than lower reach of the stream. Moderate concentrations associated with sites S-4, S-5, and S-6, all in the developed region near agricultural plots, may attribute GLY presence from surface application runoff into the stream. As S-6 had higher surface GLY (196 ng/L) than groundwater GLY (176 ng/L), surface sources for the extra concentration may be the explanation, even under baseflow conditions. The declining GLY concentrations downstream toward the bay may simply be dilution as the water enters the paved lower

village section, farther from agriculture, and possibly less domestic application near the large parking lot of the LBJ Tropical Medical Center complex.

Unlike GLY, the distribution of DDT concentrations cannot be analyzed with respect to land-use due to the method of island-wide application used several decades ago. The presence of the insecticide so long after its last usage is notable, which reflects its persistent nature as it is adsorbed onto soils and slowly leaches into groundwater. Stream bank sample S-6, however, contained below detectable concentrations of DDT, although the corresponding surface sample for the same site (**Table 4**) had a concentration comparable to all other sites. However, surface sample S-5, just downstream, showed below detectable limits of DDT, emphasizing the heterogeneous nature of its distribution on a smaller scale. Groundwater concentrations ranged from 876 ng/L at the well to 2,068 ng/L at the northern coastal spring, while surface samples similarly ranged from 839 ng/L to 2,026 ng/L. If we assume a relatively uniform spray application across the island, DDT distribution must be governed by its retardation rate within different geological substrates (soil, pH, moisture, organic content) and interaction with groundwater. Heterogeneities in the aquifer must be present that produce the observed spread in groundwater and stream concentrations. The most important conclusion of this study with respect to DDT in the Faga`alu watershed, is that it can be found in the same concentrations in both streams and groundwater, despite its assumed low mobility ("Pesticide Information Profile: DDT," n.d.). It is the conclusion of this study that groundwater via both stream baseflow and SGD is responsible for DDT delivery to the ocean. DDT may be detrimental to the riparian and reef communities in Faga`alu, due to its known ecological effects on calcifying processes of certain organisms (Kwok, 2015; Peakall, 1970).

5.1.2 Nitrogen

Measured nutrient concentrations similarly followed land-use and flow patterns across the watershed by showing increased concentrations downstream of the agricultural and populated areas of the watershed. There is no set drinking water MCL for TDN, DIN, or N+N, but MCLs have been individually set for nitrite (NO_2^-) and nitrate (NO_3^-) as 1,000 μg/L and 10,000 μg/L, respectively (**Tab.A1**) (EPA,

2009). These were not reached in any of the samples as the highest observed concentration of DIN was 252 μg/L (CS-N). In this study, between 65 and 100% of TDN consists of DIN, and thus both follow a similar distribution pattern. Nitrite and nitrate (N+N) represent between 20 and 70% of DIN. The northern coastal spring (CS-N) had the highest DIN concentration (252 μg/L) as well as TDN (333 μg/L), likely a result of the high concentration of contiguous OSDS units along the coast, along with large agricultural plots up the slope of the adjacent ridge. As the transport model predicts, and Shuler et al. (2019) suggests, OSDS is likely the primary contributor of DIN in the watershed's groundwater. Of the sites sampled, this is one of the sites in which to expect elevated concentrations of N, with 19 OSDS units located within a 0.3 km radius. The well and southern coastal spring (FG-179 & CS-S) showed the next two highest DIN concentrations (108 μg/L and 91 μg/L, respectively). The piggery near the southern coastal spring may partially be the reason for its elevated N-levels, although fertilizers from the large recreational field upstream of it could be another possible contributor. The well (FG-179) lies upstream of several OSDS units, but downslope of some high elevation agricultural fields, which may supply DIN. However, the transport model suggests that DIN from agricultural sources is only 1% of total contribution to groundwater DIN, which looks to be the only upstream source of the well. We do not have a clear explanation for this discrepancy, but can only speculate that the well samples a much deeper region in the aquifer and the slow rate of movement in deep groundwater can lead to a lack of dilution and overall accumulation of DIN (Follett, 1995; McBee, 2017), which would not be accounted for in our model. Thus either the OSDS or upslope agricultural input could contribute accumulated concentrations of DIN to the well. The upper two stream sites (S-3 and S-6) both lie near agricultural plots and OSDS units, and have moderate concentrations in comparison (61 μg/L and 71 μg/L, respectively) to the other observations. The lowest stream site (S-1) shows an inconsistency in the estimated DIN (81 μg/L), which is higher than the TDN (69 μg/L). Such results can be explained by the challenges encountered in the lab in analyzing TDN in highly reducing samples. Several stream bank pore water samples had lower N+N than NH_3, which can be explained by the reducing organic rich stream bank sediments.

It is possible that the source of nitrogen plays some role in which form DIN can be found, for example, site S-1 lies directly below a piggery and several OSDS units in the lower developed region of the watershed. The anaerobically-formed NH_3 could be sourced from manure and wastewater and it makes sense to be highest at station S-1 (67 μg/L). However, it is most likely that the amount of organic matter and reducing conditions in the aquifer govern the chemical speciation of DIN and its conversion to NH_3. Therefore it is expected that all stream bank pore water samples, which are retrieved from organic rich and low permeability sediments, have NH_3 and the coastal springs emanating from more porous alluvium are dominated by the oxidized N+N. To the contrary, the well drilling logs suggest that it taps into a basalt aquifer, which in other islands such as Oahu and Hawaii (Richardson et al., 2017), is usually well oxygenated (>90% dissolved oxygen saturation) and all of DIN is in form of N+N. The presence of NH_3 in the well is another line of evidence that groundwater may be polluted by organic rich and high nutrient water source, such as OSDS or piggeries.

Surface stream DIN levels are all comparable to the stream bank groundwater, except at S-1, where DIN is 72% higher in the surface samples, possibly due to the piggery not far upstream. Piggeries likely produce more surface runoff, as waste is not injected into the ground (Shuler et al., 2017), and may actively be washed off into the adjacent stream by pig owners. Concentrations of NH_3 are much lower in surface samples than in groundwater samples, likely due to anaerobic conditions in the subsurface, which help NH_3 accumulate to higher levels.

5.1.3 Phosphate and Silicate

Phosphate concentrations ranged between 51 and 253 μg/L, with a mean of 141 μg/L. As phosphate acts as an essential constituent of organisms, the EPA has no set MCL for drinking water (Oram, 2014a). In freshwater bodies, phosphate is known as a limiting nutrient, which in excess can lead to accelerated eutrophication and the EPA set a maximum acceptable concentration of 100 μg/L (Oram, 2014b). Above this threshold, eutrophication can occur, leading to algal blooms and lower dissolved oxygen. Four of the six stream pore water and five of the seven stream surface sites sampled exceeded

this amount (**Tables 3 & 4**) and this study suggests groundwater contribution likely plays an important role in driving these elevated PO_4 concentrations. Specifically, the well (FG-179) had the highest concentration of phosphate (253 μg/L), likely due to the accumulation of upslope agricultural inputs in the deep groundwater or simply just longer groundwater pathways obtaining enriched P from natural rock weathering. It has been shown that dissolved inorganic phosphorus (DIP) in volcanic aquifers can naturally be elevated (Porder and Ramachandran, 2013), so it is possible that natural sources (i.e. basalt weathering) are responsible for the elevated groundwater PO_4 concentrations.

Silicate in groundwater reflects water-rock interactions, as Si dissolves from silica-rich minerals within the underlying rocks. Silica content is also directly proportional to groundwater residence times within the rocks in the aquifer. This is often reflected in deeper-sourced groundwater over shallow-sourced water (Khan et al., 2015). This seems to be the case in Faga`alu, as the highest concentration of SiO_4 is found in the well (FG-179), which is sourced from the deepest groundwater in the study. This would also confirm that its residence time is longer than any of the other five locations sampled. The coastal springs showed the lowest SiO_4 values, as they are diluted by the ocean. The range of SiO_4 concentrations in groundwater was 1,944 – 20,200 μg/L, with a mean concentration of 12,948 μg/L. The stream bank sites, however, average less than 2% different from the surface stream samples taken.

5.2 Evaluation of the MODFLOW model

All calibrated head elevations of the modeled water table lie within 10% of total head values in the watershed (the highest point in water table is over 450 m according to model) (**Tab.5**). The observation point with the largest difference between modeled vs. observed values in calibration was Spring-1, near the back of the alluvial plain, which had a 27 m (63%) difference between modeled and observed heads. It is possible that the model does not capture the true geological features at the site, including the transition between the volcanic and alluvial sections of the aquifer. The four upper watershed sites, however, were all very close in range, agreeing well with observations (< 5%). Assumptions were, however, made that these represented water from the main aquifer and not a perched

layer or dike-impounded water. Additional research is certainly called for in this regard. The one site (well FG-179) where recorded water tables gave verification of the actual water table was only off by 3 m (< 1% total water table level), implying model accuracy in the lower portion of the aquifer. Reasonableness of water level estimates and the simulated flow field are confirmed by a good match between measured and modeled SGD fluxes at the land-ocean interface. No recalibration of the flow model was done to improve the match. The modeled stream baseflow measurements matched the observations to within 24% (average 11%), with absolute error ranging from 90 to 464 m^3/d across the sites. However, the RMSR of 256 m^3/d falls well below 10% of the total modeled streamflow (3,868 m^3/d). The modeled baseflow entering the bay at the lowest stream station, S-1 overestimated the total measured surface flow by 6.6%. The Faga`alu Stream gauge measurements from August 10$^{th}$, 2016 recorded a total streamflow of 3,831 $m^3/d$, with baseflow delineated at 3,665 $m^3/d$ on the day of the main Faga`alu sampling. The modeled baseflow contribution of 3,868 m^3/d had a comparatively small relative error of 5%. The small difference between actual and modeled overall stream baseflow contribution to the bay is more important than any individual stretch of stream. Contrary to measurements, the model did not calculate any of the sections to be losing water to the aquifer. Every reach of stream calculated in the model was gaining from the last, as seen in **Table 6**, while measured discharge rates showed both gaining and losing sections. Specifically going down from site S-6 to S-5, a drop by over 550 m^3/d was seen in discharge, while the model predicted a 67 m^3/d increase in flow. Such a discrepancy is again most likely due to simplifications in the conceptual model that do not accurately capture the true geologic features of the site.

The accuracy of this MODFLOW model is validated against measured fluxes during a previous study (Shuler et al., 2019), which consisted of baseflow separation in the upper and lower reaches of the stream and SGD fluxes entering the bay calculated by ^{222}Rn mass balance during similar hydrologic conditions in 2014 (Shuler et al., 2019). Shuler et al.'s 2014 stream baseflow rates were comparable as well as SGD, which totaled 6,112 m^3/d in comparison to this study's 6,547 m^3/d (**Tab.12**), a 7% difference. Even looking at groundwater flux in individual sectors (upper and lower stream reach, SGD),

the comparison holds strong at each section, with a 19% difference in the lower reach, a 3% difference in the upper reach, and a 3% difference in total SGD (**Tab.12**). Some notable differences between the current and the Shuler et al. study include: 1) the date that the data of each study was collected and 2) the location of the divide between upper and lower reaches delineated by each study. The data taken to build the MODFLOW model in this study is from August 2016, while the Shuler et al. (2019) measurement was taken in July 2014. Although both measurements occurred during American Samoa's dry season, and under baseflow conditions, some variability in the exact elevation of the water table due to preceding seasonal conditions likely exists. The second difference lies with which sampling site was determined to delineate the upper and lower reaches of the Faga`alu Stream. As has been mentioned, site S-5 (**Fig.6**) marked the divide in this study using MODFLOW, as the stream begins to gain again following this station towards the bay. In Schuler et al. (2019), site S-3 is used as the divide between upper and lower portions of the stream. Adjusting the MODFLOW results to follow Shuler's method, the total lower reach would contribute 1,377 m^3/d, lowering the relative error to 16%. The total upper reach would adjust to 2,491 m^3/d, shifting the relative error up to 5%. Overall, the change in stations does not impact the correlation, and the streamflow agreement gives further validation to the results predicted by the model.

Table 12: Direct comparison of the 2014 measured water fluxes of baseflow and SGD against the MODFLOW modeled results from this study.

	Lower reach (m^3/d)	**Upper reach (m^3/d)**	**SGD (m^3/d)**	**Total Flux (m^3/d)**
2014 Study	1,157	2,368	2,587	6,112
MODFLOW	1,434	2,434	2,680	6,547
Relative Error	19%	3%	3%	7%

A significant contribution of SGD (modeled to be 2,680 m^3) enters the coastal waters each day in Faga`alu Bay. The central coastline of the bay, according to the model, contributes more SGD than both the north and south coasts combined. Between the two coasts, the northern one contributes slightly more, which agrees with SGD measurements taken by Shuler et al. (2019). The modeled SGD predicts 18% northern, 13% southern, and 69% central coastline contribution, while Shuler et al. respectively measured 32%, 10%, and 58% SGD contribution for each coastline. This agreement between observations and the

model, supports that the water fluxes determined by the model can justifiably be used to estimate solute and contaminant transport.

5.2.1 Model-predicted contaminant fluxes

The central coast expectedly delivered the most contaminants across the land-ocean interface, with the exception of TDN and N+N (**Tab.7**), which according to the model is delivered more from the northern shoreline. As mentioned earlier, the CS-N site had the highest observed TDN concentration by far, which once input into the model, expectedly produced the similar relative results compared with other sites. The upper reach contributes much more discharge than the lower reach according to modeled baseflow rates, as it is affected by a combination of upland mountain springs and higher elevation gradient. Likewise, pesticides and contaminant amounts entering the stream from baseflow were higher in the upper reach, not because of higher concentrations, but because of much higher water discharge. The only exceptions to this were phosphate, which was distributed equally, and ammonia, which had over ten times higher concentrations in the lower reach. Realistically, on a watershed scale, the lower reach should have higher concentrations of these contaminants in groundwater, as it is urbanized with high population density and accumulation effects could be assumed. Meanwhile most of the upper reach is natural forested area, presumed to be without addition of human contaminants (with the exception of DDT, because of aerial spraying). The reason the model shows higher fluxes of contaminants added to the upper reach is that discharge rates are much higher than those in the lower reach. Ammonia seems to be the only nutrient to have the highest concentration at site S-1 at the bottom of the village.

Despite the increased recognition of SGD's importance to nutrient budgets in coastal regions, studies often emphasize that between the two, streams contribute a much higher rate of discharge (Zektser et al., 2006; Bishop et al., 2017). When comparing total amounts of SGD to stream baseflow in the Faga`alu Bay, however, the model in this study estimates that SGD contributes a comparable amount of water as does the stream in the total budget, at about a 2:3 ratio. This indicates that SGD in a small watershed with a low volume stream as the primary surface water channel, may play a much larger role

than in a coastal watershed with larger streams and rivers. The combined total flux of each contaminant entering the bay each day via SGD and baseflow thus has potential to greatly influence reef water quality and reef health in this designated priority watershed.

5.3 Interpreting the transport model

Assuming acceptable MODFLOW results, MT3DMS was used to determine contaminant flow paths over a period of time. The transport model was created by adding twelve additional data observations from six stream sites (6 glyphosate, 6 DIN). Having more parameters than sample sites can often lead to numerical instability in these types of models (Tonkin and Doherty, 2005; Zheng et al., 2012), as is the case in our study. Sensitivity analysis was used to assist in calibrating the transport model regarding four main parameters (dispersivity, porosity, the ratios of horizontal and vertical transverse dispersivity to longitudinal dispersivity). Dispersivity played the biggest factor in affecting end concentrations of both solutes at all sites in the transport model, whereas porosity affected glyphosate concentrations more than DIN. Ratios of horizontal and vertical transverse dispersivity both affected modeled solute concentrations only at certain sites, while the most sensitive site to all parameters and to both contaminants was the northern coastal spring (CS-N). Extremely high fluxes of DIN appear in this northern coastal sector compared to other regions of the watershed with similar OSDS density, which might be result of how PEST zonally estimated hydraulic conductivity in this location. Despite the use of sensitivity analysis, obtaining well-calibrated values could not be achieved in the transport model. We were, however, able to obtain order-of-magnitude estimates in both glyphosate and DIN concentrations at all sites. As long as basic processes within the aquifer were generally represented, large errors may still be acceptable, as this model will primarily be used as an analysis or screening tool in demonstrating the importance of groundwater fluxes and predicting scenarios involving variables relative to one another, rather than for precise quantitative analysis (Zheng et al., 2012). One limitation in building this model involved simplifying the assumptions in regards to underlying geology. Although hydraulic conductivity was calibrated for each geologic unit, smaller-scale heterogeneities within the aquifer were not accounted

for. This assumption disregards subsurface heterogeneities and the possibility of perched aquifers or dike-impounded water in the higher elevations. Another limitation is the use of observations collected on one day, rather than an average or trend over time. As concentrations at each site could fluctuate greatly over seasons and years, we are reporting results as "per day" and concentrations and fluxes represent dry season estimates. Most importantly, as previously mentioned, the small number of sites sampled highly limits the accuracy of a transport model. Other studies (Shuler et al., 2017; El Khattabi et al., 2018) used more observation points to obtain acceptable calibration. In the future, a wider spatial and temporal distribution of sample sites could be collected to make a more thorough assessment of Faga`alu, however, that is not possible with the currently existing number of wells (n=1). Additionally, it would be of great interest to learn of actual application rates of fertilizers and herbicides in American Samoa, along with true OSDS and piggery mass loading rates, rather than relying on data from multiple studies to make inferences and input into the model. This uncertainty likely played a large role in the discrepencies.

The transport model derived solute fluxes within the same order of magnitude as the values estimated using the hydrogeological model-derived groundwater discharge multiplied by measured concentrations (**Tab.9**). Sources of error between the two models arise from the way water fluxes and associated concentrations were predicted entirely within the cells of the MT3DMS model, while determined by multiplying modeled times measured fluxes in the MODFLOW model. Sections in the watershed where MT3DMS best matched the MODFLOW estimations include the GLY concentrations in the stream's lower reach and on the northern coastline, while DIN concentrations matched best in the stream's upper reach, and on the central and southern coastlines. The total GLY flux in the stream baseflow fell between MODFLOW-derived and observed flux values, while GLY flux was a bit lower than the MODFLOW-derived and observed fluxes in total SGD estimates (**Tab.9**). Transport model-derived total glyphosate flux across the watershed was slightly overestimated in comparison to the observed fluxes, mostly due to inconsistencies in the modeled upper reach of the stream (FG-179 and S-6), where near zero values were obtained despite calibration. MT3D model-derived DIN fluxes were overestimating both sections of the stream as well as in SGD in the northern coastline. The overall SGD

contribution of DIN was estimated to be double the measured, and triple the MODFLOW-derived results (**Tab.9**). With several OSDS units mass loading DIN directly on the coastline, the transport model took these into account, whereas the MODFLOW model used only one site to represent the entire coast. The direct measurements used only one representative concentration as well. These factors likely explain the significantly higher estimate in the MT3DMS model. Similarly, in all cases, the transport model took every application source into account in predicting its fluxes, whereas the other two methods used one representative concentration as the input for entire sections of coastline or streams.

5.4 Scenarios

As there is no recorded data for the locations and amounts of pesticides or fertilizers applied at our site, literature values for annual GLY and N application rates were used. Mass loading rates of DIN from OSDS and piggeries are adapted from Shuler et al. (2019), and are not based on direct measurements, but inferred from household and pigs per household. Increasing or decreasing glyphosate and DIN application and mass loading in the model (by ten times, both ways) proved to linearly change observed groundwater concentrations at each observation site. Using the literature values of the amount and location of application, the transport model captured GLY and DIN distribution trends and concentrations within the same order of magnitude. We can thus be sure that the application and mass loading rates used in the model are in the ballpark of actual applied amounts. It is impossible to get a better estimate on glyphosate input without further studies that assess where glyphosate is applied and how much is being applied in households and agricultural fields. More accurate cesspool data could benefit DIN inputs as well, since the OSDS data used is uncertain in both exact location and amount of cesspools, as well as in rate of leaching into the groundwater.

Scenarios were then run in the transport model to look for relative contributions of each point and non-point source, as well as situations where less contaminant is being applied to the source by improved land management practices. When determining the DIN source contribution, the transport model predicted nearly 90% of groundwater N is being contributed to the observation points by OSDS input.

Only 6% of groundwater N is associated with piggeries and a miniscule 0.1% with assumed fertilizer application from agricultural plots. Agriculture thus may play a very small role in groundwater N fluxes. In Hawai`i, it has been found that very small fractions of N leach into groundwater in the root zone of plants, such as those planted for agricultural purposes (El-Kadi and Yabusaki, 1996), which could explain why fertilizer N shows such small concentrations in the model. Interestingly, when piggeries are run as the only DIN input, the southern coastal spring's (CS-S) DIN concentration contributes 20%, indicating that the model predicts the nearby piggery to play a larger role at this site than piggeries on average at other sample sites. When running a model scenario with naturally sourced DIN across the entire watershed as the sole contributor, simulating pristine conditions, 4% of the total DIN still made it on average to each sample site, showing higher contribution than fertilizer application. The Tafuna study by Shuler et al. (2017) used MT3DMS to predict source contributions and found different contribution, 60 ± 7% OSDS, 20 ± 6% piggery, 9 ± 4% agriculture, and 11 ± 0.5% natural sources. The 2017 study, however, took place on the Tafuna Plain, a geologically different unit, with a completely different number and distribution of observation points.

In a related study, Shuler modeled the Faga`alu water budget (2019) using the SWAT model. SWAT cannot directly estimate groundwater though, as it is a surface runoff model, so inferences were made to obtain groundwater fluxes. The SWAT model estimated a range of contributions to DIN from individual sources, such as OSDS contributing 25-99% of the DIN flux, with very little (< 7%) interpreted as surface runoff. This means that 25-92% of the OSDS DIN flux could be interpreted as groundwater flux. The value of groundwater-derived DIN flux estimated by this study's MT3DMS (90%) would thus fall near the upper limit of that range. The piggery contribution via groundwater pathways was determined to be < 9% according to the SWAT model, matching closely with the MT3DMS prediction (6%) in this study. The agricultural N inputs were too small to be mentioned in Shuler's study (2019), which agrees well with the MT3DMS estimate of 0.1% total contribution. Natural N inputs had wide ranges from 1% to 70% in the SWAT model, while MT3DMS predicted 4% contribution to the total groundwater flow. Despite the limitations in the transport model due to poor calibration, the predictions

of each source contribution were reasonable in comparison to the SWAT model predictions from Shuler et al. (2019). This does not validate the MT3DMS results, but can at least illustrate the usefulness of comparing the sources' fluxes relative to each other. Scenarios regarding improved OSDS installation and decreased pesticide-use were thus run to predict their reduced impact on groundwater quality, and how improved practices might positively affect the health of an ecosystem.

When DIN mass loading rates were halved for each OSDS, simulating a two-fold improvement to the assumed cesspools that occupy the lower Faga`alu watershed, the average concentrations of the observation points improved by 46%. With the limitations of a poorly-calibrated transport model (**Tab.8**), this percent is not to be interpreted as a true estimate of actual improvement if advanced septic systems were implemented, but it can give a general sense that much less DIN would be entering groundwater pathways if better infrastructure was installed in Faga`alu.

Glyphosate-use scenarios were performed to see if any relative contributions could be assessed from urban or agricultural inputs. When domestic inputs were run, excluding agriculture, 71.5% of the total glyphosate still made it on average to all sites. When domestic inputs were excluded, agriculture contributed 28.5% on its own to all sites on average. The literature-based sorption rates and decay rate constants were added as parameters in the transport model, and results show that degradation of glyphosate may play a large role in which sources contribute the most to the observation sites. According to the model, the domestic inputs, which having half the initial concentrations as the agricultural inputs, are delivering 71.5% of the herbicide to the observation points. This indicates that proximity may be an important factor in glyphosate contamination. As glyphosate is known to undergo a rapid degradation process, the more distant agricultural plots, although assumed higher applied amount, do not contribute as much of the herbicide to the stream. Agricultural glyphosate is likely broken down before reaching observation points within the village, while the assumed lower application rates in the domestic region seem to contribute more to the estimated fluxes, based primarily on proximity to the observation sites. Scenarios were run with 1) half the domestic input of glyphosate and 2) with half the total glyphosate (domestic and agricultural) applied. Lowering the domestic input lowered average concentrations by 37%

across the watershed, while lowering all glyphosate by half, showed a 50% drop averaged across the sites. This shows that improving application techniques or limiting the use of glyphosate-based herbicides in the watershed could significantly lower the amount of contaminant in groundwater, assuming domestic use to be a more important factor because of the compound's instability. With these decay rates, it is unlikely for GLY to reach dangerous levels in the aquifer. Again, the usefulness in running scenarios for GLY primarily lies in the comparison of the degradation pathways over distance rather than interpreting the modeled against observed results (**Tab. 8**). Assumptions are made in assuming half the amount of glyphosate is applied domestically as is agriculturally, which is in no way a representation of what the true application rates may be. The spatial application of glyphosate may vary quite heterogeneously across the watershed as well, from house to house, and agricultural plot to another, leading to more model uncertainties. Finally, as mentioned previously, the underlying geology and soil properties may play a role in the attenuation of glyphosate from one location to the next.

5.5 Potential threat to reef community

Glyphosate is the most common ingredient in top-selling herbicides around the world today (e.g. Roundup), and its harmful effects have been a popular issue in recent years, specifically in regards to its carcinogenic nature to humans (Tarazona et al., 2017; Smyth and Miller, 2019). As this is a widely combative issue, the effect it has on aquatic ecosystems also needs further assessment. According to the model in this study, 900 mg/d of glyphosate are entering the Bay, with near-ocean groundwater concentrations reaching values likely similar to measured coastal spring values (154 to 301 ng/L). In a study by Diu (2016) focusing on coral being exposed to different concentrations of glyphosate, the herbicide was generally found to not have a harmful effect on reef fertilization or settlement. Only in contained studies, at concentrations above 690,000 ng/L does glyphosate show any effect on coral fertilization (Diu, 2016), which is three magnitudes higher than what was found in Faga`alu coastal spring samples. The amount of glyphosate that enters Faga`alu Bay each day via baseflow and coastal SGD (0.9 g/d, or 900,000,000 ng/d) likely dilutes relatively fast as it enters a large body of water in the bay, which

empties into the Pacific Ocean. Gallagher et al. (1996) found low concentrations of pesticides across sampled coastal sites, but detected none in the offshore surface water or sediment samples. Although glyphosate can be relatively stable in marine water, with a half-life ranging from 47 to 267 days, depending on the type of microbial communities present (Mercurio et al., 2014), it is not known to bioaccumulate into organisms as it has low lipid solubility (Schuette, 1998). Diu (2016) though, found that lower fertilization rates in coral can be attributed to the runoff of Roundup (Monsanto ®) into marine environments. Roundup is the primary herbicide in which glyphosate is often linked to as the main ingredient. However, in the study, it was found that glyphosate by itself is not detrimental to reef health, but that the Roundup solution was in fact linked, indicating that other ingredients in its formulation are likely to have toxicity to the reef (Diu, 2016). Thus, monitoring glyphosate is important in Faga`alu, for as it is an ingredient in other more harmful pesticide recipes, such as Roundup, which may pose a threat to the reef community. That being said, the chronic effects of the glyphosate itself are likely not a factor on reef health, as the dilution and degradation of glyphosate is relatively rapid in open water (Schuette, 1998). One limitation in this study, is that no marine samples from Faga`alu Bay itself were taken during the study, thus actual offshore concentrations of glyphosate are not known to directly compare with other studies.

DDT, however, has a much longer residence time than glyphosate and is able to bioaccumulate in the tissues of organisms that uptake it. Studies have shown that DDT likely has an effect on the calcification of adult corals and other calcifying organisms in the reef community (Kwok, 2015; Porter et al., 2018), similar to the effects it had on the calcium-related eggshell thickness of bird eggs in prior studies (Peakall, 1970; Porter and Wiemeyer, 1969). The fact that 840 mg of DDT is contributed to Faga`alu Bay via stream baseflow and SGD each day, highlights its persistence and ubiquity in the environment decades after the 1972 ban by the EPA (2016). The assumption that it is no longer sprayed indicates that DDT's long half-life gives it much time to accumulate in the ecosystem, and has the potential to affect growth and reproduction of marine organisms within the reef as its daily load into the bay has spanned several decades, and may continue several more.

Excess nutrients have already been documented in Faga`alu Bay in other studies (Whitall and Rice, 2015; Shuler et al., 2019). No MCLs have been set for nutrients such as N and P, as they are often limiting to ecosystems under natural conditions (Oram, 2014b). However, corals are sensitive to excess nutrients, and levels above 14 μg/L-N (nitrate or ammonia) and 3 μg/L-P (orthophosphate or organophosphate) can be considered unhealthy for a reef ecosystem, as it could promote more algal growth over the reef, outcompeting the coral (Goreau and Thacker, 1994; Mosley, 2005). Total N entering the bay each day is 701 g (7.01e+8 μg) and total P is 815 g (8.15e+8 μg) via baseflow and SGD according to our model. It can be assumed that high concentrations, especially in particulate form as it tends to fall to the bottom with sediment, could be accumulating in the reef ecosystem and leading to algal competition for resources with the coral. Unfortunately, the bay itself was not sampled during the 2016 investigation, so observed coastal concentrations are not available to analyze and compare to suggested healthy levels.

6. Conclusions

By integrating field-collected groundwater concentrations with a hydrogeological model of the Faga`alu watershed in American Samoa, relative SGD and baseflow fluxes of pesticides and nutrients were determined for each sector of coastline and each reach of stream, respectively. Although flow rates modeled in this study are only calibrated against a snapshot of observations, the model-estimated contributions reasonably capture water flow to within 7% of the total Faga`alu water budget from previous dry season observations by Shuler et al. (2019). Modeled stream baseflow was also within 5% of what the Faga`alu Stream gauge recorded during the seepage run, which provides confidence in model estimated groundwater fluxes. The model predicted the central coastline to be contributing 119% more SGD to Faga`alu Bay than both the northern and southern coastlines combined, while the upper reach of the stream is contributing 70% more baseflow than the lower reach.

Field investigation confirmed pesticides to be present in the groundwater, and by incorporating their concentrations into the MODFLOW hydrogeological model, fluxes across the land-ocean interface

could be estimated. The model estimated a delivery of just less than 1g of glyphosate to the bay each day, while delivering nearly 9g of DDT to the bay. With a relatively fast degradation process, and such small amount of GLY entering the bay each day, and based on the study by Diu (2016), it seems that the impact on the reef may not be significant. The continued presence of DDT, however, could have chronic effects on the health of the reef though, as it accumulates in fatty tissues of organisms and has been shown to have negative effects on calcium carbonate-building species, such as the coral itself (Kwok, 2015; Porter et al., 2018). Nutrient investigation revealed that 713 g of TDN and 842 g of PO_4 are crossing the land-ocean interface each day. Although concentrations of N at any individual sampling site do not exceed EPA recommended values (Table A1), the constant N flux into the bay may cause algal growth to compete with and thus harm a healthy coral reef. The amount of OSDS units and piggeries in the coastal region likely play a large role in this excess N. Concentrations of PO_4 are above the acceptable limits (Oram, 2014b) in many locations, and thus its delivery to the bay may also be impeding the health of the reef, although some of the PO_4 is suspected to come from natural erosional sources.

The transport model developed in this study provided useful qualitative analysis of contaminant transport and tested hypothetical scenarios for contaminant loadings. Despite limitations in the transport model, concentrations within an order of magnitude of the observed were estimated. The model proved useful in signifying the importance of groundwater transport pathways, and calibration indicated which model parameters most affected transport of contaminants with their specified attenuation rates and degradation processes. A scenario was run where the representative pesticide GLY simulated transport via agricultural and urban zones provided unanticipated results, where it was estimated that domestic application of GLY, although assigned 50% less that of agricultural application in the model, delivered 150% more GLY to the observation sites. A scenario where a 50% decrease of GLY application was added to the model, showed a linear decrease in GLY arriving at observation sites. Scenarios were then run with the representative nutrient DIN, revealing that its groundwater fluxes primarily traced back to OSDS-related sources (90%), while all other N-sources were estimated to contribute only 10% to the total N-flux at observation points. Improvement of OSDS units in the future (i.e. upgrading from cesspools to

septic systems) was then simulated to demonstrate the improvement that could be accomplished with better land-management practices. A 46% improvement showed how upgrading this one source of DIN across the watershed could significantly improve groundwater quality in the future.

The combined field and model-based characterization used in this study demonstrates the importance that groundwater plays in solute transport during baseflow conditions. Very little rain is present to create surface runoff and elevated streamflow under these conditions. To give perspective, the delineated stream baseflow from the day of sampling calculated by the stream gauge at Faga`alu was 95% of the total daily flow. This means that 95% of the streamflow was derived from groundwater pathways feeding the stream in gaining sections. Additionally, SGD produces 41% of the total water budget, and is completely groundwater-derived. With this said, considering the fluxes predicted in this hydrogeological model, it is evident that groundwater plays a significant role to pesticide and nutrient fluxes into the coastal reef ecosystem at all times of the year, especially during the dry season of July through September. Better land-use practices can help reduce the leaching of pesticides and fertilizers into this sizable subsurface reservoir, while improved wastewater management can help mitigate nutrient overloading into the aquifer. As Faga`alu has been designated a priority watershed in monitoring reef health, it is important to consider not only pollutants and trash being thrown into the stream or running off properties via surface pathways, but also as demonstrated by this study to consider groundwater via SGD and stream baseflow as a significant pathway for pesticide and nutrient loading into the bay.

APPENDICES

Table A1: The EPA has set MCLs for nitrate and nitrite, but not for other N-species. Ranges of these other parameters are listed, by guidelines according to the sources listed below the table.

	Nitrates (mg/L)	Nitrites (mg/L)	NH3 (mg/L)*	Range of Measured TDN,DIN, or N+N (mg/L)	Range of Measured NH3 (mg/L)
EPA Maximum Contaminant Level (MCL)	10.0	1.0	None	Range: 0.014 – 0.333	Range: 0.002 – 0.067
Threat to Fresh Water Aquatic Life – acute **	32.8	0.06	Range: 0.102 - 2.08		
Threat to Fresh Water Aquatic Life – chronic (30-day average) **	3.0	0.02			
Threat to Marine Aquatic Life – acute **	None	None			
Threat to Marine Aquatic Life – chronic (30-day average) **	3.7	None			

* Range given for NH3, depending on combination of pH and Temperature

**https://www2.gov.bc.ca/assets/gov/environment/air-land-water/water/waterquality/wqgs-wqos/approved-wqgs/nitrogen-overview.pdf

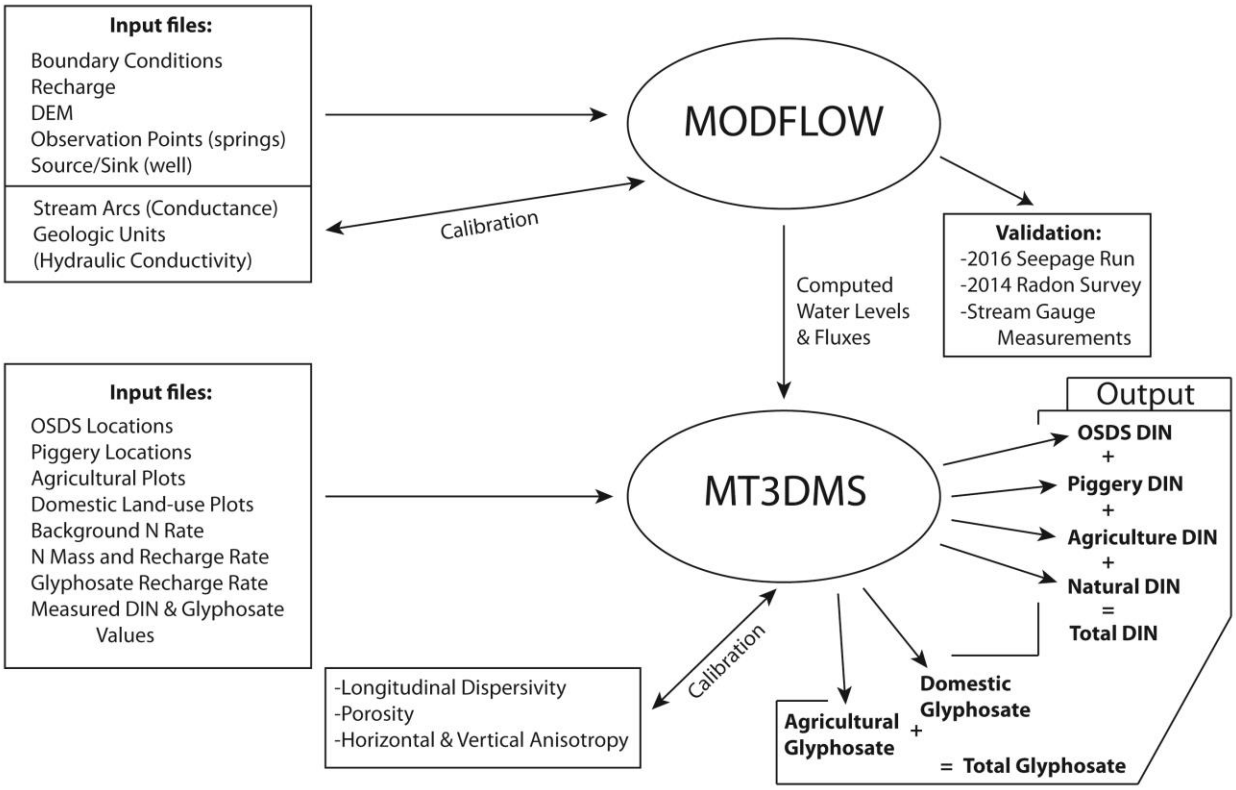

Figure A1: Flow chart describing the models used in this study, including inputs, the hydrogeological model (MODFLOW), the transport model (MT3DMS), and model outputs.

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