

FIELD ASSESSMENT AND GROUNDWATER MODELING OF PESTICIDE
DISTRIBUTION IN THE FAGA'ALU WATERSHED ON TUTUILA, AMERICAN
SAMOA

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ABSTRACT

Pesticide use is prevalent worldwide and their dispersal across water resources has been gaining increased attention. Pesticides in natural waters can be toxic not only to terrestrial and aquatic biota, but also to humans. Pesticide studies usually focus on surface waters since surface runoff and sediments are considered their primary migratory pathways. Groundwater pathways, however, have not been as thoroughly investigated since most pesticides are not commonly considered mobile and persistent enough for subsurface dispersal. Pesticide transport through aquifers may take several decades, eventually reaching drinking water sources or the marine environment.

Groundwater and surface water interactions were investigated as a vector of pesticide migration on the island of Tutuila in American Samoa in August 2016. For the island-wide study that looked at pesticide spatial variation, samples were collected from groundwater wells and springs as well as streams, for selected pesticides (glyphosate, imidacloprid, azoxystrobin, DDT/DDE). A more detailed pathway-specific study was conducted in the Faga`alu watershed, where field data were integrated into a groundwater model to reconstruct flow paths and pesticide discharge from the groundwater aquifer to the stream and the coastline. In combination with land-use maps, groundwater models were used to identify potential pesticide sources.

All measured pesticide concentrations on Tutuila were well below EPA regulated limits. They were found at the same frequency and in the same concentration ranges in surface and groundwater samples. DDT was uniformly distributed, but there was a variation in glyphosate and imidacloprid spatial distribution that followed population density. In Faga`alu, groundwater pathways were responsible for a majority (~70%) of glyphosate and DDT discharge (350 & 482 mg/d and 2990 & 5519 mg/d) to the stream and coastline, respectively, in comparison to surface runoff according to my model and field measurements during dry season. The timescale of the transport spans from many decades (DDT applications were banned in the 1970s) to most recent applications of glyphosate that were traced back to populated regions, where this herbicide is probably applied in backyard-scale agriculture rather than large-scale farming operations. This study shows the significance of groundwater flow for pesticide transport and discharge into the coastal ocean.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASCC	American Samoa Community College
AS-EPA	American Samoa Environmental Protection Agency
ASPA	American Samoa Power Authority
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
ELISA	Enzyme-linked immunosorbent assay
EPA	Environmental Protection Agency
GIS	Geographical Information System
GMS	Groundwater Modeling Systems
HHP	highly hazardous pesticide
HRP	horseradish peroxidase
LD ₅₀	Lethal Dose in 50% population
MCL	Maximum Contaminant Level
MT3DMS	Modular Transport Three Dimensional Model Simulator
NASDA	(American Samoan) National Association of State Department of Agriculture
²²² Rn	Radon-222 isotope
SGD	Submarine Groundwater Discharge
SWAT	Soil and Water Assessment Tool
USCRTF	United States Coral Reef Task Force

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1. Introduction

American Samoa, a heavily populated group of islands in the southern Pacific Ocean, roughly 4200km (2610mi) south-southwest of the Hawaiian archipelago, has persistent issues with contaminated drinking-water. Since 2009, boil-water notices have impacted much of the population whom rely on the municipal water supply in this American territory, as water quality problems have become a growing concern (ASPA 2014). Contamination from non-point sources in American Samoa include elevated nitrate levels in water resulting from nitrogen releases from private on-site wastewater disposal systems (OSDS), agricultural runoff, and livestock waste (piggeries), as well as pathogens likely originating from those same sources (ASPA 2012, AS-EPA 2016). Tracing of OSDS and piggery-related pollutants was covered extensively in a study by Shuler (2016). Agricultural applications of potential pollutants such as pesticides, which are also a cause for concern in bodies of water, were explored in previous studies by Polidoro et al. (2017). The latter study focused on selected organic-based pesticides and pollutants, mostly in surface waters, because streams and sediments are considered their primary pathways. In general, groundwater pathways of pesticides have not been investigated in the past because most pesticides are not considered mobile enough to disperse in aquifers (U.S. Congress 1990). Pesticides are produced with the sole purpose of destroying specific living organisms, but are known to collaterally and negatively affect other non-target biota as well (Watts 2016). Pesticide-use is a growing concern in society today, not only for its effects on the flora and fauna with which it may come in contact with, but also because of its effects on humans (U.S. Congress 1990).

Imprudent agricultural techniques can ultimately lead to the leaching of chemicals into aquifers (Polidoro et al. 2017). Pesticides can percolate into groundwater from sprayed agricultural fields overlying an aquifer. Leaching rates can depend on many factors, such as soil properties (i.e., hydraulic conductivity, porosity, adsorption capacity), climatic factors (i.e.,

precipitation, temperature), farming practices (i.e., amounts and frequency of application), and specific pesticide properties (i.e., propensity for sorption, degradation). Drinking water pulled from groundwater resources can expose humans to the risks posed by these chemicals (Geisler 2004). Tutuila, the largest island in American Samoa, obtains about 90% of its drinking water from groundwater sources (Shuler 2017). Thus, it is timely to examine the presence and transport of pesticides through surface water and groundwater reservoirs on Tutuila.

The Faga'alu watershed on the island of Tutuila is a perfect study site for examining pathways of pesticide migration into and within groundwater aquifers, because of its relatively human-perturbed land-use and large population gradients, which have resulted in water quality problems. Pesticide distribution in streams and sediments has been studied previously (Polidoro et al. 2017), and the Faga'alu Stream has been found to discharge fertilizers and nutrients into the harbor. As a consequence, high concentrations of these compounds accumulate near the stream mouth (Fenner 2008). However, pesticide distribution has not yet been investigated in the context of surface water-groundwater interactions. For example, the role of baseflow (groundwater discharge into the stream) has not been studied as a vector of pesticide migration. Stream baseflow (see **Figure 31** in Appendix B for illustration) serves as a direct link between groundwater and the surface water that eventually discharges into the ocean. The stream channel, therefore, acts as an effective conduit for contaminants, and plays a role in the diminishing health of coral reefs (Fenner 2008). In addition, submarine groundwater discharge (SGD) has been shown to deliver nutrients into the harbor (Shuler, unpublished 2018), and it may also contribute pesticides across the terrestrial-marine interface. Using measured pesticide concentrations and modeled groundwater pathways through the aquifer, SGD fluxes can be estimated for the Faga'alu watershed to provide a more comprehensive understanding of surface-groundwater interactions, and total pesticide leakage into the harbor.

1.1 RESEARCH OBJECTIVES

The research presented in this thesis aims to investigate pesticide fluxes across the watershed with a specific focus on surface water - groundwater interactions as a vector of pesticide delivery to streams and the coastal ocean. The specific objectives of this research are:

- 1) Compile an inventory of selected pesticides in groundwater and selected streams across the island of Tutuila to identify which pesticides are of concern and which areas are most affected by their presence.
- 2) In a targeted study focusing on Faga`alu watershed, locate and quantify the contribution of groundwater and associated pesticide fluxes to the baseflow in streams, and as submarine groundwater discharge (SGD) to the ocean.
- 3) Based on measured fluxes and other hydrological parameters, create a hydrogeological model of the Faga`alu watershed, and determine pesticide fluxes across the land-ocean interface; use this model to infer contaminant sources and pathways.

To achieve these objectives, surface and groundwater samples have been collected island-wide and analyzed using enzyme linked immunosorbent assay (ELISA) kits for specified pesticides. Pesticides were selected based upon information obtained from collaborators at the American Samoa Community College (Dr. Mark Schmaedick, ASCC), the American Samoa Environmental Protection Agency (AS- EPA), and the American Samoan National Association of State Departments of Agriculture (NASDA). One important objective of the project is to provide feedback to these agencies, to report back the findings of this study so that they can be applied to improve management practices in contaminant control on the island.

In the focused study of the Faga`alu watershed, to investigate the potential of groundwater as a vector of pesticide transport into Faga`alu Bay, two processes were evaluated:

- 1) groundwater contribution to the stream and associated pesticide fluxes, and 2) direct

groundwater discharge into the bay via springs and seepage, and associated pesticide fluxes. These processes were identified and quantified using radon as a groundwater tracer (Burnett and Dulaiova 2003). Combining pesticide distribution in Faga'alu with a MODFLOW numerical model, groundwater pesticide fluxes were determined, enabling the source, the site of application, to be identified. This research contributes new insights into the understanding of pesticide fluxes, which are often assumed to be associated with sediment and surface runoff alone. I hypothesize that the investigation of groundwater and surface water interactions, as a vector of pesticide migration, will demonstrate the importance of groundwater contribution to contaminant transport across a watershed such as Faga'alu.

1.2 REGIONAL SETTING AND FEATURES OF THE STUDY SITE

1.2.1 Tutuila, American Samoa: Population, geology, and climate

Tutuila (14S, 170W), located roughly halfway between Hawai'i and New Zealand, is the largest (137 km²) of the seven islands that comprise the U.S. territory of American Samoa. Aside from being the most populated of the islands, Tutuila hosts the capital city of Pago Pago, and acts as the center of government and business ("Demographic Baseline Report..." 2007). The population of the territory has remained at approximately 55,000 people since the late 1990s ("American Samoa: Data." 2017). The most densely inhabited areas lie on the Tafuna-Leone Plain of southwestern Tutuila, and along the coastlines of the island. In 2008, the population density was estimated at 460 people per square kilometer. If one includes only habitable non-mountainous regions, where the majority of people reside, the density is much greater ("Demographic Baseline Report..." 2007).

Geologically, Tutuila rose from the ocean approximately 1.5 Mya in similar fashion to Hawai'i, as a mid-ocean volcanic hotspot (Craig et al. n.d.). The eroded shield volcanoes remain

today, with dense igneous rocks comprising their cores, and alkalic igneous rocks derived from lava flows and pyroclastic deposits lying on top. Much of the pristine interior of the island is mountainous and forested, with alluvial valleys spaced regularly along the coastline (Izuka et al. 2007). These mountainous regions are known as the ‘Older Volcanic’ region of Tutuila. The Tafuna-Leone Plain stands out as the relatively flat southwestern portion of the island, and is geologically much younger than the rugged interior. The highest elevation on Tutuila is Matafao Peak at 653m (2,142 ft.), which is located between the capital Pago Pago and the Tafuna-Leone Plain (Craig et al. n.d.). Hydrologically, the two regions vary considerably. The mountains host a greater number of perennial streams fed by groundwater discharge, while the plain has larger, more well-developed streams that discharge into the ocean (Izuka et al. 2007).

In regards to climate, Tutuila lies within the South Pacific Convergence Zone (SPCZ) and experiences seasonal fluctuations in rainfall and cloud cover. Rainfall also varies geographically, from the orographic zone over the interior mountains to the drier southern and eastern coastlines (Izuka et al. 2007). Annual average rainfall island-wide can range from 3,000 to 6,000 mm/yr, which leads to a highly productive groundwater flow beneath the ground surface of the island (Shuler 2016). Generally, a longer and warmer wet season lasts from October through May, while a shorter and cooler dry season lasts from June through September (Craig et al. n.d.).

Agriculture is widespread in American Samoa. Consequently, the distribution of non-point source pollution is widespread, as well. A significant portion of the food consumed is grown locally in a self-supporting manner, and over half of the arable land is currently under cultivation. Certain farms are suspected of using illegally-imported synthetic fertilizers and pesticides due to poor regulation (Shuler 2017). NASDA has been enforcing stricter policies since 2016, banning certain farmers from selling their products if they are suspected of using illegal substances (Sagapolutele 2016).

1.2.2 Faga`alu watershed: Details of study site

The Faga`alu watershed in central Tutuila was chosen as the site of focused investigation of surface water-groundwater interactions because it is considered a priority watershed for conservation and remediation by the U.S. Coral Reef Task Force (USCRTF). The watershed (1.78 km²) includes a main stream (Faga`alu Stream), with many branching ephemeral streams. The main stream runs approximately 3 km, from the high elevations of Matafao Peak, down an alluvial valley, to finally empty into Faga`alu Bay of the outer Pago Pago Harbor region of the island (Messina and Biggs 2016). The undisturbed upper watershed is steeply sloped and heavily forested, while the lower watershed consists of a flat alluvial plain where the developed Faga`alu village lies. The stream in this developed region is heavily disturbed by human activity. Whereas the slopes consist of dense rocks from the Pago volcanic series, the more porous alluvial plain of the lower valley consists of well-drained silty clay loams to fine sandy loams (Messina and Biggs 2016). Not far upstream from the bay, the LBJ Tropical Medical Center (the primary medical facility of Tutuila) occupies a significant area of Faga`alu village. Along with housing structures and paved roads in the lower valley, increased urban runoff may result from overland flow and lower recharge rates in soils near the ocean. At the boundary of the developed area, in the direction of the mountains, lies a quarry with exposed rough terrain, which is prone to erosion. Until recently, this quarry had contributed large amounts of sediment runoff into nearby Faga`alu Stream. Retention ponds were installed in 2014, however, to mitigate much of the particulate-laden runoff (Messina and Biggs 2016). One groundwater well (regulated by ASPA) used for municipal water is also present in the watershed, just west of the hospital and adjacent to the stream.

Faga`alu Bay, part of the outer Pago Harbor, has a fringing coral reef that extends 50-400 m offshore. Water quality of the bay is currently a major concern, due to turbid, nutrient-enriched waters from the high-sediment runoff of the anthropogenically polluted stream (“American

Samoa Watershed...” 2000). As a consequence of this concern, the USCRTF has begun a remediation program in the watershed.

In this study, Faga’alu serves as the watershed-scale focus area for which the hydrogeological model, built using MODFLOW software, is constructed. The model is used to create simulations of possible contaminant transport pathways in the aquifer that pesticides may follow. The seven major sample collection stations in the Faga’alu Stream, one well and two coastal springs, are shown in **Figure 1**.

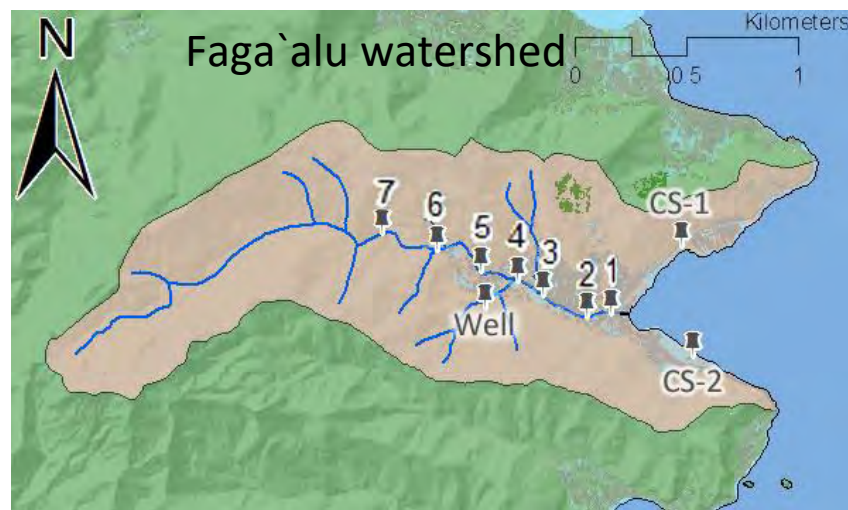


Figure 1: Seven stream study sites, 1 well, and 2 coastal springs make up the detailed watershed-study of Faga’alu.

1.3 PESTICIDES

1.3.1 Pesticide-use in American Samoa

Pesticides designed to kill specific unwanted life forms can ultimately have adverse effects on humans who come into contact with them. Pesticides can negatively impact non-target flora and fauna in an ecosystem, as well. Since living organisms often share similar biochemical processes, all may be susceptible to dangerous synthetics intended for other species; whether the chemical mode of action acts analogously or not on separate species (Watts 2016). For example, roughly 70 percent of applied pesticides from a study in Thailand were washed off plants into surface

runoff and the vadose zone, leaving excess residue to easily enter the food chain (Watts 2016). On Pacific islands such as Tutuila, which share a physical relationship with the marine environment, pesticides that wash off land may affect coastal as well as riverine communities. Pesticides may play a role in weakening the health of coral reef systems, for example, causing them to be more susceptible to natural stresses such as climate change (Watts 2016).

According to the National Toxics Network, American Samoa currently has 21 actively registered pesticides in use on its islands. Of the total, six are considered highly hazardous pesticides (HHPs) by the Joint Meeting on Pesticide Management (JMPM). The HHPs in use on Tutuila include carbaryl, glyphosate, lambda-cyhalothrin, malathion, paraquat, and permethrin (Watts 2016).

In my study, four pesticides were measured in surface and groundwater samples taken across the island of Tutuila using the ELISA screening method. The HHP glyphosate was included in this study, as it is the most widely-used herbicide on the planet. Glyphosate is distributed by Monsanto as a key ingredient in 'Roundup.' The other three pesticides were selected based upon advice of local experts, as mentioned earlier. These included two pesticides that are suspected of being applied illegally, or in excess, on Tutuila: imidacloprid and azoxystrobin. Imidacloprid, although considered an HHP, is not registered or known to be in use in American Samoa, so its presence, if found, would indicate illegal use. Azoxystrobin is not considered an HHP, and is one of the 21 registered pesticides in American Samoa, and thus could be expected to be found in samples. The fourth pesticide evaluated is DDT, also an HHP (Watts 2016). DDT is no longer registered for use in Samoa (banned since 1972), but evidence exists of widespread use in the 1940s and 1950s, as it was sprayed heavily on many other Pacific islands. The 1949 annual report on American Samoa, prepared by the U.S. Navy, gives a brief indication that DDT was being prepared for an extensive program to combat mosquito populations in the islands (Report on American Samoa... 1949). Although no literature directly mentions its use, it can be implied

based upon the report that DDT was likely sprayed island-wide via airplane, following the 1949 report. The characteristics of each of these four pesticides are summarized briefly below.

Prior to summarizing each pesticide, certain terminology and abbreviations must be introduced, as these will be used in the following descriptions. To begin, pesticides can be subdivided into several classes, each of which are aimed at terminating different types of pests. In this study, the three classes of pesticides tested for are herbicides, insecticides, and fungicides. These are aimed at destroying unwanted plants, insects, and fungus, respectively. The United States Environmental Protection Agency (US-EPA) often sets standards and limits of consumption for each pesticide based on toxicity, and thus the following terms will be used to describe the toxicity of each of the four pesticides. The maximum contaminant level (MCL), set by the Safe Drinking Water Act (SDWA) in 1974, is the highest level of contaminant allowed to be consumed by an individual from a public water system (<https://www.epa.gov>). In this study, parts per billion (ppb) was used as the unit of measure. A second standard, the ‘lethal dose’ (LD_{50}) is the amount of contaminant which causes death in 50% of tested animals (Schuette 1998). In each case, for this study, the LD_{50} pertains specifically to rats, and is measured in units of mg/kg (equivalent to ppm).

1.3.2 Glyphosate

Most commonly known for being the primary ingredient in ‘Roundup,’ glyphosate has been distributed by the Monsanto Company since its introduction in 1974. It has become the most heavily used herbicide in the history of the planet, and will likely remain popular in the coming decades. A total of 8.56 billion kg has been used worldwide between 1974 and 2014 (Benbrook 2016). Glyphosate is a non-selective, non-residual, and broad-spectrum herbicide used primarily on grass, weed, and brush overgrowth, and undergoes a unique degradation pathway in the environment as seen in **Figure 2**.

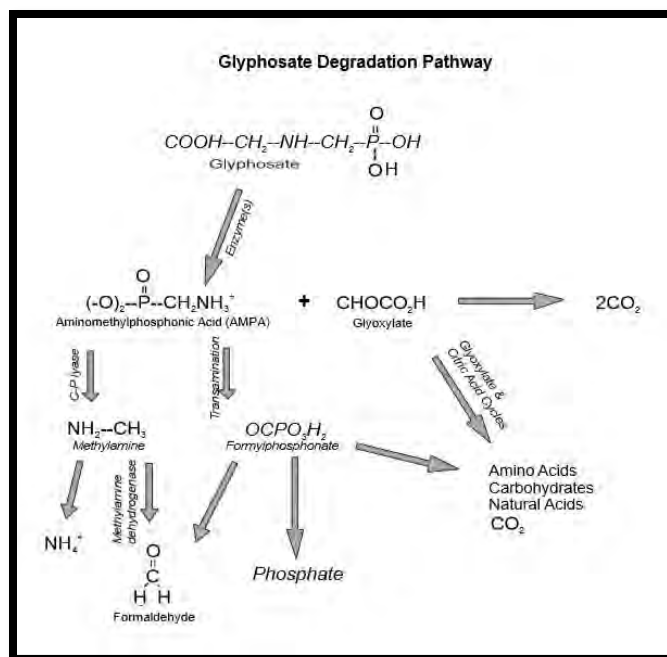


Figure 2: Degradation pathway of glyphosate, as the herbicide is broken down from parent form back to CO_2 , NH_4^+ , PO_4^{3-} , and other end forms (Schuette 1998).

In performing its function on target plants, glyphosate accumulates more efficiently in regions of active cell division, where it stunts plant growth via inhibition of the biosynthesis of essential primary proteins. These affected proteins include enzymes such as 3-phosphate synthase (EPSPS), 5-enolpyruvylshikimate, and aromatic amino acids L-tryptophan and L-phenyl-alanine. Disruption of these enzymes and proteins can affect many physiological processes, from disease immunity to sprout-suppression in plants (Paul 2017). The symptoms develop relatively slowly in hosts, gradually wilting the leaves and leading to a yellow discoloration, and eventual browning and drying of exposed vegetation. Half-life for glyphosate varies considerably (1.5 to 130 days) depending upon: 1) the pathway it takes, and 2) the conditions under which it is exposed (Schuette 1998).

Glyphosate has an LD_{50} of 4320 mg/kg in rat test subjects (Schuette 1998), and the EPA has set an MCL of 700 ppb (0.7 mg/L) for human consumption in drinking water (*National Primary Drinking...* 1995). Because it is water soluble and inactivated by microbial degradation in soil and water, glyphosate is generally non-toxic to fish, birds and mammals; and does not

bioaccumulate in the food chain (Schuette 1998). There are, however, chronic effects due to prolonged exposure. Glyphosate has been linked to kidney and reproductive damage, for example, although evidence is inadequate to link it to cancer (*National Primary Drinking...* 1995). Many recent studies have encouraged its inclusion on the list of carcinogens (Myers et al. 2016). As of July 7, 2017, the state of California has agreed to list glyphosate as a carcinogen, after the World Health Organization (WHO) International Agency for Research on Cancer (IARC) labeled it a “probable carcinogen” (Hogue 2017).

Glyphosate was chosen as the first pesticide tested on water samples from Tutuila, due to its wide use and the likelihood of its occurrence in a large proportion of sample sites. These characteristics render glyphosate an ideal tracer of dispersion in the hydrogeological model. Presence and concentration of glyphosate was used as an indicator of which sites to prioritize in testing for the other pesticides.

1.3.3 Imidacloprid

Imidacloprid is an insecticide that belongs to the neonicotinoid family of pesticides, and is currently the most extensively used insecticide worldwide (Abraxis LLC. *Imidacloprid* n.d.). It specifically targets sucking, chewing, and soil insects, and is even used in flea treatments for domestic pets. Imidacloprid is highly water soluble, suggesting potential to leach into groundwater. Some studies, however, suggest a level of immobility in silty loam soils (Bacey n.d.), similar to those found in the Faga`alu alluvial plain. Half-life of imidacloprid can range under different conditions in soil from 27 to 229 days, and is only 3 hours under aqueous photolysis. The degradation pathways of the insecticide are illustrated in **Figure 3** (Bacey n.d.).

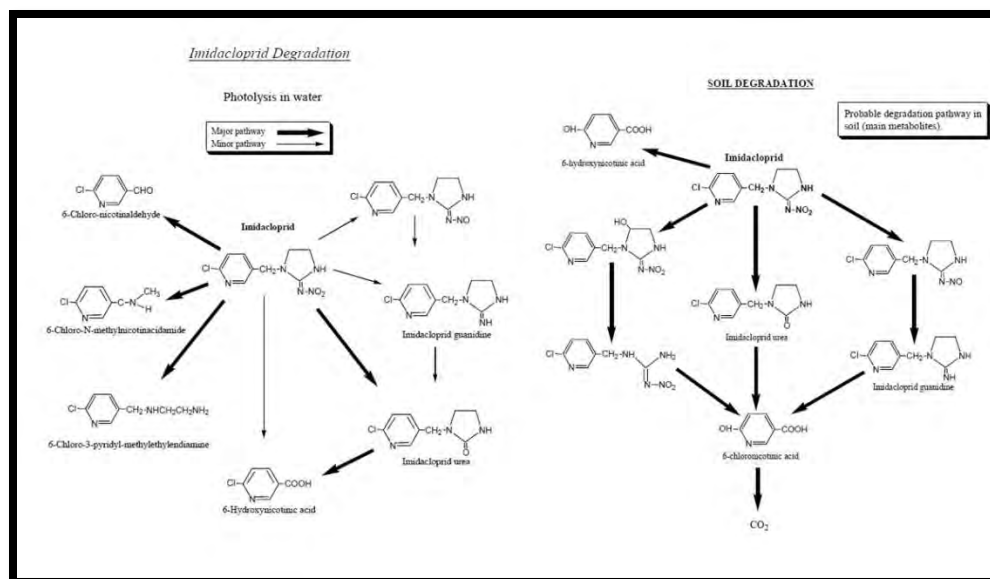


Figure 3: Degradation pathways of imidacloprid via photolysis and in the soil (Bacey n.d.).

The active sites in an imidacloprid molecule act selectively in insects as agonists to nicotine acetylcholine receptors (nAChRs) (Abraxis LLC. *Imidacloprid* n.d.). Imidacloprid attacks cholinergic receptors in the central nervous system (CNS) of an insect, competing for receptor sites with acetylcholine (an excitatory neurotransmitter at synapses in the CNS) (Johnson 1994). The active sites do not react in the same way with vertebrate nAChRs as they do with insects, and are thus viewed as presenting little toxicity to mammals and other macrofauna (Abraxis LLC. *Imidacloprid* n.d.). Although the U.S. EPA has not assigned an MCL to this insecticide in regards to human health, other measures have been assigned via animal testing. The LD₅₀ ranges from just under 100mg/kg to >5000mg/kg in tested mice, rats, and rabbits (Koshlukovam 2006).

In honeybees by comparison, the LD₅₀ is 0.039 mg/kg, which indicates a much higher toxicity level at lower doses (Johnson 1994). The lower LD₅₀ threshold for honeybees may be (in part) responsible for the diminishment of their populations, and may have similarly impacted other beneficial insect species around the world. Reports in 2006 describe the collapse of the western honeybee colonies across North America, Europe and Asia (Abraxis LLC. *Imidacloprid* n.d.). This collapse was first thought to result from a parasite, but has since been attributed to

neonicotinoids. These insecticides, which are carried by wind, contaminate the pollen and nectar that bees collect (Abraxis LLC. *Imidacloprid* n.d.). Although considered relatively non-toxic to humans, a case of nonfatal gastrointestinal difficulties and respiratory problems in humans has recently been reported in India, due to inhalational exposure to imidacloprid (Kumar 2013).

1.3.4 Azoxystrobin

Azoxystrobin is a broad-spectrum fungicide, designed to combat several major groups of fungal diseases, and is in use worldwide. It is known to contaminate drinking water sources via surface runoff and infiltration into groundwater, and can linger in soil for a considerable time (Abraxis LLC. *Azoxystrobin* n.d.). Azoxystrobin is relatively immobile, and is relatively non-persistent under most conditions. Although it degrades relatively fast, it has the potential to leach into groundwater. Its half-life can range from 11 to 17 days under photodegradation, and 72 to 164 days in soil (*Azoxystrobin: Pesticide...* 1997).

Although no MCL has been set for Azoxystrobin, other consumption regulations such as the maximum residue limit (MRL) have been set, although they vary depending on the country, as well as on what type of food contains the fungicide (Abraxis LLC. *Azoxystrobin* n.d.). The LD₅₀ in rats is over 5000mg/kg, a level which is relatively non-toxic. It is also relatively harmless to humans (*Azoxystrobin: Pesticide...* 1997), although it has been shown to irritate human skin with extended contact. Azoxystrobin has, however, been shown to be acutely toxic to many aquatic species, both freshwater and marine, and even some plants (Abraxis LLC. *Azoxystrobin* n.d.).

1.3.5 DDT/DDE

Dichlorodiphenyltrichloroethane (DDT) is a well-known and once commonly used organochlorine insecticide, currently banned for use in much of the world. During World War II (WWII), in the 1940s, the military sprayed DDT heavily to protect troops from mosquito and lice-borne diseases such as malaria and typhus. It was also used by farmers to protect crops and as pest control in residential buildings (*DDT (General Fact Sheet)* 1999). The pesticide works by

causing insect sodium ion channels within neurons to fire spontaneously, leading to uncontrolled spasms and eventual death (DeCarvalho 2013). The overwhelming popularity of DDT in the mid-20th century was a result of its relative low cost, and its long residence time where sprayed. DDT is fat soluble, meaning that it accumulates in fat cells of an organism and does not pass through the digestive system. This leads to bioaccumulation through the food chain and presents adverse effects to an ecosystem. The half-life of DDT is very long compared to other pesticides, estimated between 2 to 15 years in soil and up to 150 years in the aquatic environment (DDT (General Fact Sheet) 1999). Between its fat solubility and lengthy half-life, the ban of DDT across much of the world can be well understood. DDT itself has no known toxic effects on most species when stored in fatty tissue, but when the fat is broken down by metabolic reactions, DDT can degrade to byproducts such as Dichlorodiphenyldichloroethylene (DDE) or Dichlorodiphenyl-dichloroethane (DDD) (all three forms will be referred to simply as ‘DDT’ in this study), which may be released into the blood and affect the nervous system (DDT (General Fact Sheet) 1999). A basic degradation pathway of DDT into its common breakdown products is displayed in **Figure 4**.

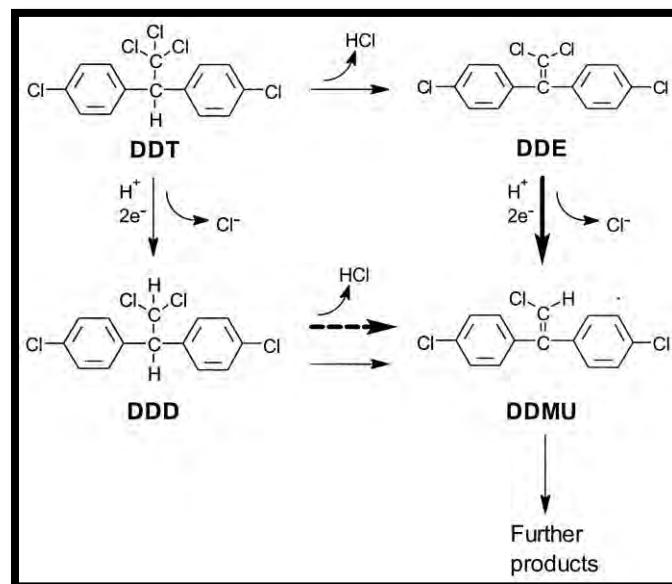


Figure 4: Degradation pathway of DDT to its breakdown products of DDE and DDD, and so on (Quensen 1998).

No assigned MCL level has been designated by the U.S. EPA for DDT, but regulations for water quality have been determined in New York State, where DDT may not exceed 5 ppb in drinking water. The LD₅₀ for DDT in rats is approximately 113 mg/kg, which is markedly lower and more toxic than the other pesticides targeted in this study (*Toxicology and Exposure...* 2003). Known effects of DDT and its breakdown products (DDE, DDD) include reproductive effects, such as eggshell thinning in avian species; convulsions, lesions and liver damage in tested mammal species; and nausea, fatigue, trembling, nervous tension and weakness in exposed humans (*DDT (General Fact Sheet)* 1999).

Planes were spraying DDT all over the South Pacific to control malaria in combat areas during WWII, and it was often applied in weekly treatments to make sure mosquitoes had been eradicated (Travis 1946). As mentioned earlier, a report from American Samoa in 1949 indicated that DDT spraying was to be undertaken on Tutuila in the fashion of the WWII applications (American Samoa Report 1949). Because of its lengthy residence time in an environment, and known application in the South Pacific, DDT is an ideal pesticide to search for in American Samoa.

1.4 HYDROLOGICAL MODELING, COLLECTION OF DATA FOR MODEL CALIBRATION, AND LAND-USE ANALYSIS

1.4.1 Modeling the Faga`alu watershed

To understand groundwater flow in the Faga`alu watershed on Tutuila, a numerical model was created using the United States Geological Survey (USGS) MODFLOW model. Only sparse data are available on subsurface geology and groundwater flow paths in the area. Therefore, additional data was collected to build a conceptual model, and to calibrate the hydrological model. This project used stream discharge measurements (along with a ²²²Rn survey) and known head levels as calibration parameters.

1.4.2 ^{222}Rn Analysis

The noble gas radon (^{222}Rn) was used, along with seepage runs, to determine locations of groundwater discharge into Faga`alu Stream for model calibration of groundwater level. ^{222}Rn is an unreactive gas, often used as a natural geochemical tracer for the presence of groundwater input into riparian and coastal zones. Because it is generally not present in atmosphere-exposed marine, surface or rain waters, it is a powerful tracer of subsurface water (Burnett and Dulaiova 2003, Dulaiova et al. 2009). It is produced by radioactive decay of uranium-bearing minerals in rocks through an alpha-recoil process (see **Figure 5** for decay chain) (Mehta 2016). ^{222}Rn itself is radioactive, with a relatively short half-life ($t_{1/2} = 3.83$ days), ideal for tracing groundwater sources (Burnett and Dulaiova 2003). ^{222}Rn can be easily quantified in the field or in the laboratory. Once produced via alpha-recoil from rocks in the aquifer, radon diffuses into groundwater and pore spaces, where it remains until it decays radioactively or evades to the atmosphere. Once discharged from the aquifer to surface water, radon concentrations can be used to assess groundwater presence. Because of its ideal half-life and detectability, radon is widely used as a groundwater tracer, and can complement seepage runs to compare where a stream (in this case) may be gaining or losing groundwater (Burnett and Dulaiova 2003, Dulaiova et al. 2009).

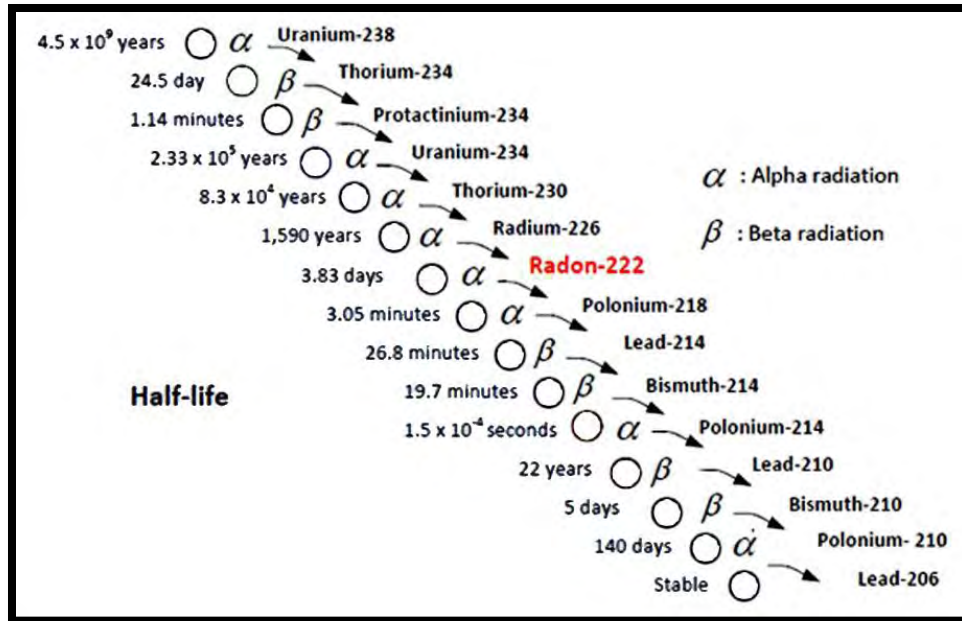


Figure 5: ²²²Rn is the sixth step in the uranium-series of decay, and has a 3.83 day half-life, making it ideal for tracing groundwater, as it is not too long (weeks to years) and not too short (seconds to minutes) to reliably measure its alpha decay radiation. *Image modified from: ("Radioactive Decay" n.d.)*

1.4.3 Determination of groundwater flux and contaminant transport

Groundwater Modeling System (GMS) software is the platform used to simulate the MODFLOW, MODPATH and MT3DMS models used in this study (<http://www.aquaveo.com>). MODFLOW is a modular hydrologic model used to predict surface-groundwater interactions and groundwater conditions ("MODFLOW and Related Programs" 2018). MODFLOW can be calibrated by: 1) using known water table levels as observation points in the model, and/or 2) assigning measured stream discharge rates to specified stream arcs in the model.

Following calibration of MODFLOW, the MODPATH advection model can be run in conjunction to simulate projected pathways from groundwater sample sites back to potential sources. The advection process, however, does not act alone in the subsurface, and thus the model must be generalized to include the dispersion process. Using the multi-species contaminant transport model (MT3DMS), MODFLOW outputs are then used to simulate groundwater flow via dispersion and advection to determine contaminant transport through the

aquifer (Shuler 2016). The contaminant in this model represents pesticide flowing from agricultural sources in the watershed, and the objective is to assess the relationship between measured pesticide levels and location of potential pesticide sources across the watershed.

The Faga`alu watershed was graphically subdivided into model cells of dimension 38 m x 30 m in order to implement the model. Estimated flow paths and concentrations of contaminant were determined at specified cells to estimate source locations and concentrations over time. Contaminant fluxes were estimated for the watershed by utilizing the measured pesticide concentrations (via ELISA analysis) in the modeled system.

1.4.4 Land-use spatial analysis using ArcGIS

ArcGIS (Esri) is a geographic information system (GIS) program used to spatially analyze and compile geographic data (“Work Smarter...” Esri). Several terms associated with the GIS and modeling programs used in this study will be applied in subsequent sections and thus must be defined. Definitions for these terms are listed in **Table 1**.

ArcGIS has been used for spatial analysis of the pesticide concentration distribution across Tutuila, as well as more focused distribution of pesticides in the Faga`alu watershed. Existing shapefiles describing land-use (such as forest/urban/etc.), stream, watershed boundaries, and village locations have been used in coordination with newly-created shapefiles representing pesticide concentration and submarine groundwater discharge (SGD) in the ArcGIS analysis. Shapefiles representing agriculture, the stream, wells, and recharge were all used as well, to build the hydrogeological model in GMS.

Table 1: A list of modeling and GIS-related definitions as a reference for subsequent reading.

<u>Arc Groups</u>	Arc groups are created from a set of selected arcs (see <i>Stream Arcs</i>). Assigned properties to the entire group can simplify the model, instead of assigning properties to each individual arc. An arc group can be selected to display the computed flow (of a stream in this case) through the arc group (“GMS: Feature Objects.” 2017).
<u>Coverage</u>	Feature objects in the MODFLOW model are grouped into coverages. Coverages are grouped into conceptual models and represent a particular set of information. Often derived from shapefiles (i.e.-used to define recharge zones, or zones of hydraulic conductivity. These cannot be included in same coverage as polygons would overlap) (“GMS: Coverages” 2017).
<u>Polygons</u>	A polygon is a type of shapefile which is enclosed, signifying an areal region with representative assigned attributes to the encompassing region.
<u>Shapefile</u>	A shapefile is a vector-based storage format used to help visualize the location, shape, and attributes of geographic features in GIS programs such as ArcGIS (“Shapefiles.” 2017).
<u>(Stream) Arcs</u>	Arcs are sequences of vector-based line segments grouped together as a single "polyline" entity (a type of shapefile) in a modeling program to represent a feature object, in this case a stream. They contain unique IDs and can be assigned attributes (“GMS: Feature Objects.” 2017).
<u>Stress Period</u>	A stress period is a group of one or more time steps in which stress input data are constant (Reilly and Harbaugh 1996).

2. METHODS

2.1 FIELDWORK ON TUTUILA, AMERICAN SAMOA

2.1.1 Island-wide collection of surface and groundwater samples

In August 2016, during the dry season, an island-wide collection of water samples was performed on Tutuila, American Samoa. Samples were obtained during a two-week period from stream surface waters, stream bank groundwater, wells and coastal springs. Sampling dates, locations and sample types are summarized in **Table 2**.

Table 2: Samples taken on Tutuila in August, 2016. Sampling date and location are noted as well as the type(s) of sample. The sample type is given, separated by commas; their order correlates to the respective number of each type of sample taken.

Date	Location	Type of Sample	# Samples Collected
08/09/2016	Tafuna-Leone Plain	W	4
08/10/2016	Faga`alu Stream	L, P, T, D	7, 3, 2, 1
08/11/2016	Vaitele Stream	L, P, T, D	6, 2, 1, 1
08/12/2016	Faga`alu Stream	H	3
08/13/2016	West-side Tutuila	W, D	21, 2
08/14/2016	Pala Lagoon	C	1
08/15/2016	Central & eastern Tutuila	W, C, D	16, 2, 2
08/16/2016	Island-wide	L, W, D	16, 1, 2
08/17/2016	Vaipito (Pago) Stream	L, P, C, D	4, 2, 1, 1
08/18/2016	Oa	C, L	3, 1
08/19/2016	Faga`alu	C	2
Total			107

L=Stream Low Flow, W=Well, P=Peizometer, T=Tributary, D=Duplicate, H= Stream High Flow, C=Coastal Spring

Three detailed stream studies were conducted during the sampling period. On August 10th, 2016, sampling of the full accessible reach of Faga`alu Stream was completed. A total of nine sites on the stream were sampled (7 main stream, 2 tributaries). Samples from the full reach of the Vaitele Stream on the Tafuna Plain (6 main stream, 1 tributary) on August 11th, and from Vaipito Stream in Pago Pago (4 main stream) on August 17th, were also collected. Stream surface water samples were collected using an SP200 variable speed portable peristaltic pump sampler (Global Water[®]) using silicon tubing. Water was fed from a steady flowing portion of the stream

into tubing submerged in the central part of the channel. Streambank groundwater samples were collected using a push-point sampler with silicon tubing attached to a peristaltic pump. Tubing was inserted as far into the ground as allowed by the pebbly terrain (~0.3-0.6 m depth). Coastal springs were also sampled using push-point samplers, which were pushed into sandy or pebbly material on the shoreline. At all wells, permanently installed wellhead collection ports were used for sample collection. Access was allowed via ASPA personnel, who assisted in well collection port operation. Duplicate samples were collected for 8.4% of samples. Duplicates were used in determining precision of measurements.

2.1.2 Sample sets collected at each study site

At each station, samples were collected in 250 mL glass bottles for radon (^{222}Rn) analysis, and in 25 mL glass amber vials for pesticides. A YSI 6820 V2-2 multiparameter water quality sonde was used to determine conductivity, temperature, and dissolved oxygen of the water being sampled. Pesticide samples were stored refrigerated (4°-8°C); radon was tested immediately, and thus was not refrigerated.

2.1.3 Radon sample collection and measurement

The 250 mL glass bottle designated for ^{222}Rn collection was submerged and capped in an overflowing container no less than three times sample volume to reduce the presence of air bubbles in the sample. The peristaltic pump was used to collect water from surface and push-point sampling locations into the sample containers. Time was noted when radon samples were sealed in order to adjust for radon decay occurring between time of collection and time of measurement.

Each sample was analyzed on the day of its collection to obtain maximum sensitivity of measurements. Radon was analyzed using a 'RAD-H₂O' radon instrument, which includes a radon-in-air monitor (RAD7 manufactured by DurrIDGE[®]), a small drierite tube to extract moisture from the air being pumped from the sample to the monitor, and a bubbler to extract radon gas from the water sample. The decay of ^{222}Rn and its daughter ^{218}Po were counted during

a four-run cycle programmed on the RAD7. At the end of the four cycles (approximately 30 minutes), a dataset of radon counts is saved onto the RAD7 device and uploaded later onto a computer for analysis.

2.1.4 Pesticide sample collection and storage

Unfiltered water was collected from each site into a 25 mL amber vial. The amber vials exclude sunlight to prevent photodegradation or light-sensitive decay of any pesticides that may be present in the samples. Gloves were worn during collection to prevent any contamination. Samples were stored in a cooler on site, and transported later to a refrigerator ($\sim 4^{\circ}$ - 8° C) to inhibit chemical degradation. Samples were stored refrigerated until analyzed in the laboratory at UH Mānoa, which occurred within five to ten months of collection. Analytical methods are detailed below.

2.1.5 Seepage Runs

A seepage run consists of multiple measurements of streamflow during one sampling period across a stream reach. Assuming that the difference in flow rate between stations is due to net groundwater discharge to the stream, or loss of stream water to the aquifer, groundwater-surface water exchange on a watershed scale can be assessed (“Hydrologic Activity” 2015).

Seepage runs were conducted at each location on the Faga`alu Stream using a SonTek Flow Tracker device to quantify stream discharge. Upon locating a clear and flowing area of the stream (or creating one by adjusting rocks), the instrument was used at each sampling location. By transecting the cross-section of the channel, stream flow was determined using the Flow Tracker, and recorded for later use in determining where the stream was gaining or losing water.

2.2 LABORATORY SAMPLE ANALYSIS

At the University of Hawai`i (UH) at Mānoa, in Honolulu, HI, samples were stored under specific conditions (refrigerated, frozen, room temperature, darkness) according to protocols

detailed above. Analysis of pesticide, ion, nutrient concentrations, and deuterium and oxygen isotopes, were run at later dates. Pesticide testing was performed in the Dulai Lab, while the other sample-types were sent for analysis in other labs, as specified below.

2.2.1 Glyphosate test

In the Dulai Lab at UH Mānoa, water samples were tested for the herbicide glyphosate using an enzyme linked immunosorbent assay (ELISA) procedure (Abraxis LLC *Glyphosate* n.d.) on January 4, 2017; approximately 5 months after the collection date. A microtiter plate with 96 wells, each coated in Goat Anti-Rabbit Antibody, was provided in a commercially available glyphosate kit (Abraxis[®]). Standards for glyphosate were set at 0, 0.075, 0.2, 0.5, 1.0, and 4.0 ng/mL. 50μL of each derivatized standard, control and water sample were then pipetted into assigned wells on a microtiter plate. After antibody solution (50μL) was added, the plate was covered with Parafilm[®] and allowed to sit at room temperature for 30 minutes to incubate. 50μL of the enzyme conjugate (horseradish peroxidase (HRP)) was then added and allowed to incubate, covered, for 60 minutes, to allow a competitive reaction to occur between the enzyme and any glyphosate present in each sample. Enzyme-reacted glyphosate binds to the antibody-coated walls in the microtiter wells. The solution was then discarded and the wells were washed three times with a washing buffer. A color solution containing an enzyme substrate (hydrogen peroxide) and chromagen (3,3',5,5'-tetramethylbenzidine) was then added to each well, producing a blue tint (Abraxis LLC *Glyphosate* n.d.). After incubating once again for 30 minutes under Parafilm[®], a stop solution (diluted acid) was added to the blue-colored solution, causing each sample to turn yellow in color. The intensity of yellow is inversely proportional to the concentration of glyphosate in each sample. Thus, the clearer a sample appears in the end, the more glyphosate it contains. The more intense the yellow color, the less glyphosate is present. To determine the concentration in each sample, an ELISA microplate reader reads the absorbance of each sample on the plate, at a wavelength of 450 nm, within 15 minutes of adding the stop

solution. Results were calculated using a standard calibration curve and applying an appropriate dilution factor (Watanabe and Miyake 2013, Abraxis LLC *Glyphosate* n.d.).

2.2.2 Imidacloprid test

The insecticide imidacloprid was tested using a similar ELISA procedure (Abraxis LLC *Imidacloprid* n.d.) on June 1, 2017, approximately ten months after the collection date. Standards for imidacloprid were set at 0, 0.075, 0.15, 0.30, 0.60, and 1.2 ng/mL. 50 µL of each sample, standard, and control were added to their assigned wells along with 50 µL of buffer solution and 50 µL of enzyme conjugate, before a 60 minute incubation period under Parafilm® to allow the competitive reaction to take place. Following incubation, the solution was discarded into the sink and the wells were washed three times with washing buffer solution. 150 µL of color solution was then added and allowed to sit for 25 minutes, covered, at room temperature, as the solution was allowed to turn a shade of blue. Finally, 100 µL of the stop solution was added turning the solution yellow, and then the absorbance was read at a wavelength of 450 nm using the ELISA microplate reader, within 15 minutes of its addition (Abraxis LLC *Imidacloprid* n.d.). The intensity of yellow was inversely proportional to the concentration of imidacloprid.

2.2.3 Azoxystrobin test

Unlike the previous two tests, water samples devoted for azoxystrobin analysis had to be diluted by methanol to a final concentration of 10% of methanol, prior to analysis. The appropriate amount of methanol was pipetted into samples and a vortex mixer (Vortex Genie®) was used to thoroughly mix samples, after which they were allowed to incubate overnight (Abraxis LLC *Azoxystrobin* n.d.).

The fungicide azoxystrobin was then tested using the ELISA method (Abraxis LLC *Azoxystrobin* n.d.) on June 16, 2017, approximately ten months after the collection date. Standards for azoxystrobin were 0, 0.01, 0.025, 0.05, 0.1, and 0.25 ng/mL. Standards, controls and samples (diluted to 10% methanol) were added at 50 µL per assigned well. An amount of 50 µL mouse anti-Azoxystrobin antibody solution was added, as well, and the tray was allowed to

incubate for 30 minutes at room temperature. HRP-conjugate solution at 50 μL was then added, covered and allowed to incubate an additional 30 minutes. Following this period, the solution was discarded into the sink and the tray was washed three times with washing buffer solution. Next, 150 μL of color solution (blue) was added to each well and allowed to sit for 20 minutes before adding 100 μL of stop solution (yellow). The ELISA microplate reader was then used to read the plate at a wavelength of 450 nm to obtain the concentrations (Abraxis LLC *Azoxystrobin* n.d.). Once again, the intensity of yellow in each sample was inversely proportional to the concentration of the azoxystrobin present.

2.2.4 DDT/DDE test

Already having been prepped with methanol from the previous test, a separate aliquot of the same samples was used to perform an ELISA test for DDT/DDE. This test (Abraxis Inc. *DDT/DDE* n.d.) was performed on June 20, 2017, approximately ten months after the collection date. Standards for DDT/DDE were 0, 0.625, 1.25, 2.5, 5, 10, and 25ng/mL. Standards, controls and samples (diluted to 10% methanol) were added at 25 μL per assigned well. Mouse anti-DDT/DDE antibody solution (50 μL) was added and the tray was allowed to incubate for 30 minutes, covered, at room temperature. All the following steps from adding conjugate, washing, adding color and stop solutions, and the reading of the plate at a wavelength of 450 nm, followed the exact same protocol as the above azoxystrobin test (Abraxis Inc. *DDT/DDE* n.d.).

2.3 MODELING AND GIS METHODS

2.3.1 Modeling framework

Numerical models within the MODFLOW family of programs were used to quantify pesticide fluxes from non-point sources in the Faga`alu watershed on Tutuila and tracked their movement and concentrations throughout the aquifer. A model of the watershed was created using MODFLOW. The MODFLOW model was calibrated using seepage runs and measured

head levels. The simulated water level results were utilized to run the MODPATH model, which enables projection of advective flow lines. The model MT3DMS was then run, using MODFLOW input to simulate both advective and dispersive transport in the aquifer, and to determine the respective contaminant concentrations. The GMS software was employed as a graphical user interface to build a conceptual model, run the numerical models, and process model results (Zheng and Wang 1999). A flow chart of the integrated framework of these models, indicating inputs and outputs, is illustrated in **Figure 6**.

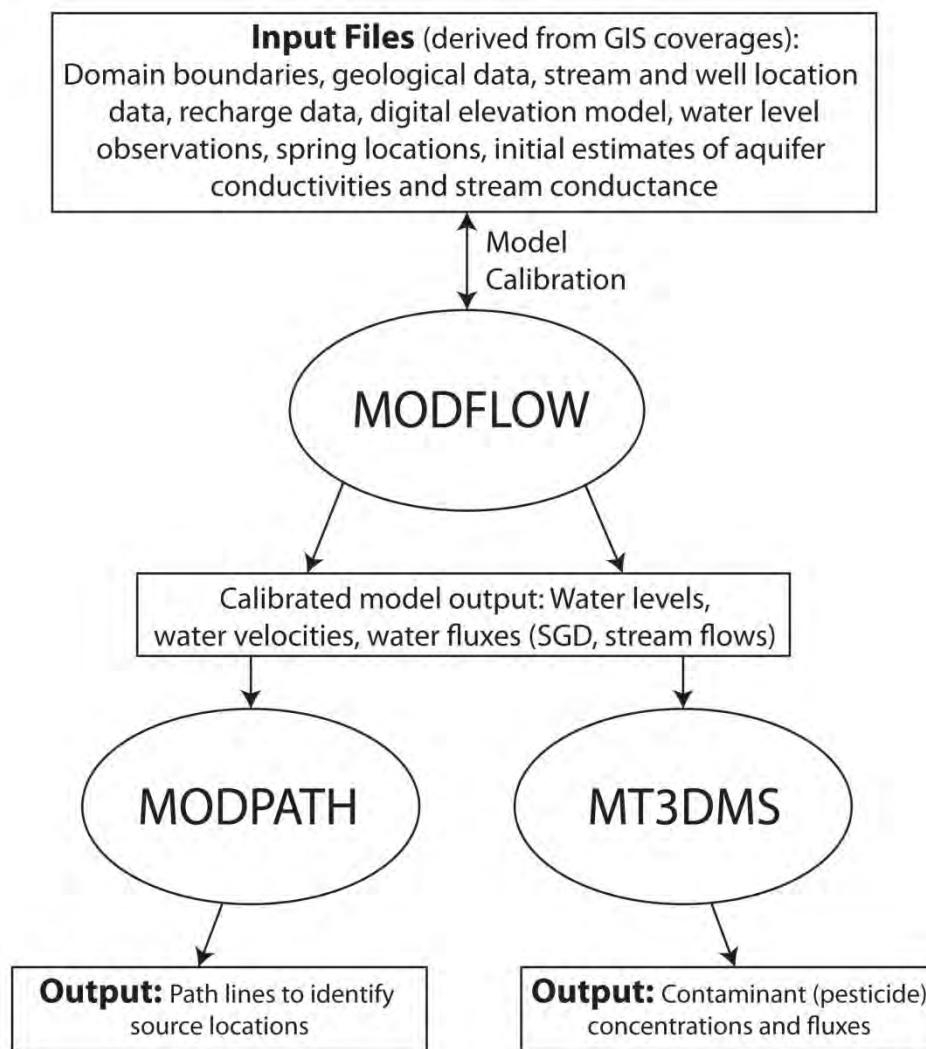


Figure 6: Flow Chart describing the framework of the three models used in this study. MODFLOW is calibrated by using available input data listed in the chart mainly to estimate aquifer conductivity and stream conductance that provides the best match between measured and estimated observations. The calibrated MODFLOW model was then used to provide data necessary to run the transport models MODPATH, and MT3DMS.

2.3.2 Conceptual Model

Faga`alu is a relatively small aquifer ($< 2 \text{ km}^2$), surrounded by older volcanic basalt formations which are likely low in permeability to water movement (Izuka 2007, Shuler 2016). The borders of the watershed on the mountain ridges were designated as no-flow boundaries in the model, assuming that a groundwater divide exists there. However, actual field conditions can invalidate such an assumption and additional information is needed to confirm this assumption. The boundary of the land-ocean interface was set as a specified (known) head of mean sea level (MSL). Although dikes in the mountains likely cause discontinuity in aquifer properties, the lack of knowledge about their distribution required the use of effective hydraulic conductivity values for portions of the aquifer, where dikes exist. It was assumed that the alluvial plain in lower Faga`alu would have higher permeability to water, as it does not consist of the solid igneous components seen in the upper watershed, but rather of loosely consolidated substrate.

The shapefile used for the stream and its tributaries running through Faga`alu was delineated in GMS as a “drain,” and various available stream data were used in the calibration of the model. In-situ baseflow measurements were inserted into stream arc groups in MODFLOW to represent the observed stream flow in the model. Such values were tested against computed values during model calibration. Well #179 is the only well in the Faga`alu watershed, and was included in the conceptual model as a “source/sink” coverage. Geologic units, where hydraulic conductivity was assigned, were also included in the conceptual model (more details given later in **Figure 8**). All of the components of the conceptual model, including boundaries with assigned conditions, the stream and tributaries, Well #179, and the geologic units of different conductivity are illustrated in **Figure 7**.

Faga`alu Watershed Conceptual Model

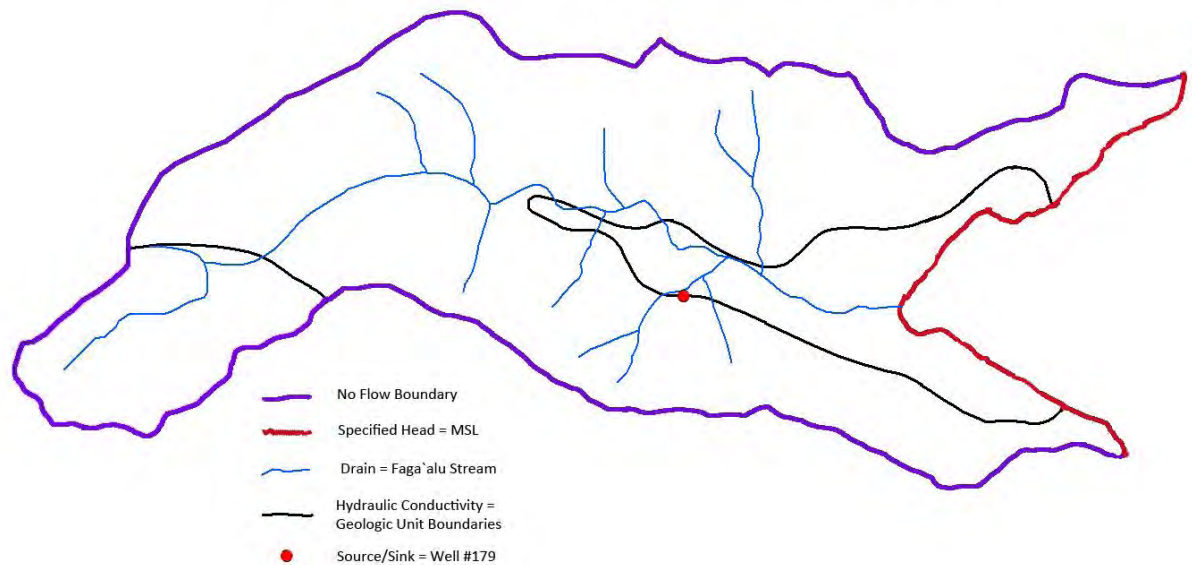


Figure 7: Conceptual Model of the Faga`alu Watershed, as described above.

2.3.3 Building the MODFLOW model

Using the MODFLOW-2000 model, groundwater flow was simulated at steady-state, under forward-running conditions in an unconfined aquifer. A two-layer grid was created, with a total of 10,000 cells (that is, 50 x 100 cells in plain view). Among these, only 4221 cells were active, as they are located within the boundary of the aquifer. Each cell measured 38 m x 30 m in width and length. In the vertical direction, the top layer covered the zone between MSL and the terrain elevations above MSL. The lower layer covered the zone between the MSL, extending to 500 m below MSL. The zone below 500 m depth was not considered in the model, as it is assumed that flow activities will not be significant there (El-Kadi 2016). Initial head levels were set at 10 m above MSL in each cell before running the model.

Coverages that were created for the model within GMS included recharge, drain (the stream), source/sink (the well), hydraulic conductivity (geologic layers), observation points (known head values), boundary (specified head), and agriculture (indicating contaminant sources). The precipitation recharge coverage for Faga`alu was provided by Leta (unpublished

2018), developed by using the Soil and Water Assessment Tool (SWAT) model; recharge ranged from 0.0018 - 0.0035 m/d across the watershed. Water withdrawal from well #179 was added as a sink, assuming a value of -163.53 m³/d based on converting measurements provided by Shuler (personal communication) from past pumping rates. A top screen on the well casing was added at 10 m depth, and a bottom screen at 25 m depth, according to information obtained from ASPA.

A map of Faga'alu showing the three major subdivisions of geologic units, provided by the American Samoan National Park Service, can be viewed in **Figure 8**. A smaller unit existed within the 'B'-unit of geology, but was combined and set at the same conditions as the encompassing unit to simplify the model. This map (**Figure 8**) illustrates the nature of the geologic shapefile used as the coverage determining various properties of Layer 1 and 2 of the grid in the hydrological model. As an approximation, and due to the absence of detailed information, all properties were kept identical between the two layers (**Table 3**). Hydraulic conductivity (K) was adjusted during the calibration process of the model to obtain the best match between computed and observed head levels and stream discharge rates (**Table 3**).

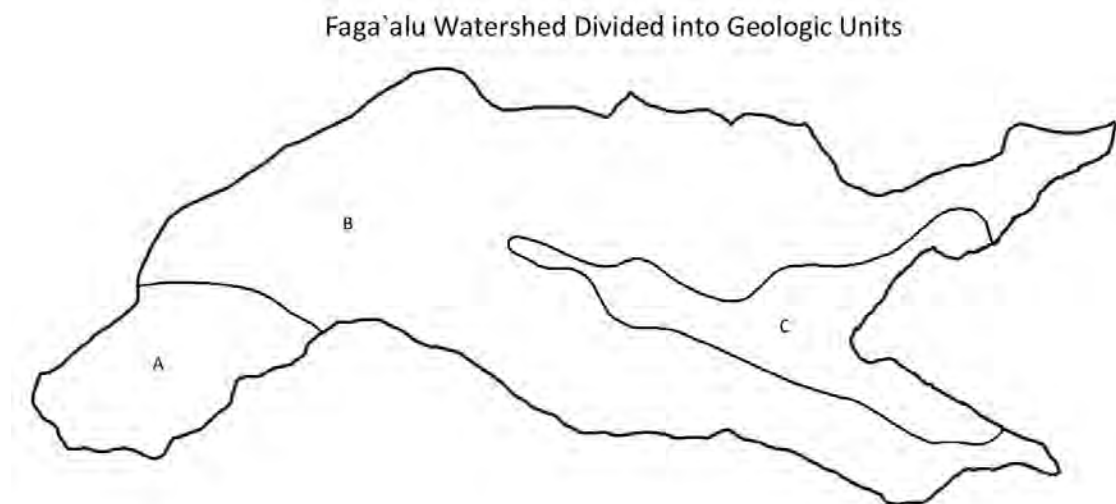


Figure 8: Geologic units of the Faga'alu watershed: (A) Pago Volcanic Series, intra-caldera, trachyte plugs and dikes, (B) Pago Volcanic Series, intra-caldera, (C) Beach sand and alluvium ("Geologic Map of A. Samoa" 2008).

Table 3: Attributed hydrologic properties of each geologic unit in the two model layers after calibration of the model.

Geologic Unit	Hydraulic Conductivity (m/d)	Porosity	Longitudinal Dispersivity (m)	Vertical Anisotropy	Horizontal Anisotropy
A	0.0300	0.3	20.0	3.0	1.0
B	0.0165	0.3	20.0	3.0	1.0
C	85.00	0.3	20.0	3.0	1.0

2.3.4 Calibration of the MODFLOW model

Documented head values from past observations, from the Faga`alu well and several mountain springs, were used to calibrate the model. The values of these head levels are estimates only, as they are obtained from different sources and are subject to uncertainty regarding dates of collection. The points used and their observed head levels are shown in **Figure 9**.

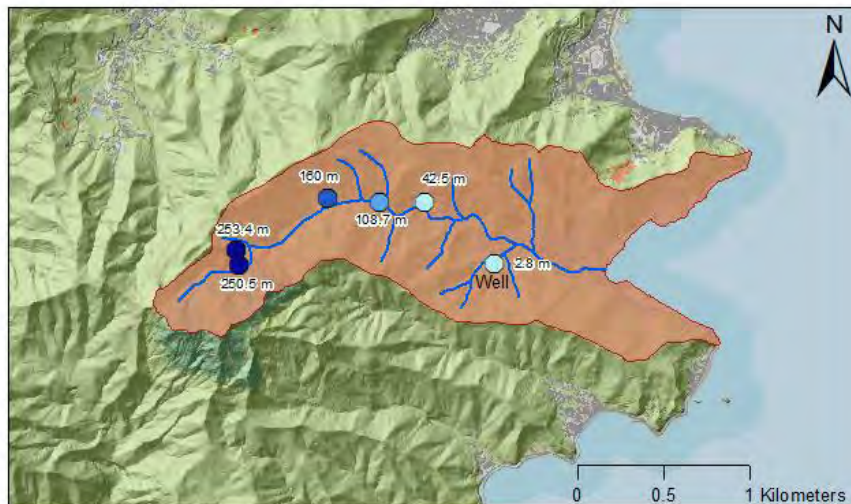


Figure 9: Documented head levels of the Faga`alu aquifer, based on locations of mountain springs and recorded well water levels. Lighter blue is lower head and darker blue is higher.

Stream discharge rates were also included to calibrate the MODFLOW model. The divisions of stream and tributary arc groups used in MODFLOW, based upon measured stream discharge rates recorded during seepage runs in August 2016, are shown in **Figure 10**.

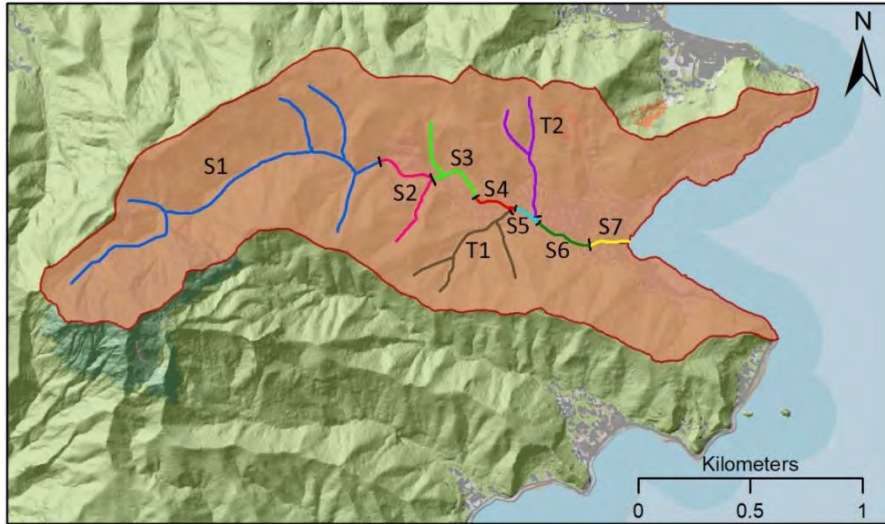


Figure 10: The Faga'alu Stream and tributaries were broken into seven separate stream sections (S1-S7), and two tributary arcs (T1-T2), based upon location of discharge measurements recorded during baseflow in August 2016 seepage runs.

The stream arc groups were simulated as drains with observed flow rates in the model. Treating a stream as a drain assumes that water only moves to the stream from the aquifer, and not vice versa. Details of stream flows, such as sections losing water, are ignored in this case. Conductance is a parameter that is assumed to control water flow to the stream from the aquifer. In the calibration process, streambed conductance was adjusted as a method of calibration at each arc (sub-portions of each arc group). Along with adjusting hydraulic conductivity, modifying this conductance is the only other possible means by which reasonable calibration can be achieved. The observed (measured) flow, adjusted conductance, flow interval (relative error of flow rate), and standard deviation for each respective arc and arc group are shown in **Table 4**.

Table 4: Data used for stream arc calibration including the observed flow rate, streambed conductance (rate at which water permeates stream bed), the observed flow interval (measure of error bars in computed vs. observed flow rate), and standard deviation (sd = CI/z where CI is confidence interval [95%] and z is “z statistic” based on specified confidence and normal distribution). (“GMS: Calibration Targets” 2017, “GMS: Observations” 2017). *d = day

Arc Group	Arc #	Observed Flow Rate (m ³ /d)*	Obs. Flow Interval (+/-) (m ³ /d)*	Standard Deviation	Conductance (m ² /d/m)*
Stream (S1) Arc Group 1	Arc 1	2384.64	119.20	60.82	1.00
	Arc 2				0.05
	Arc 3				5.00
	Arc 4				0.05
	Arc 5				1.00
	Arc 6				0.05
	Arc 7				0.05
	Arc 8				20.00
Stream (S2) Arc Group 2	Arc 9	2531.52	126.60	64.59	20.00
	Arc 10				0.50
Stream (S3) Arc Group 3	Arc 11	1969.92	100.00	51.02	5.00
	Arc 12				0.50
Stream (S4)	Arc 13	2367.36	210.00	0.51	5.00
Stream (S5)	Arc 14	2289.60	210.00	0.51	0.050
Stream (S6)	Arc 15	2894.40	210.00	0.51	20.00
Stream (S7) Arc Group 4	Arc 16	3628.80	181.44	92.57	20.00
	Arc 17				20.00
Tributary (T1) Arc Group 5	Arc 18	82.08	4.10	2.09	0.50
	Arc 19				0.50
	Arc 20				0.50
Tributary (T2) Arc Group 6	Arc 21	164.16	8.20	4.18	0.50
	Arc 22				0.50

Manual calibration was used for MODFLOW model calibration. Hydraulic conductivity and streambed conductance were adjusted manually until head levels were acceptably close to observed values. The model was considered successfully calibrated when a regression coefficient (R^2) close to 0.99 was achieved. Applying measured stream discharge rates to stream arcs and adjusting conductance, proved a more difficult task than expected. As a result, observation points based on hydraulic head were used as the primary means of calibration of the model. After completion of MODFLOW calibration, the next stage included utilizing the MODPATH and MT3DMS models for contaminant transport assessment.

2.3.5 Estimating pesticide fluxes in stream and SGD

To estimate pesticide fluxes in Faga`alu Stream, the stream was divided into two sections: 1) the upper reach, and 2) the lower reach. Stations 1, 2, 3, and 4 in **Figure 1** represent the lower reach of Faga`alu Stream, while stations 5, 6, and 7 represent the upper reach. Pesticide flux into the stream by groundwater discharge was calculated by multiplying modeled groundwater flow of each of the two stream arc groups by the concentration of the pesticides in stream bank groundwater measured from push-point samples collected in the corresponding reaches of the stream. The average pesticide concentrations at stations 1 and 3 were used for the lower reach, while for the upper reach only station 6 was available. DDT concentration at station 6 was below the detection limit, but it is unlikely that the entire reach has zero DDT flux, as stream concentrations were non-zero. An average was taken of two of the push-point samples from the upper reaches of adjacent watersheds (Vaipito and Vaitele) to approximate upper reach DDT levels. Although this average does not represent a true measurement of DDT for the upper reach in Faga`alu, it can provide a representative assessment of how much of the contaminant may be present in groundwater in the upper reaches of the watershed. In order to compare groundwater discharge-derived pesticide flux to total stream flux, the latter was calculated by multiplying stream water pesticide concentrations at the station furthest downstream (station 1 for lower reach, station 4 for upper reach) by the measured stream discharge (of August 2016). Once the groundwater-derived and total stream pesticide fluxes were estimated, the fraction of groundwater contribution to total flux was determined.

To estimate pesticide fluxes at the land-ocean interface via SGD, the coast was divided into three sections: 1) the northern coastline, 2) the central coastline, and 3) the southern coastline (**Figure 11**). The total flow for each of the three sections was estimated from the flow budget of MODFLOW by summing flows from the coastal cells in each stretch of coastline. As with estimating the pesticide flux in streams, similar calculations were made by multiplying the flow budget of the combined coastal grid cells of each section by pesticide concentrations measured in

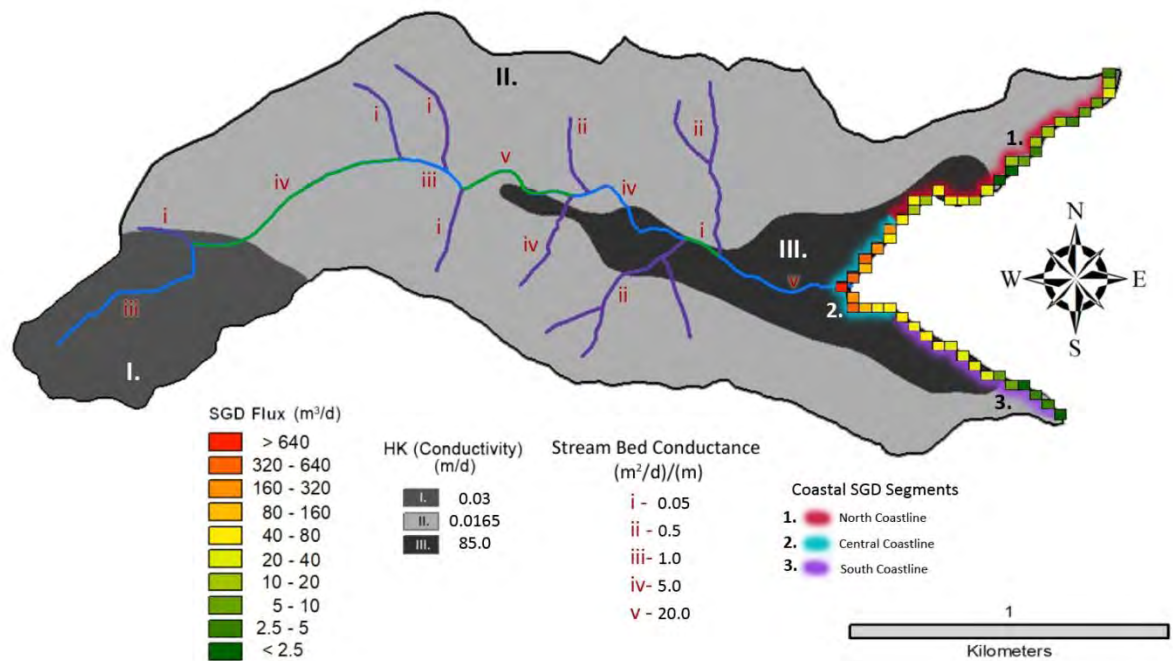


Figure 11: Map of the Faga'alu watershed, including calibration data (Hydraulic Conductivity and Streambed Conductance), measured SGD rates, and the subdivided sections of the coastline (north, central, south).

springs and groundwater collected by push-point samplers in each section. Estimates taken from the southern and northern portions of the coast of the bay used pesticide concentrations from the southern and northern coastal spring push-point measurements, respectively. The central coastline estimate used the push-point measurement from station 1, which is not very far upstream, and should provide a reasonable representation of concentrations in that sector.

2.3.6 MODPATH

Using grid cells located at each groundwater sample location (well, coastal springs, stream bank push-points) as starting points to generate water flow path lines, MODPATH was run for particle tracing in a backward-mode to simulate the advection process. MODPATH can also be set to create forward-running flow paths, but this option was not explored. As described earlier, MODPATH assesses contaminant transport without factoring in dispersion. This was carried out to identify potential sources of contaminants in the aquifer, to link such sources to known land-use data. The groundwater sample sites used can be seen in **Figure 12**.

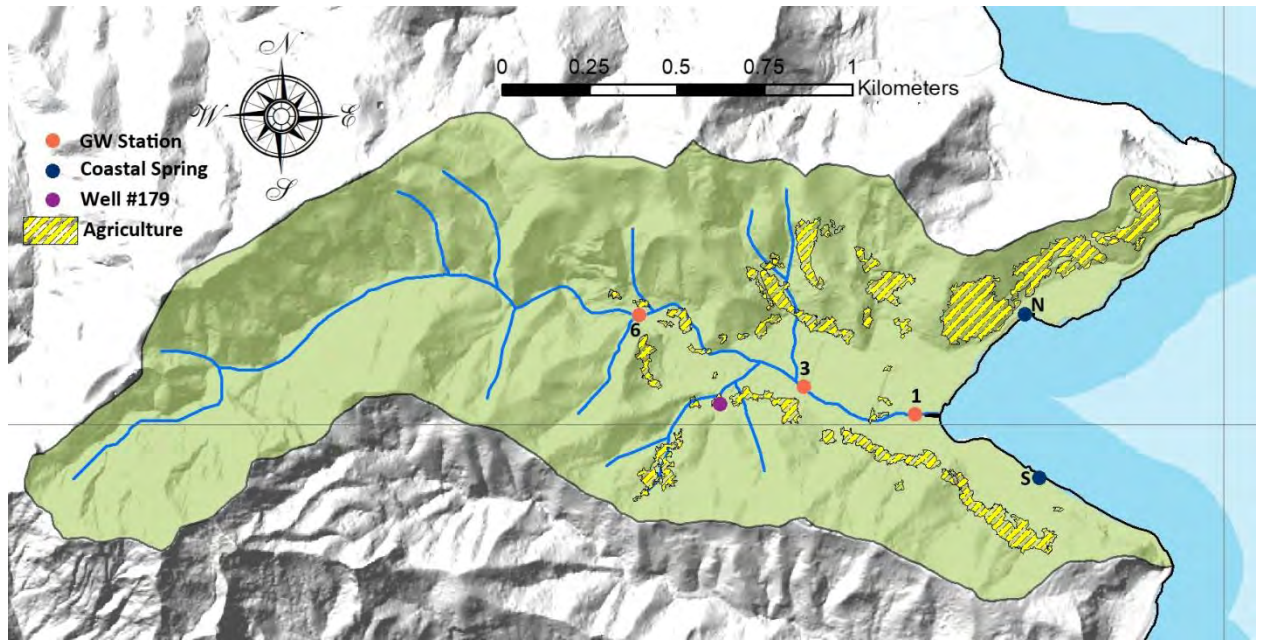


Figure 12: Groundwater push-point sample sites, well location, and land-use for agriculture practices in the Faga'alu watershed are shown. Data for agriculture may not be fully accurate due to limited available information.

2.3.7 MT3DMS

In order to account for dispersion, the MT3DMS model was used to simulate contaminant transport in the aquifer. Rather than simulate particle transport, as was done with the MODPATH model, the MT3DMS model solves the governing transport equation, which accounts for both advection and dispersion (Zheng and Wang 1999, El-Kadi 2018). The MT3DMS model thus is superior to MODPATH, because it accounts for dilution due to dispersive effects. The MT3DMS model can also simulate certain chemical reactions, such as adsorption and decay (Gusyeve 2014, El-Kadi 2018), but for simplification purposes and due to lack of information, a conservative chemical was simulated in this study to represent pesticides. The modeling process introduces known contaminant sources and calculations are made to predict contaminant concentrations at various aquifer locations at different times. The sources of contaminant (pesticides in this case) based on agriculture land-use (adapted from 'Faga'alu land-use map' 2012) are shown in **Figure 12**. To facilitate calculations of aquifer concentrations as percentages, all agriculture polygons were assigned 100 ppm as an initial concentration of a hypothetical pesticide. The model was run

for stress periods of 10,000 days (~27.3 years), with concentration measurements recorded at 365 day (1 year) intervals. The longitudinal dispersivity value was set at 20 m. The ratios of horizontal and vertical transverse dispersivities and longitudinal dispersivity were set to 0.2 and 0.1, respectively. Longitudinal dispersivity and transverse dispersivity ratios of similar magnitudes were used in a USGS study by Zheng et al. (2001). MT3DMS requires the flow field information as input, specifically hydraulic head and porosity, which are used to estimate flow velocity (Zheng and Wang 1999, El-Kadi 2018). Flow field information was provided by the calibrated MODFLOW model, which was run for a steady state condition. The MT3DMS model was run subsequently to simulate contaminant transport through the aquifer over time.

2.3.8 ArcGIS and spatial analysis

ArcGIS was used to plot data into maps to visualize the results of this study. Maps ranging in focus spanning from island-wide to watershed were generated. Accumulated data was used to illustrate pesticide concentration levels, Rn measurements, stream discharge measurements, and model calibration methods.

Numerous shapefiles were adopted from Shuler (unpublished 2018) (agriculture, geology, land-use, coastline, watershed, etc.) and Leta (unpublished 2018) (recharge) to build the MODFLOW model, and to provide a basis for analyzing patterns of pesticide distribution. Several shapefiles were also created from the measurements made in this study (sample points, observation points, elevation-based scatter points), using the ArcMap program. These shapefiles were used as coverage input files in the GMS software for use in the MODFLOW model. Spreadsheets were used to compile all data collected in this study, as well as to complete calculations and to plot graphs.

3. Results

3.1 ELISA PESTICIDE TEST RESULTS

3.1.1 Island-wide glyphosate distribution

In January 2017 the ELISA test was used to analyze glyphosate concentrations in all (107 total) water samples collected in August 2016. The highest recorded value of glyphosate was 0.301 ppb at the southern coastal spring groundwater sample in the Faga`alu watershed. This concentration falls well below the EPA set maximum contaminant level (MCL) of 700 ppb. Glyphosate was detected in 56% of the collected groundwater samples and in 62% of the collected stream samples. In total, 59% of the total combined samples showed detectable glyphosate levels (**Table 5**).

Table 5: Percent occurrence of each pesticide (% of samples where present) in ground and surface water samples, and in total samples taken. Individual data (sample locations, concentrations) are listed in Appendix Table A.

Pesticide	Positive Hits (%)		
	Groundwater	Streams	Total
Glyphosate	62	56	59
Imidacloprid	72	36	57
DDT/DDE	98	97	97
Azoxystrobin	0	0	0

Concentrations of glyphosate from several undeveloped regions of the island were below detectable limits, and thus when choosing a more focused survey for the remaining three pesticide analyses, these sites were omitted from analysis due to technical constraints (the microtiter plates allowed the analysis of 79 samples per kit). Maps of observed glyphosate concentration across the island of Tutuila from the August 2016 survey, were separated as surface sites at baseflow

(**Figure 13**) and as groundwater sites (**Figure 14**) to illustrate the observed concentration distribution.

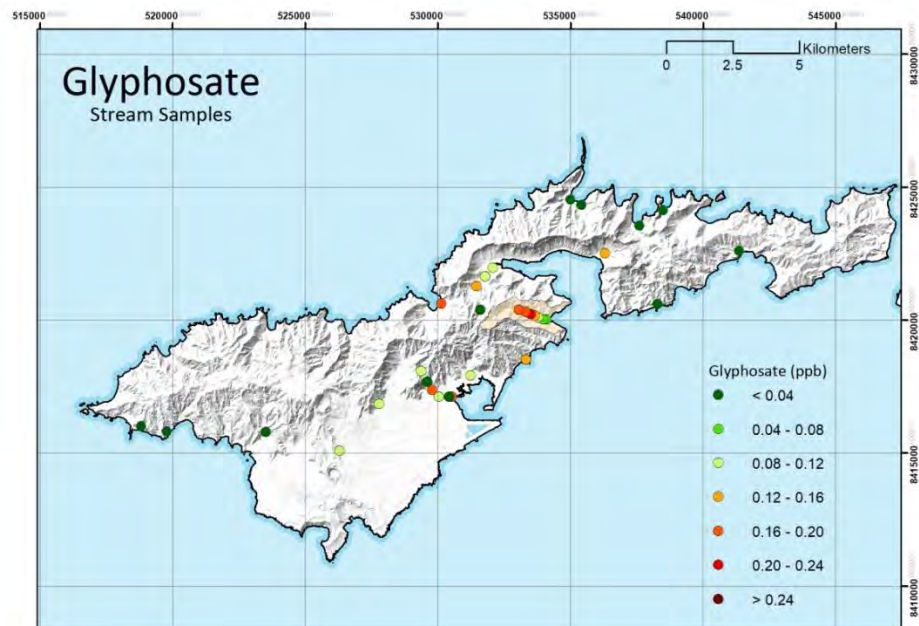


Figure 13: All stream sample concentrations of glyphosate (n=44) across Tutuila. These represent an analysis of surface water at baseflow conditions during the August 2016 survey.

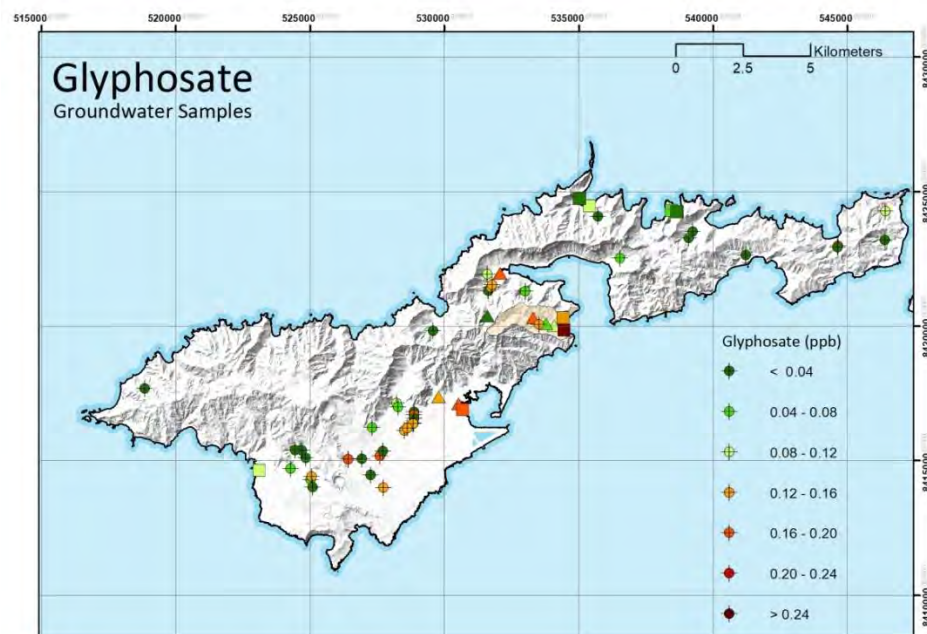


Figure 14: All groundwater sample concentrations of glyphosate (n=63) across Tutuila, including groundwater wells (circle with cross), coastal springs (squares), and stream bank push-point samples (triangles) taken during the August 2016 survey. The Faga'alu watershed is indicated by the tan shaded area.

3.1.2 Glyphosate concentrations in the Faga`alu watershed

In the Faga`alu watershed, concentrations of glyphosate are mostly above the island-wide average (0.075 ppb). The highest concentration in the watershed (0.301 ppb) was observed in a coastal spring on the southern portion of coastline, while the highest concentration in baseflow surface samples was observed at station 6 (0.196 ppb). Faga`alu well #179 had a concentration of 0.156 ppb. A side-by-side comparison of herbicide concentrations of stream samples at baseflow stream conditions and at high flow conditions, as well as in tributaries and stream bank groundwater samples as a function of distance upstream from the stream-ocean interface, is shown in **Figure 15**. The high flow concentration at station 2 (green point in **Figure 15** located 200 m upstream) is 0.240 ppb, also relatively high compared to baseflow and groundwater near the same coordinates (near harbor).

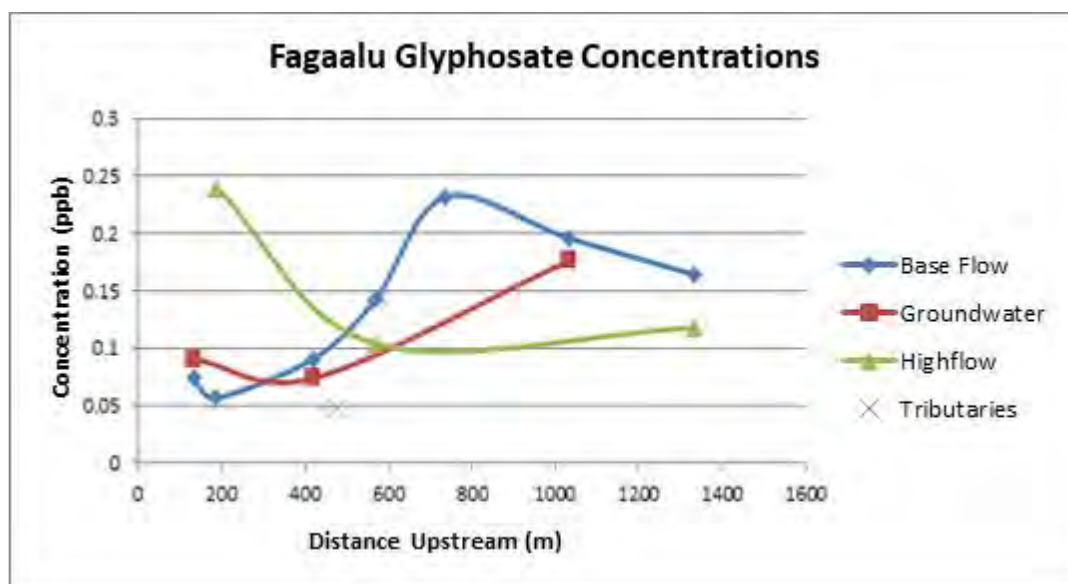


Figure 15: Glyphosate concentrations at seven stream and two tributary sites of the Faga`alu watershed. Stream bank groundwater and high flow measurements are included to compare with stream and tributary baseflow concentrations.

3.1.3 Imidacloprid island-wide distribution

On June 1, 2017 the ELISA analysis was used to measure imidacloprid concentrations in 79 of the total 107 water samples taken. The number of sites chosen for analysis was dictated by the number of available wells in the ELISA microtiter plate; priority was given to samples where

glyphosate was present in the island-wide study. The highest recorded concentration of imidacloprid on island was 0.172 ppb in well #66 on the Tafuna Plain. This concentration lies well below the LD₅₀ level of 450 mg/kg (4.5×10^5 ppb) that poses danger to laboratory rats in some studies (*Imidacloprid (Technical Fact Sheet)* 2010). For humans it would likely be less toxic yet. Imidacloprid was detected in 72% of the collected groundwater samples and in 36% of the collected stream samples, with a 57% occurrence in total combined samples. Distribution maps of imidacloprid concentrations across the island of Tutuila in surface and groundwater collected during the August 2016 survey are shown in **Figures 16 and 17**.

3.1.4 Imidacloprid in Faga`alu

Aside from its presence in one high flow sample at station 2 (0.087 ppb), all other Faga`alu watershed samples from the stream, well, and coastal springs contained imidacloprid concentrations below the detection limit (0.075 ppb). Imidacloprid was more prevalent on the Tafuna-Leone Plain portion of the island than in the Faga`alu watershed.

3.1.5 Azoxystrobin island-wide distribution

On June 16, 2017, the ELISA test was performed in the laboratory to measure azoxystrobin concentrations in the same 79 water samples that were used for imidacloprid analysis. This test was run over ten months since the water was collected on Tutuila, and samples were stored refrigerated in dark amber vials. In the case of this pesticide, methanol was added just prior to analysis. Methanol is an essential part of the preparation in that it acts as a water-miscible solvent in the assay buffer, which increases maximum absorbance and decreases the sensitivity of the immunoassay (Wang 2012). The methanol addition is recommended as soon as possible after sample collection, but this was not possible in the field sampling due to practical reasons. Across the island, all 79 samples that were tested for azoxystrobin had concentrations below detectable limits, showing no detectable trace of the fungicide.

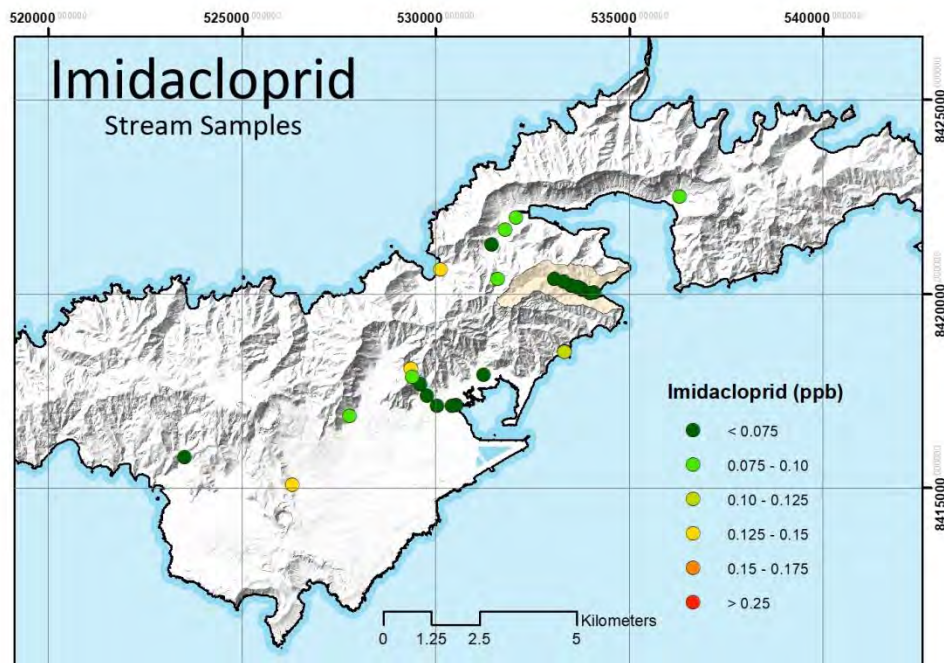


Figure 16: Stream sample concentrations of imidacloprid (n=32) across Tutuila. These represent an analysis of surface water at baseflow conditions during August 2016.

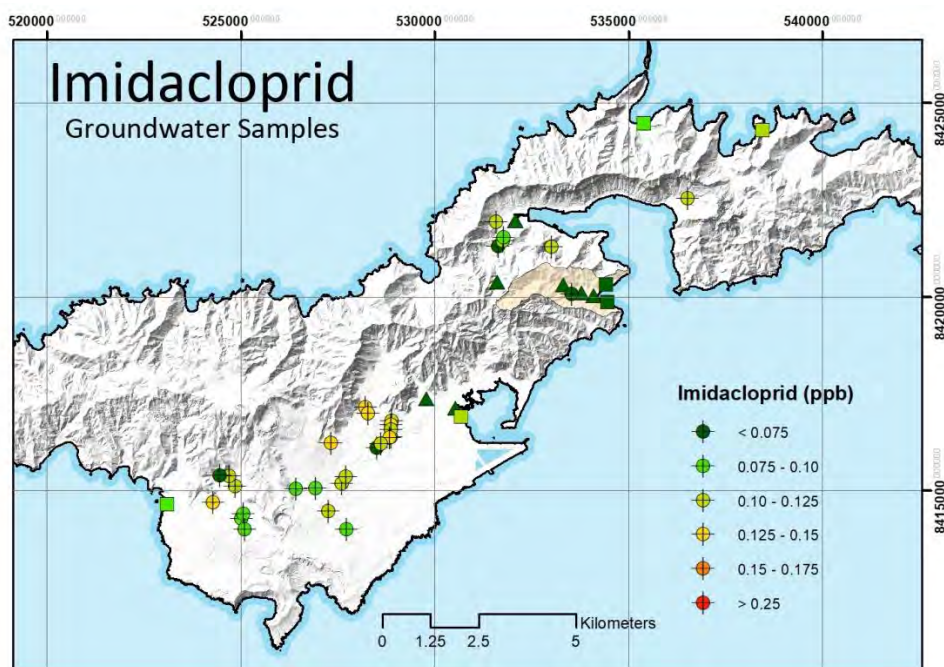


Figure 17: Groundwater sample concentrations of imidacloprid (n=46) across Tutuila. This includes groundwater wells (circle with cross), coastal springs (squares), and stream bank push-point samples (triangles) taken during the August 2016 survey.

3.1.6 DDT/DDE island-wide distribution

On June 20, 2017, the ELISA procedure was used to analyze for DDT/DDE (which will be referred to as ‘DDT’ from this point forward) concentrations in the same 79 water samples analyzed in the two previous tests. It had been approximately ten months since the collection and refrigeration of samples. Methanol was added to samples prior to analysis, in the same manner as for the azoxystrobin analysis. DDT was detected in nearly all samples tested. The highest recorded value of DDT in the samples was 3.717 ppb from well #66 on the Tafuna Plain, the same well where the highest concentration of imidacloprid was recorded. This concentration lies well below the LD₅₀ level of 113 mg/kg (1.13×10^5 ppb) that could pose danger to laboratory rats (*Toxicology and Exposure...* 2003). DDT was present at detectable concentrations in a high percentage of wells and streams, with occurrence in 98% of the collected groundwater samples and in 97% of the collected stream samples, and a 97.4% occurrence in all combined samples. Distribution maps of DDT concentration distribution across the island of Tutuila from the August 2016 survey are shown in **Figures 18** and **19**.

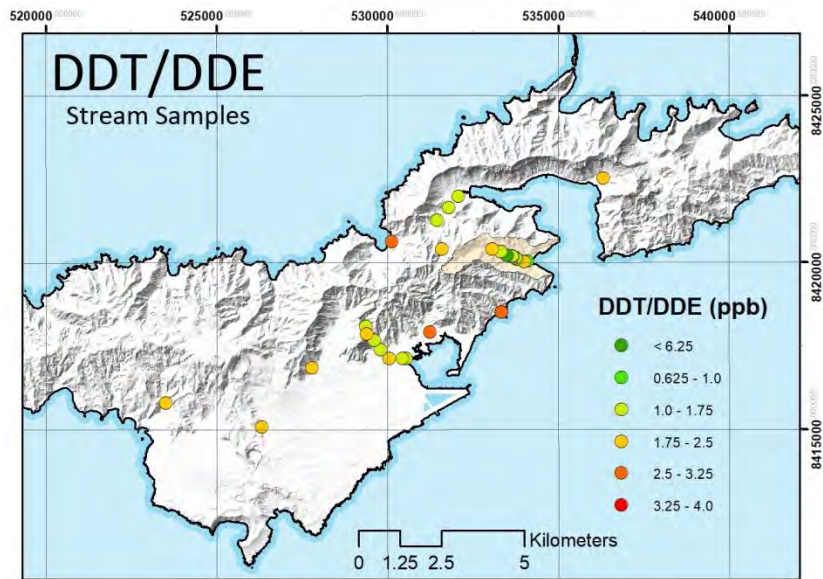


Figure 18: Stream sample DDT concentrations (n=32) across Tutuila. These represent an analysis of surface water at baseflow conditions during the August 2016 survey.

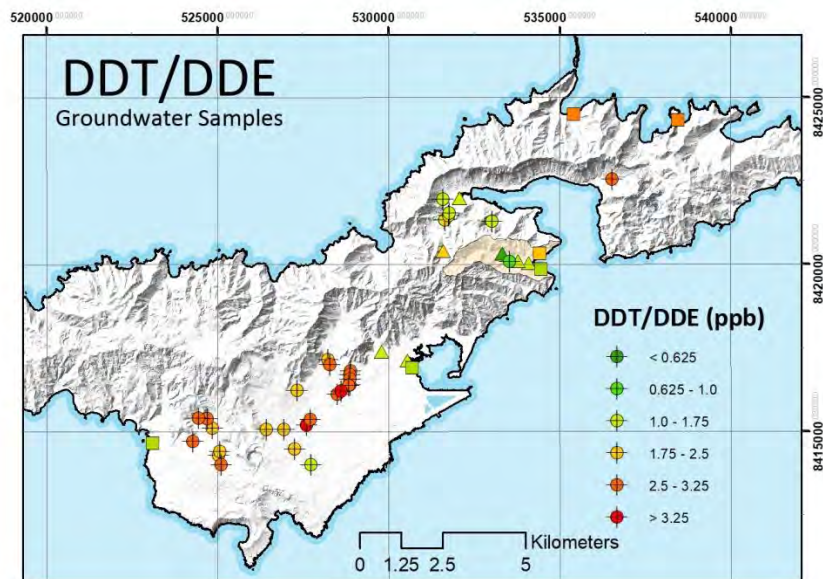


Figure 19: Groundwater sample DDT concentrations (n=46) across Tutuila. This includes groundwater wells (circle with cross), coastal springs (squares), and stream bank push-point samples (triangles) taken during the August 2016 survey.

3.1.7 DDT/DDE in Faga`alu

Levels of DDT in the Faga`alu watershed were relatively low (0 - 2.091 ppb) compared to concentrations found in Tafuna (1.672 – 3.717 ppb), however presence was documented in 89.5% of the Faga`alu samples. The only locations on the entire island that lacked DDT were two Faga`alu sites; one groundwater stream bed sample, and one surface sample in the Faga`alu Stream at baseflow. The highest concentration of DDT in a baseflow surface sample (2.026 ppb) was at station 7, while the high flow sample at the same location showed increased concentration (2.091 ppb). The northern coastal spring also had higher than average (relative to all samples in the watershed) concentration at 2.068 ppb. DDT concentrations in the different types of samples in relation to distance upstream from the ocean are displayed in **Figure 20**.

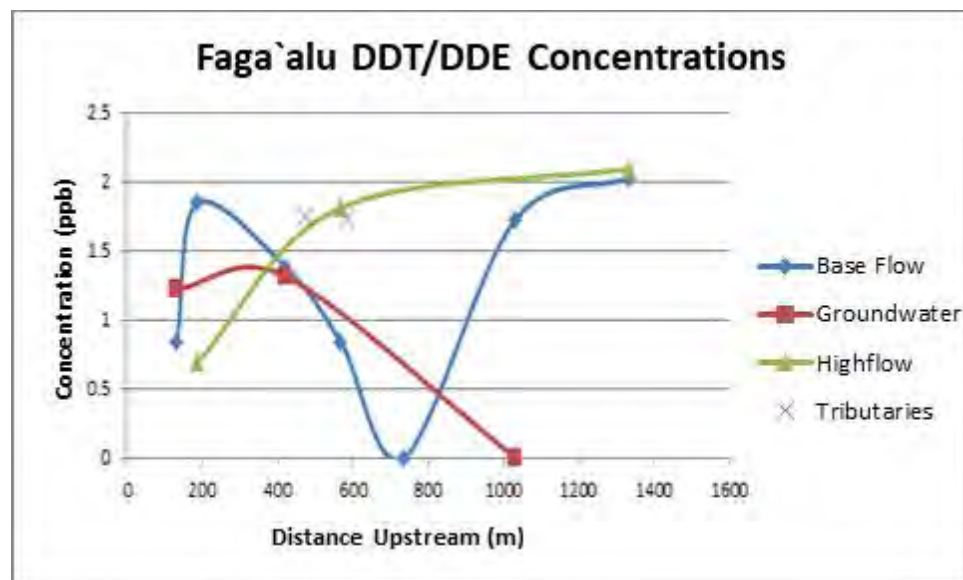


Figure 20: DDT concentrations in seven stream and two tributary sites of the Faga`alu watershed. Stream bank groundwater and high flow DDT concentrations are included to compare with DDT in stream and tributary baseflow samples.

3.1.8 Summary of Faga`alu Stream Survey

Table 6: An overview of the samples taken from the Faga`alu watershed is given below. The data is divided into sample type. Station numbers with coordinates, pesticide concentrations, radon levels, and stream flow rates are given. (*Data for the full island-wide survey is in Appendix A, **Table A**)

Stream			Glyphosate	DDT	Radon	Stream Flow
Station #	Latitude	Longitude	(ppb)	(ppb)	(dpm/L)	(m³/s)
STREAM - Baseflow						
1	-14.29137	-170.68379	0.076	0.839	121.78	0.42
2	-14.2915	-170.68479	0.057	1.844	85.12	0.0335
3	-14.29074	-170.68668	0.091	1.382	18.80	0.0265
*	-14.29044	-170.68707	0.048	1.742	10.58	0.0019
4	-14.29006	-170.68778	0.142	0.839	19.21	0.0274
*	-14.29002	-170.68791	0.143	1.726	79.51	
5	-14.2897	-170.68926	0.232	0	14.90	0.0228
6	-14.28878	-170.69109	0.196	1.722	34.28	0.0293
6	-14.28878	-170.69109	0.112	1.041		
7	-14.28813	-170.69337	0.164	2.026	28.94	0.0276
STREAM - High Flow						
2	-14.28878	-170.69109	0.24	0.692		
4	-14.28813	-170.69337	0.104	1.808		
7	-14.28878	-170.69109	0.118	2.091		
STREAM- Groundwater						
1	-14.29137	-170.68379	0.091	1.219	586.89	
3	-14.29074	-170.68668	0.074	1.313	77.23	
6	-14.28878	-170.69109	0.176	0	55.76	
WELL						
#179	-14.29104	-170.68895	0.156	0.876	333.7	
COASTAL SPRING						
S	-14.29294	-170.68039	0.301	1.509	32.4	
N	-14.28879	-170.68079	0.154	2.068	91.3	

*Tributary sites, without a station #

3.2 INTERPRETING HYDROGEOLOGY AND BUILDING A HYDROLOGICAL MODEL FOR THE FAGA`ALU WATERSHED

3.2.1 Seepage Runs

Segments of the stream that gained or lost volume due to groundwater flux were physically determined by measuring stream discharge rates during baseflow at each of the seven main study sites of the Faga`alu Stream. Stream discharge ranged from 0.023 m³/s to 0.042 m³/s ; and **Figure 21** shows the discharge pattern along the stream (site #1 being closest to the ocean, site #7 being farthest into the valley). The Faga`alu Stream gains groundwater where the mountains meet the floor of the valley (sites #7-6), then loses water to the underlying aquifer over a large portion of the alluvial plain (sites #6-5). The stream then increasingly gains water near the bottom of the basal lens, where the land meets ocean and the stream exits into the bay (sites #4-1). A basal lens, also commonly referred to as freshwater lens, is often found on coral-fringed islands and forms when fresh groundwater rests on top of denser salt water near the coastal plain (Ryan 2008). A coastal aquifer and its basal lens are illustrated in Appendix B (**Figure 30**).

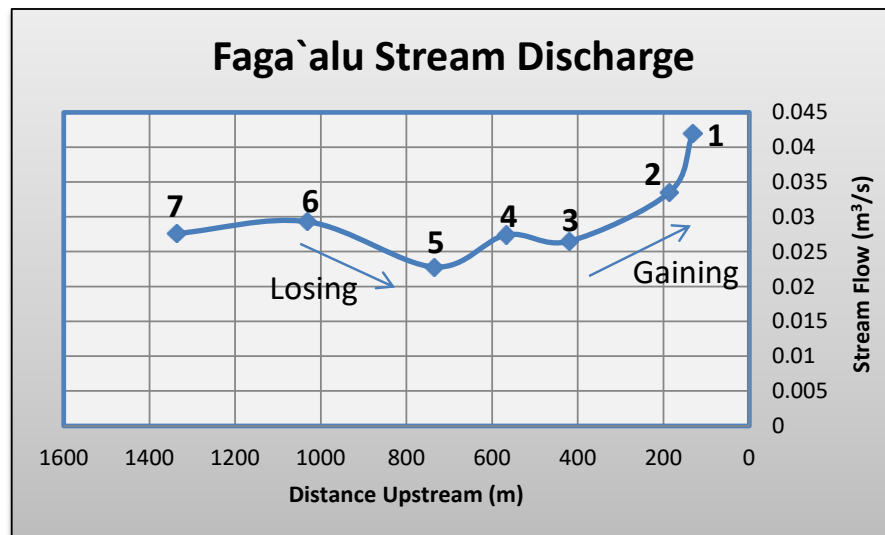


Figure 21: Stream discharge measurements, showing where the Faga`alu Stream is gaining and losing water from and to the aquifer.

Where the stream is gaining in discharge, groundwater from the aquifer must be adding to the stream, thus the stream level must intersect the water table near these points. Where the

discharge decreases, the stream is losing water to the aquifer below, as the water table is lower at these points. These results were used to calibrate the hydrological model (MODFLOW), as described in the Methods section.

3.2.2 Radon (Rn) survey

A radon survey can provide evidence of groundwater contribution to a stream, just as direct seepage runs can. Since higher ^{222}Rn concentrations indicate groundwater contributions specifically, the amount of ^{222}Rn found in a sample of surface water can tell one where groundwater is being added to a stream. Radon concentrations in the stream should correlate with gaining and losing locations in the stream. As can be seen in **Figure 22**, the ^{222}Rn levels in the Faga`alu Stream and push-point samples follow a similar pattern to the stream discharge measurements shown in **Figure 21**. Radon levels ranged from 15 – 122 dpm/L (*dpm = disintegrations per minute) in surface waters, and from 56 – 587 dpm/L in stream bank groundwater samples.

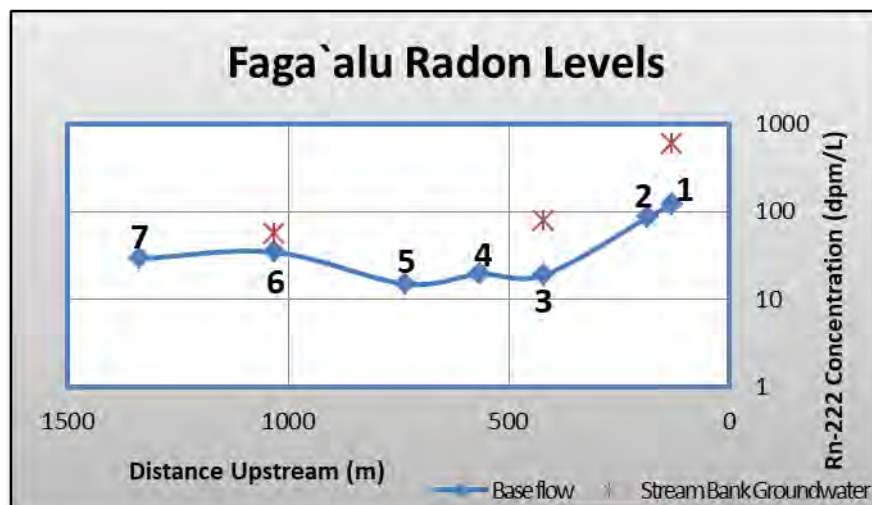


Figure 22: Radon-222 levels in surface (diamond) and groundwater (cross) at each Faga`alu stream study site. The higher the radon in the stream, the more groundwater input the stream is receiving.

The seepage run measurements are graphed alongside the radon concentrations in **Figure 23** to show coincident locations of increasing discharge and radon. The two parameters are

reported on different axes and on different scales, but they show coherent variation. These two measurements were thus used in calibrating the MODFLOW model to determine groundwater flow in the Faga'alu aquifer.

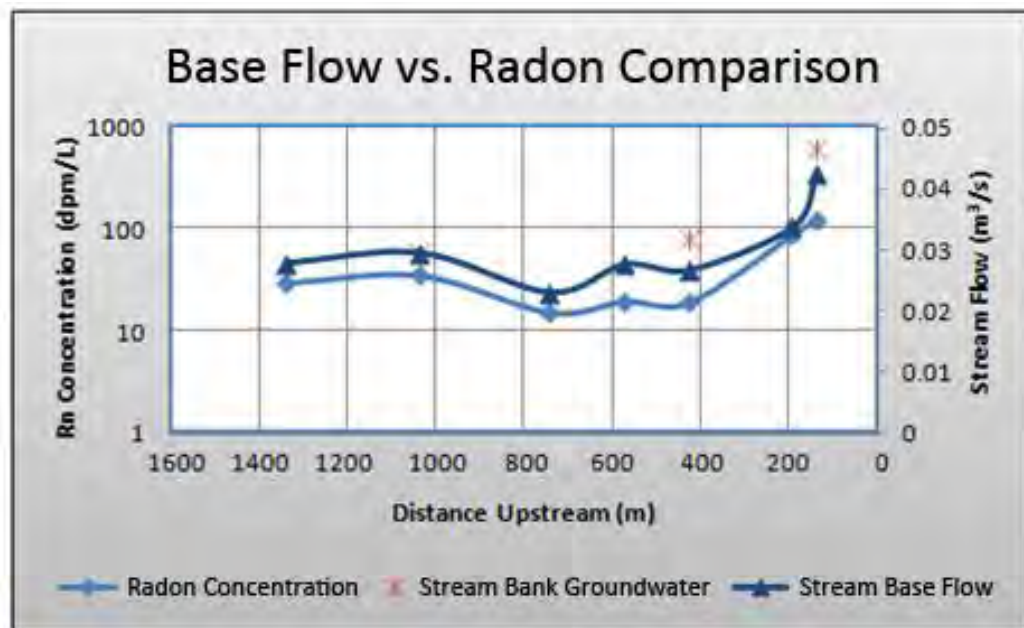


Figure 23: A side-by-side comparison of radon concentration to stream discharge, to show correlation of the measurements, and thus validation of the results.

3.2.3 MODFLOW model development

The MODFLOW model was developed as described in the Methods section. The model was then calibrated by using: 1) stream measurements from locations of gaining reaches of the stream and 2) six calibration points for head level. A water table was created by MODFLOW, and the computed vs. observed groundwater levels followed a relatively straight trend-line with a regression line slope of 0.9216 and an R^2 -value of 0.9899 (**Figure 24**). Observed water table head levels are shown side-by-side with the computed levels after hydraulic conductivity was optimized in each quadrant (**Table 7**). Calibration was obtained by manually adjusting the hydraulic conductivity and stream bed conductance values until computed head values closely matched observed values. According to the model, water head elevation ranged from 0 m at the ocean to ~280 m at the back of the watershed. The limited number of observation points casts

some uncertainty on the results. The water table created by MODFLOW can be seen in **Figures 25 and 26**.

Table 7: Observed vs. Computed head levels according to the calibrated MODFLOW model.

Observation Point	Observed Head Level (m)	Computed Head Level (m)
1	2.53	7.36
2	42.46	71.78
3	108.72	110.03
4	160.00	167.29
5	253.37	245.39
6	250.48	249.60

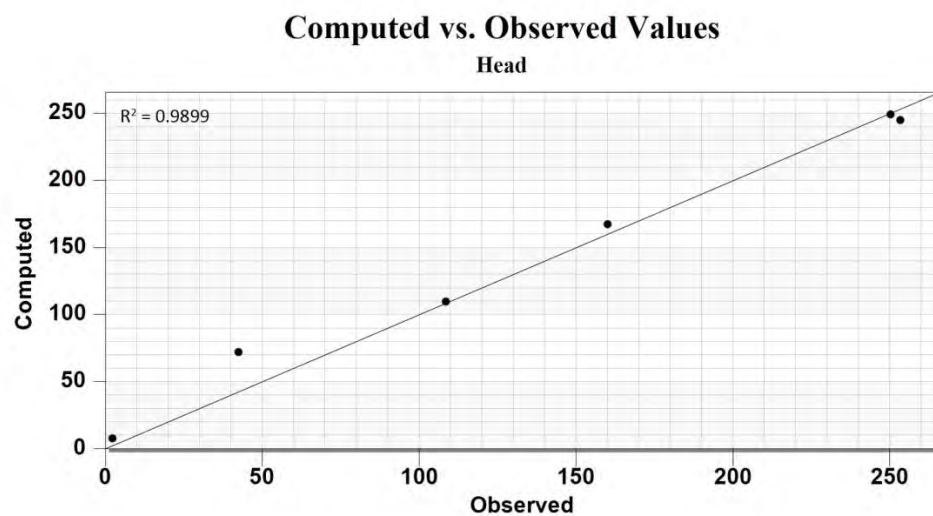
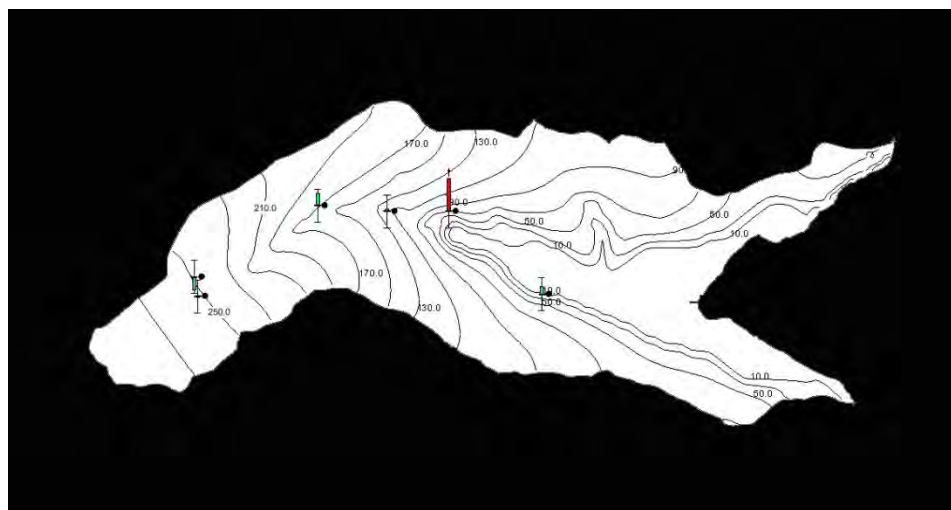


Figure 24: Computed vs. observed head values used in calibration follow regression line, with an R^2 value of 0.9899..



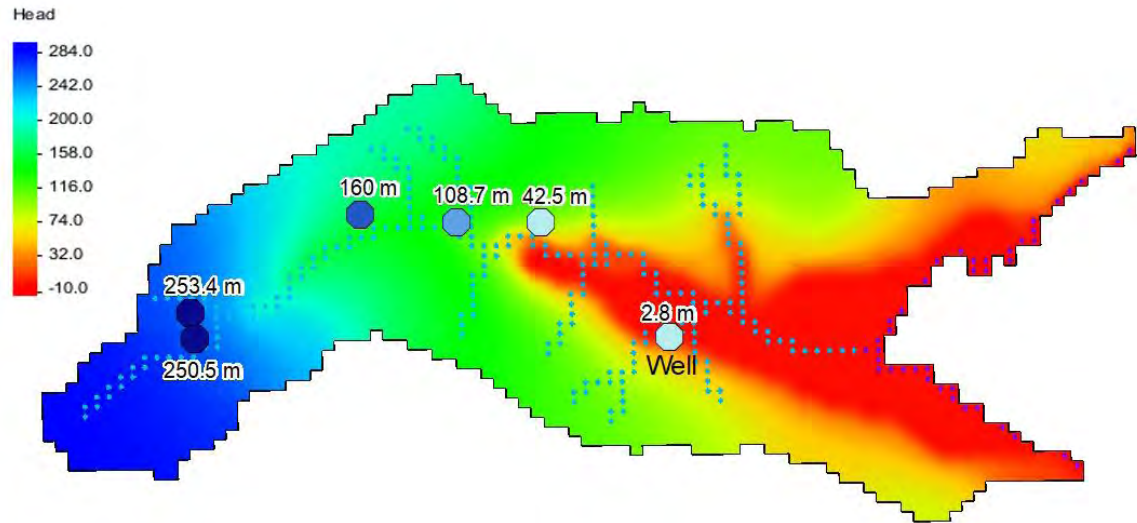


Figure 26: Contoured representation of the water table surface in the Faga'alu aquifer superimposed on known head levels (circles).

3.2.4 Surface-groundwater interactions

The MODFLOW model was used not only to estimate groundwater flow paths, but also to quantify groundwater-surface water interactions. Specifically, I was interested in: 1) groundwater discharge into the ocean as SGD, and 2) groundwater contribution to baseflow in the Faga'alu Stream. Using this information, pesticide discharge in the stream and across the land-ocean interface could be attained. Stream and SGD fluxes are shown in **Table 8**, with estimated pesticide fluxes for each. Since azoxystrobin was absent island-wide in the samples, and imidacloprid was generally absent from the Faga'alu aquifer, only glyphosate and DDT were used for the focused study.

The stream was divided into an upper and lower reach to delineate the upper section, which was gaining water, from the rest of the stream. The coast was divided into northern, central, and southern sections. The upper reach of the stream had a modeled groundwater contribution of 91% of the total flow rate. Glyphosate was estimated to be 89% derived from groundwater in this reach, while DDT was estimated as 91% groundwater derived. The flow rate in the lower reach had a 24% contribution by groundwater. Glyphosate was 27% and DDT was 28% derived from groundwater feeding the stream in this section. It will be discussed later why

the lower section (basal lens) of the stream showed lower fractions of groundwater in the modeled stream flow. Coastal SGD was determined by dividing the land-ocean boundary into three segments, as described earlier (**Figure 11**). The total submarine groundwater discharge rate was estimated by MODFLOW to be 4129 m³/d across the land-sea boundary. Total glyphosate flux was estimated at 482 mg/d, while total DDT/DDE flux was estimated at 5519 mg/d, at the offshore boundary to the reef region.

3.2.5 MODPATH simulation

The path lines created by MODPATH do not predict realistic contaminant distribution in the aquifer, considering the role that the dispersion process plays in natural systems. Injecting and tracing particles from or to a source is used in MODPATH to predict such path lines. In reality, particles will spread forming a plume of varying solute concentrations. Still path lines can provide an approximate direction along the plume centerline that can be used in identifying the sources of contaminants (El-Kadi 2018). In current simulations, injected particles were traced backwards from groundwater sample locations to determine possible source locations. Simulated path lines following a steady state MODFLOW run are shown in **Figure 27**. Flow lines from the Faga'alu well #179 originate from upslope where agricultural polygons were present in the Faga'alu land-use map (2012). Although none of the other flow paths created for other push-point locations correlate to the agriculture, the path from station 3 is short and may reflect direct residential application as it lies on the developed alluvial plain.

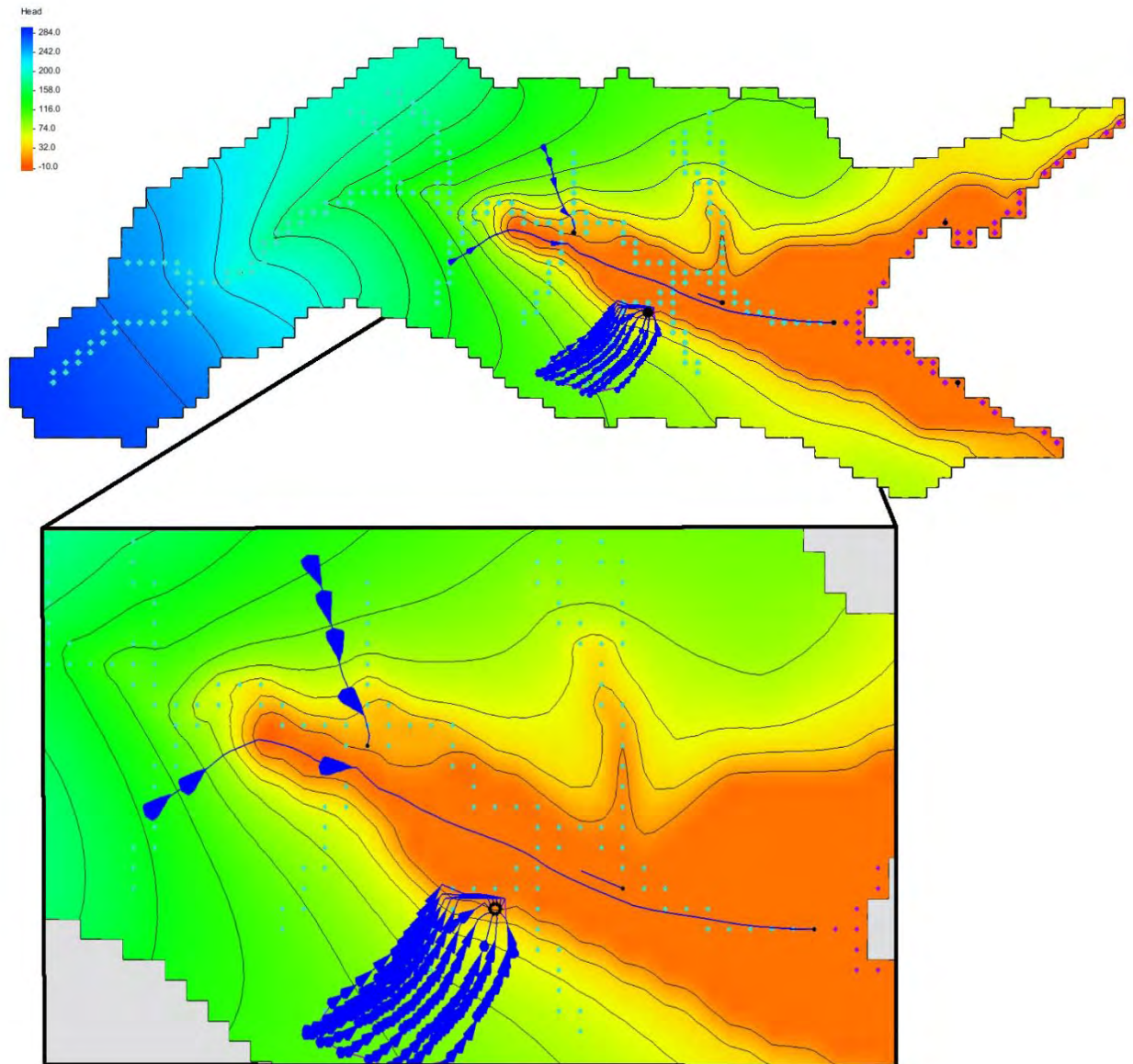


Figure 27: Path lines shown in blue, trace particles from groundwater sample locations in Faga'alu. Each arrow on the line represents a period of 10 years. The coastal springs did not show movement in backwards advection as did the other sites.

Table 8: MODFLOW-derived groundwater (GW) discharge into Faga`alu Stream is compared to total measured stream discharge at baseflow conditions. Total discharge for upper and lower reaches of the stream is shown, as well as the sum for both reaches; these values are derived from in situ measurements. GW contribution as percent of total flow is calculated by dividing GW by total flux. Pesticide fluxes by groundwater discharge as well as total per stream are calculated by multiplying the corresponding water discharge by the measured pesticide concentrations. The fraction of pesticides contributed by groundwater into the stream is also provided. MODFLOW-derived coastal SGD input into Faga`alu Bay was divided into 3 sectors.

	Discharge (m ³ /d)			Glyphosate flux (mg/d)			DDT flux (mg/d)		
	GW	Total	GW as fraction of total (%)	GW	Total	GW as fraction of total (%)	GW	Total	GW as fraction of total (%)
Stream									
Upper Reach	1798	1970	91	316	355	89	*2476	2721	*91
Lower Reach	406	1659	24	34	126	27	514	1842	28
Sum	2204	3629	61	350	481	73	2990	4564	66
Coastal SGD									
Northern	446			69			922		
Central	3312			301			4037		
Southern	371			112			560		
Sum	4129			482			5519		

*As DDT concentration at station 6 was below detection limit, the mean DDT concentration of two upper reach sites from neighboring watersheds was used in its place as an estimate (see text).

3.2.6 MT3DMS model

The MT3DMS model simulates transient convective-dispersive contaminant-transport in the aquifer once initial contaminant concentrations are defined for different source polygons. Such polygons are shown in panel A of **Figure 28** representing agricultural units that were adapted from a land-use shapefile ('Faga'alu land-use map' 2012). A contaminant, which is a pesticide in this case, is assumed to leach at a constant rate from the polygons at defined initial concentrations. Panels B through E in **Figure 28** show the contaminant concentrations in the aquifer at different simulation times. The model was run for 9125 days (25 years) following the calibrated steady state MODFLOW run. On the northern side of the bay, concentration levels rise higher than source concentrations (100 ppm), in certain cells by over four times (panels C,D, and E, in red). Concentrations estimated in some cells at the coastline exceed 3,000 ppm; these are likely due to numerical errors in the model, and will be discussed later.

Simulation results were continuously recorded at monitoring points, including the push-point stations and the well (**Figure 29**). The expected changes in concentration over time are observed at designated sample locations; these are known as breakthrough curves. These curves show transient contaminant concentrations in specified grid cells. Unfortunately, there were no data available for concentration measurements at these locations for model validation. However, the results can potentially be useful for assessing the relative sensitivity to contamination at various locations, and for helping in future assessments as additional data become available.

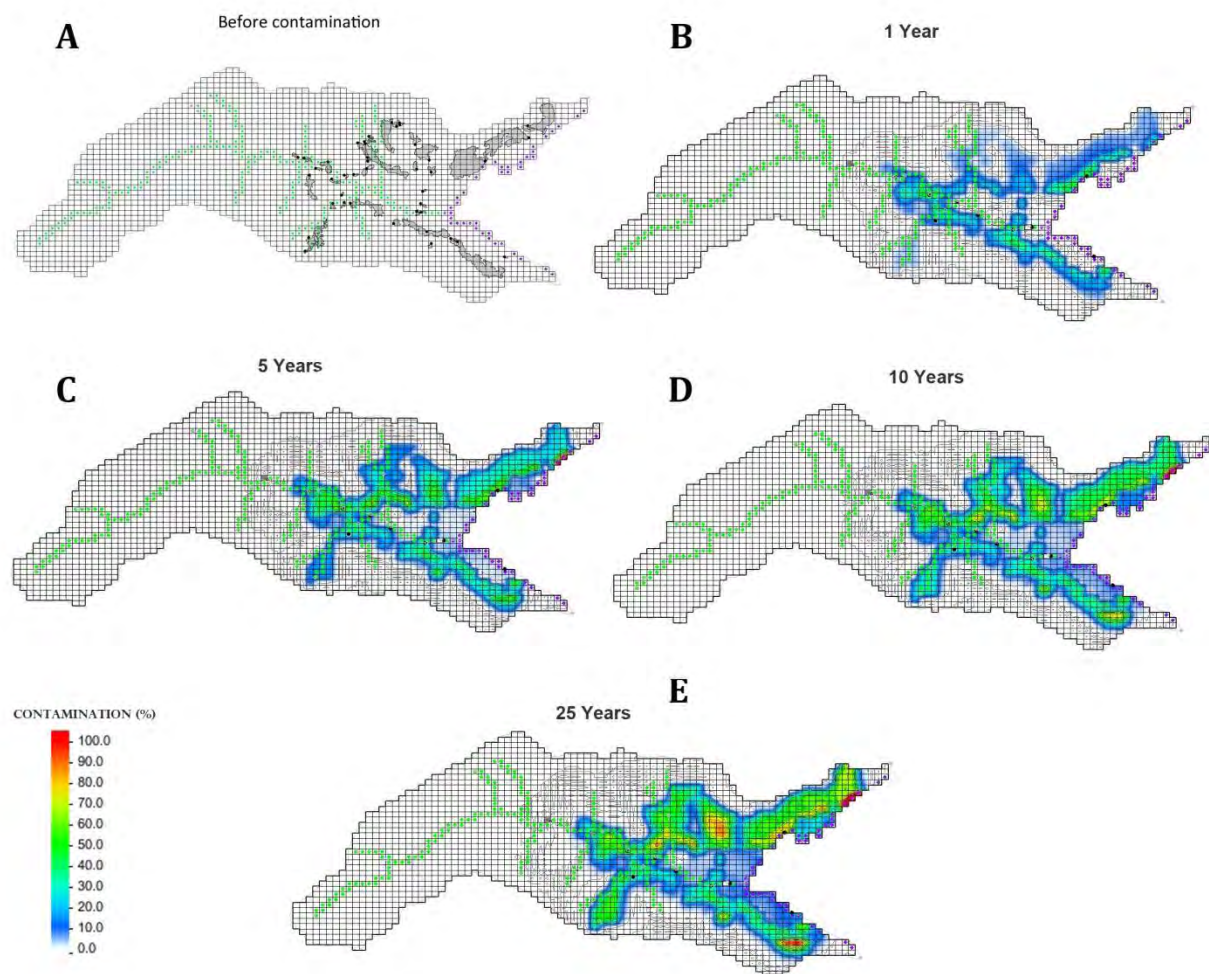


Figure 28: Results for the transient MT3DMS model runs are displayed at the given simulation times. Agricultural contamination was set at the sources (Panel A) and concentrations are simulated following a steady state MODFLOW run. As should be expected, concentrations increase as time progresses.

MT3DMS Concentration Active Time Series at Groundwater Locations

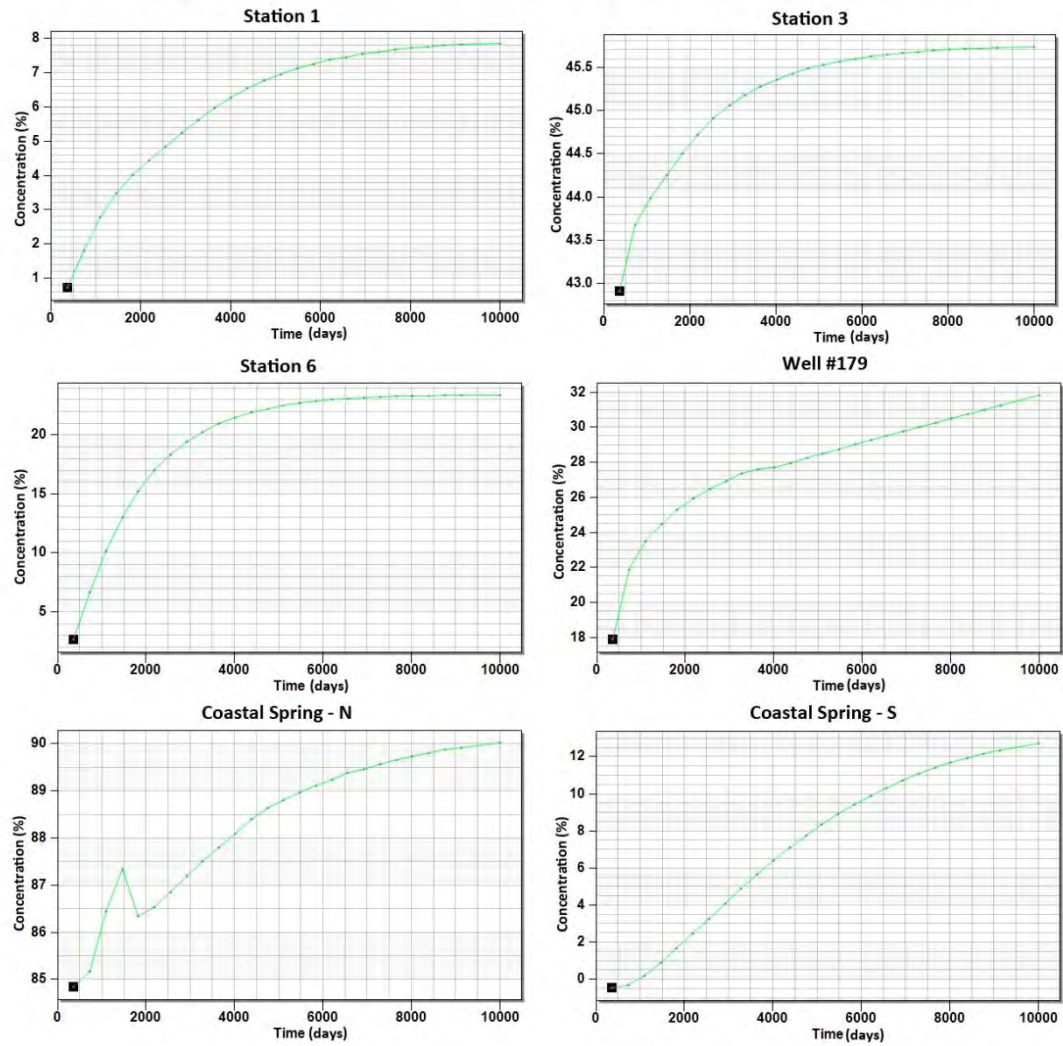


Figure 29: Breakthrough curves for contamination at the Faga`alu groundwater and coastal sites.

4. Discussion

4.1 PESTICIDE SAMPLE TYPE AND SPATIAL DISTRIBUTION ANALYSIS

Statistical analysis of island-wide pesticide concentrations using analysis of variance (ANOVA) revealed at the 95% significance level that there is no difference in surface and groundwater glyphosate concentrations across the island of Tutuila (F-critical = 3.9316, F = 0.8339). ANOVA results indicate that imidacloprid and DDT, however, are dissimilar in surface and groundwater concentrations across the island (F-critical = 3.9668, imidacloprid: F = 11.9095, DDT: F = 11.0460), with higher concentrations present in groundwater.

4.1.1 Glyphosate spatial distribution

Glyphosate was detected in low concentrations in samples from the eastern and western coastal regions of Tutuila, relative to the central region of the island spanning from the Tafuna Plain to the Pago Pago Harbor, which showed more elevated concentrations (64% higher than the island-wide average of 0.075 ppb). The Faga`alu watershed, in particular, showed higher concentrations of the herbicide than anywhere else sampled. The watershed average was 0.141 ppb, which is 88% higher than the island-wide average. The highest concentration found on island during this study was the southern coastal spring in Faga`alu, which had 0.301 ppb of glyphosate. Although this is considered generally low by EPA standards (700 ppb MCL), its presence relative to the rest of the island demonstrates the value of studying contaminant flow in this priority watershed. In a similar study by Gourcy et al. (2009), glyphosate was found in concentrations ranging from 0.094 ppb to 0.323 ppb on the Caribbean tropical island of Martinique, which also has a volcanic history. In a 2014 study on the island of O`ahu in Hawai`i, the highest concentration of glyphosate found in water samples was 0.14 ppb, also comparable to this study (*2013-14 State Wide Pesticide 2014*).

In the past, glyphosate at low levels has been considered non-toxic to humans as well as fish, mammals and birds (*National Primary Drinking Water* 1995). However, glyphosate has recently been classified as a probable carcinogen in several recent studies (Myers 2016). The company that originally formulated glyphosate, Monsanto, has disputed these claims (Hogue 2017). Kidney, liver and reproductive problems are also a concern in the bioaccumulation of the herbicide over long period exposure, for certain organisms (Myers 2016). Half-life estimates have also recently undergone revision, and are possibly longer than previously recognized in water and soils. Many believe that estimates on daily intakes are based on outdated science, and should be re-analyzed with modern methodology (Myers 2016).

In the Faga`alu watershed study, glyphosate concentrations peaked in stream surface waters about 0.75 km upstream from the bay during baseflow (as seen in **Figure 15**). Further up the stream, concentrations dropped, although it is surprising that glyphosate was present at all at station 7, which is located on undeveloped land on top of a waterfall behind the quarry. No logical use for a glyphosate-based herbicide behind the quarry is evident. Glyphosate concentrations peak where developed land begins (station 5) and becomes further diluted down the stream at three consecutive stations (stations 4, 3, and 2) toward the bay. At the very bottom near the bay, where the basal lens contributes baseflow to the lower stream, concentrations rise by 30% between station 2 and station 1.

Within the developed part of the watershed, the pattern of glyphosate distribution could be due to the spatially variable baseflow contribution to the stream, where glyphosate concentrations correlate with the locations where the stream is gaining or losing water. Where the Faga`alu Stream is gaining, according to seepage runs, concentrations of glyphosate are slightly higher, suggesting its addition to the stream via groundwater-dependent baseflow. This was confirmed by finding matching concentrations of this herbicide in corresponding stream bank groundwater samples. Upstream, at the back of the valley, the stream is gaining water flow from volcanic basalts. Here, the elevated concentrations of the herbicide could result from the slow

moving groundwater in the aquifer in basalts (possibly dikes) that have a relatively lower hydraulic conductivity. Where the stream is losing water, resulting from a drop in the water table in the central section of the watershed, glyphosate concentrations decrease as well. This may be due to degradation of glyphosate without new inputs or due to dilution by tributaries. As the stream moves further down the alluvial plain toward the bay, where hydraulic conductivity is greater, according to my conceptual model, a larger subsurface flux of water would dilute concentrations. A decrease in glyphosate concentrations was observed in groundwater between push-point samples from station 6 to station 3, reflecting this pattern. As the water nears the mouth of the stream, at Faga'alū Bay, concentrations of glyphosate spike up again (by 30% in surface and 23% in groundwater samples). This elevation in concentration at the bottom of the alluvial plain could be due to increased subsurface water contributions. As the groundwater body forms a biconvex lens, known as a basal lens, it may intrude into the stream bed and contribute additional baseflow (Macdonald 1983). The correlation of glyphosate concentrations with the gaining and losing sections of the stream is consistent with a link to groundwater contributions to the baseflow. Baseflow into the stream, and then stream transport, are thus important in the overall flux of the herbicide through the watershed. The half-life of glyphosate in streams (~3-14 days) is shorter than its half-life in soils (~44-60 days) (Schuette 1998). Thus, the glyphosate concentration observed in the baseflow of Faga'alū stream could be attributed to its higher persistence in soils, as its patterns reflect surface and groundwater interactions.

The high flow stream studies showed an opposite trend to low flow conditions, with higher glyphosate levels near the mouth of the stream, and decreasing levels farther up the valley. Since high flow is a result of overland flow joining the stream during heavy rainfall, concentrations of glyphosate relate more to surface runoff than to added baseflow. As more agriculture, and thus greater herbicide-use occurs farther down the valley, it can be surmised that runoff from properties in the lower valley may have contributed higher concentrations of glyphosate to the stream flow. Higher glyphosate concentrations sorbed onto soil surfaces are

expected where human development is more densely distributed, such as in the lower Faga`alu watershed. This is expected not only due to small and large-scale agriculture, but also from personal use on property and roadside spraying to clear vegetation. Overland flow may explain why surface samples at high flow condition displayed the opposite pattern than that observed at baseflow.

Although fewer push-point groundwater samples ($n=3$) were taken along the stream than surface water samples ($n=7$), the trend in stream bank groundwater glyphosate concentrations generally agrees with that observed at the same locations in the stream surface water, at baseflow condition. A slight increase in concentration appears in the estuary at the saline-freshwater boundary, while showing a drop in concentration in the mid-alluvial region and an increase near the back of the developed region. This trend in groundwater contribution correlates to the results observed in stream surface water measurements at baseflow condition.

Groundwater flow paths feeding the coastal springs are separate from the stream system (see modeling results below), and show slightly elevated glyphosate concentrations. The southern spring, in particular, displayed the highest concentration of this herbicide on the island during this study. The basal lens feeds this spring, so there is a possibility that groundwater carries glyphosate from upstream of the spring, where residential and agricultural land-use may affect its composition. However, local inputs must also be considered from application of this herbicide near the springs, and its percolation into the groundwater locally. Direct spraying of vegetation (cleared grass areas) nearby, although not documented directly during this study, may contribute to the higher concentrations recorded in the springs.

While observed concentrations agree with levels found in other studies from the Caribbean to Hungary (Gourcy et al. 2009, Mörtl et al. 2013), it must be acknowledged that ELISA is used more as a screening tool for glyphosate analysis, rather than as a quantitative tool. While considered a robust analysis, several factors may impact accuracy of the glyphosate test. The first is the time elapsed between sample collection and analysis. Samples were stored

refrigerated in dark vials, so the in-situ half-life of glyphosate documented in groundwater in the literature (44-60 days (Schuette 1998)) is not directly applicable. It is possible that preservation was not fully effective, and the concentrations measured five months after collection, were lower than in the actual samples at the time of collection. No half-life estimate exists for glyphosate stored under dark, refrigerated conditions, so the measurement results were not corrected in any way. Relative error over duplicates, which represented 7% of the glyphosate samples analyzed, was $\pm 22\%$. Other possible sources of error during analysis are detailed in the Supplementary section in Appendix B. Finally, it is important to note that this study was a one-day sampling event, so it did not capture any transient processes or changes over time in glyphosate concentrations.

4.1.2. Glyphosate fluxes obtained from MODFLOW-derived groundwater fluxes

The MODFLOW model was created for the Faga`alu aquifer, as described earlier, to estimate the direct discharge of groundwater into the coastal ocean. This process is called submarine groundwater discharge (SGD). The flow budget from the coastal grid cells to the bay was determined, providing SGD across the land-ocean boundary of 4129 m³/d (**Table 8**). The coastline was divided into three sections (northern, central, southern), and using the SGD flux in addition to glyphosate concentrations from three push-point sample sites (coastal spring north, coastal spring south, station 1 in the estuary), the glyphosate contribution to Faga`alu Bay was estimated (**Table 8**). The central section that includes the estuary had the largest SGD, as well as the largest glyphosate fluxes. The total glyphosate flux by SGD from all three sectors was 482 mg/d. This is the amount of glyphosate estimated to be discharging from the aquifer directly to the ocean.

To show the importance of groundwater pathways, the objective of the study was to also estimate groundwater discharge into the stream. The flow budget for the upper reach of the Faga`alu Stream and associated glyphosate fluxes were dominated by groundwater inputs of glyphosate, representing a contribution to stream flow of 91% and to total glyphosate flux of

89%. Since the estuary was included in the SGD portion, groundwater contribution to the stream was only 24% in the lower reach, with glyphosate fluxes accounting for 27% of the total stream discharge. There are no defined boundaries at which groundwater feeding the stream and estuary ends and direct discharge to the ocean begins (Dulaiova et al. 2006). For this study, it was decided to keep all grid cells as coastal SGD and stream arcs as stream flow. This is supported geochemically by the fact that pesticides discharging into the estuary most likely end up directly in the bay. Therefore, I decided to include the estuary in the direct discharge to the ocean (SGD), so the lower reach of the stream that is being fed with the basal lens ends up being dominated by surface discharge. Overall, when total groundwater discharge to the stream-coastline continuum is accounted for, the assignment of the estuary boundary does not matter. Total stream discharge at the time of this study was 3630 m³/d, from which 2204 m³/d was fed by groundwater. Total SGD was 4130 m³/d. SGD dominates water inputs into the bay.

Despite relatively low concentrations of glyphosate in Faga`alu, groundwater contributes a considerable fraction of this contaminant to the reef via SGD and stream baseflow. Submarine groundwater discharge has a slightly higher glyphosate contribution to Faga`alu Bay, with 482 mg/d compared to the riverine addition of 350 mg/d via groundwater. The total glyphosate flux in stream water is 481 mg/d; groundwater contributes roughly 73% of this flux, as opposed to 27% contributed via surface runoff. Overall, groundwater seems to contribute a much larger flux of the herbicide each day than surface flow (701 mg/d to 130 mg/d). While these inputs are of the same order of magnitude, with higher amounts contributed via groundwater than is often given credit for, glyphosate fluxes show that contaminant flux in general may owe more to subsurface water flow than to surface flow.

4.1.3 Imidacloprid spatial distribution

The insecticide imidacloprid was found at low concentrations (< 0.172 ppb) relative to toxicity standards; highest concentrations were observed on the Tafuna Plain in the central part of the island. From nineteen samples collected in the Faga`alu watershed, it was present at

concentrations above detection limit (0.075 ppb) in only one sample. The one Faga`alu sample where imidacloprid was present was in a high flow stream sample, indicating possible recent application, since pesticides in surface runoff may indicate freshly sprayed areas. The majority of surface and groundwater samples collected at the Tafuna Plain had detectable amounts of imidacloprid. The highest concentration at any site on island was at Tafuna well #66, which at 0.172 ppb was well below the LD₅₀ level set by the EPA. The data analysis using ANOVA revealed that concentrations of imidacloprid were different at a statistically significant level between surface and groundwater sampling sites. Groundwater tended to have two times the mean concentrations of surface samples (0.08 ppb to 0.04 ppb respectively). As imidacloprid was not detected in the Faga`alu watershed, no analysis could be made for its flow through the modeled aquifer, aside from the note that it was recorded in the stream at high flow conditions. A study in upstate New York by Phillips and Bode (2002) found imidacloprid in surface waters ranging from 0.07 ppb to 0.2 ppb, which agrees well with the concentration range in my study (0.078 pbb to 0.172 ppb).

An interesting note about imidacloprid is that it is illegal in American Samoa (Watts 2016), and thus banned for use completely. The presence of the insecticide at all suggests that illegal imports of pesticides containing the chemical are being brought in and used on the island. ASPA and NASDA have suspected its illegal use (personal communication).

Imidacloprid was analyzed in the lab ten months after its collection in the field, thus adding a level of uncertainty to the results. Many half-lives may have passed between its collection and analysis time, and a significant decrease in concentrations may have occurred during storage. Its half-life estimates are quite variable in the literature (Bacey n.d.), and thus no corrections were made to measured concentrations. Based on the 6.3% of duplicate samples analyzed, the relative error for this analysis was $\pm 24\%$.

4.1.4 Azoxystrobin spatial distribution

Although the fungicide azoxystrobin is listed as legal for use in American Samoa, no traces of the chemical were found in any samples tested across Tutuila in this study. Several reasons could factor into the absence of this fungicide. Azoxystrobin may not have been in use to combat fungal diseases at the time of sample collection. According to a report from the Integrated Pest Management (IPM) database of the USDA, the most common fungal pest on island, the black streak leaf disease (BLSD) of banana plants, is commonly treated with three other fungicides; Tilt (propiconazole), Calixin (tridemorph) and Punch (flusilazole) (Brooks 2001). There is no mention of azoxystrobin in the report.

It is also possible that this chemical was not detected due to a problem in the ELISA analysis. It had been over ten months since the collection of samples on Tutuila before the analysis was performed in the lab at UH. This may have been enough time for azoxystrobin to degrade in the water samples. Laboratory half-life has been estimated to be up to 4 ½ months (*Azoxystrobin: One of the Active..* 2005), so the 10-month holding period would equal a little over two half-lives, and should not result in diminishing all traces of the compound in all samples from the island-wide survey. Perhaps the late addition of methanol affected the analysis. It is suggested that samples be preserved in a 10% methanol solution immediately after collection. Any of these factors may have led to the lack of azoxystrobin detection across Tutuila. It is also possible that azoxystrobin has not been detected because it was not applied on the island around the time of this study.

4.1.5 DDT/DDE spatial distribution

Although in higher concentrations on the Tafuna Plain, DDT was found in all samples tested across the island, except for two samples (one stream and one groundwater) from the Faga'alu watershed. The ubiquitous presence of the insecticide, across developed to undeveloped sites, is likely a result of plane flyovers for island-wide spraying consistent with mid-twentieth century practices (American Samoa Report 1949). Although DDT has been banned for use in

American Samoa, as well as the United States since 1972 (*DDT- A Brief History* 2017), its persistence continues to be observed in the soils and waters of Tutuila. Although its half-life is estimated to be between 2 and 15 years in the environment (*DDT (General Fact Sheet)* 1999), the large quantities that may have been sprayed could easily account for its present concentrations. DDT concentrations present are not at threatening levels, according to the EPA. The ability of DDT to bioaccumulate in fatty tissues of animals may, however, still cause chronic problems throughout the lifetime of organisms under constant exposure (*DDT (General Fact Sheet)* 1999).

The highest concentration of DDT on the island was at Tafuna well #66, at 3.717 ppb. A study by Whitall and Holst conducted in Faga'alu in 2015 measured DDT concentrations in marine and terrestrial sediments from the bay and watershed. This study found a mean of 0.23 ppb DDT, with a maximum concentration of 2.287 ppb near the location of the northern coastal spring (2.068 ppb) (Whitall and Holst 2015). Although taken from sediment rather than water, and using a different testing procedure, the 2015 results reflect similar concentrations to mine, in the same region. In a study on the Hawaiian island of Kauai, sediment near a specific pumping station contained a DDE concentration of 1.1 ppb, which falls within a similar range to my results, as well (*2013-14 State Wide Pesticide* 2014). To compare a study using water samples similar to my own method, the Sibali et al. (2009) research in South Africa found water samples with DDT ranging from 1.20 ppb – 3.25 ppb in concentration, also a level comparable to the range in this study.

Tafuna well #66 displayed the highest concentration of both DDT and imidacloprid from all island sites. Despite both being insecticides, there is probably no connection between their application at this common location. Imidacloprid was first registered for use in the mid-1990s (Kumar 2013), decades after DDT had been banned in most countries (*DDT (General Fact Sheet)* 1999). In addition to the temporal difference, methods and patterns of application likely differed as well. Unless the groundwater near the source of well #66 is somehow downstream of a sink or retention area (a thick soil layer, for example) for certain contaminants, it is likely a coincidence

that the site contains the highest concentration of both. This region is, however, characterized by a high population density and fast infiltration rates, which could contribute to similarities in the pesticide concentrations (Izuka et al. 2007). Although the highest on island, concentrations from this site are within comparable range to the island average (Imidacloprid: well #66 = 0.172 ppb, island average = 0.063 ppb; DDT: well #66 = 3.717 ppb, island average = 1.98 ppb). The data analysis using ANOVA revealed that concentrations of DDT were variable between surface and groundwater sampling sites. Groundwater tended to have higher mean concentrations than did surface samples (1.7 ppb to 2.2 ppb respectively). As DDT has been allowed to percolate into groundwater for over half a century, its higher concentrations found in groundwater (which follow a normal distribution) are expected.

In the focused watershed study, DDT concentration distribution (**Figure 20**) differed quite a bit from the patterns displayed by glyphosate in Faga`alu Stream (**Figure 15**). The data show an absence of DDT in the stream about 0.75 km upstream (station 5) from the bay, where glyphosate was at its peak. In the groundwater samples, DDT was absent just over 1 km upstream (station 6) from the bay, also a point at which glyphosate concentrations were high. Stations 5 (surface water) and 6 (groundwater) were the only two sites tested on the entire island where DDT was absent. The stream was losing water to the water table in the vicinity of station 5. Without baseflow feeding this portion of the stream, DDT in groundwater would not feed the surface, as in other locations. Samples collected in the losing section of the stream show no or low DDT presence, as the pesticide is probably absent from the surface of the soils or vegetation, since it had not been applied for decades. The absence of DDT in the groundwater at station 6, however, cannot be easily explained, because it represents the high level groundwater in the aquifer. As such, it would be expected to show concentrations at elevated levels, as all other groundwater samples did. At this site, as well as one more upstream where seepage runs indicate higher baseflow contributions, stream DDT concentrations were present. Downstream, within the coastal plain, baseflow contributions were measured and elevated concentrations of DDT were

observed as well. A general rise in concentrations occurred near the mouth of the stream, by comparison to the middle stretch where the basal lens intercepts the stream bed.

The three Faga`alu sites where high-flow conditions were sampled (stations 2, 4, and 7), however, showed a gradual increase all the way to the back of the valley in DDT concentrations, indicating possible surface runoff contributions to the stream insecticide inventory. As decades have passed since DDT-spraying, leaching into the groundwater would be a more expected route than its presence near the surface. Having undergone lesser contact by human activity and erosion, however, surfaces in the back of the valley may have retained the pesticide longer than those undergoing the anthropogenic pressures on the alluvial plain below. The high-flow samples displayed a decrease in DDT concentrations from upper to lower valley locations, likely representing a dilution of the pesticide as it travels downstream from the mountains to the ocean.

The following sources of error in DDT analysis should be considered. Similar to azoxystrobin, methanol was recommended to be added to samples shortly after collection for sample preservation. The combination of the ten-month storage period and the significant delay in addition of methanol may have affected the results. But unlike the other pesticides analyzed, DDT has a long half-life, so the storage time should not cause sample degradation. The methanol, although possibly having affected the azoxystrobin analysis, for which all recorded concentrations were below detection limit, did not seem to have the same effect on the DDT analysis. DDT was present in more sites than any other pesticide tested, however it cannot be determined whether the late addition of methanol had an effect on the recorded concentrations. The relative error estimated from the duplicates collected at 6.3% of locations tested for DDT was $\pm 15.7\%$, a lower uncertainty than for the other pesticides analyzed.

4.1.6 DDT/DDE groundwater fluxes according to MODFLOW

The MODFLOW estimation of $4129 \text{ m}^3/\text{d}$ as SGD in Faga`alu was used to determine DDT flux in the same way that glyphosate flux was estimated. The DDT contribution to Faga`alu Bay via SGD was estimated to be 5519 mg/d . In taking the flow budget for the upper and lower

reaches of the Faga`alu Stream, and calculating DDT fluxes, the groundwater fraction of its contribution to stream flow was 91% to the upper stream and 28% to the lower stream. Similar to prior discussion of glyphosate, if the grid cell overlying the stream mouth was added to stream flow rates, DDT contributions would show higher fluxes coming out of the lower reach, due to contributions from the basal lens. Between SGD and riverine fluxes, groundwater contributes a considerable amount of DDT over time to the reef system, despite the low levels relative to the EPA-set LD₅₀. Although DDT has not been in use for many decades, the riverine and coral reef ecosystems still face the consequences of the persistent insecticide long after its last application.

Submarine groundwater discharge contributes more DDT to Faga`alu Bay (5519 mg/d) than does the stream groundwater fraction (2990 mg/d). As mentioned earlier, there was no good direct estimate for upstream groundwater DDT concentration, as station 6 had no detectable DDT. Instead, DDT values from neighboring watersheds were used to estimate groundwater-derived DDT flux into the upper reach of the stream. With the total discharge of the stream being 4564 mg/d, groundwater is estimated to contribute roughly 66% of the DDT content from the stream into the bay. The combined stream and SGD fluxes show that, according to the hydrological model water fluxes, groundwater contributes a larger flux of the insecticide than surface flow (8509 mg/d vs. 1552 mg/d). As with glyphosate, once again a larger amount of DDT is contributed to the bay via groundwater than surface water. DDT, glyphosate, and other potentially untested contaminants may be dominated by subsurface water flow to the ocean, than by surface flow through the Faga`alu watershed.

4.2 NUMERICAL MODEL EVALUATION

4.2.1 MODFLOW calibration (Computed vs. Observed)

The calibration process yielded a higher estimate of hydraulic conductivity in the alluvial plain of the aquifer than in the basaltic mountains of the upper valley, resulting in higher

groundwater flow rates in the lower part of the valley. The resulting model supports field observations that the more permeable (higher conductivity) sandy loams persist in the alluvium, while the relatively more impermeable (lower conductivity) volcanic rocks comprise the valley slopes (Messina and Biggs 2016). The combined modeled riverine and SGD fluxes agree with the total recharge applied via the modeled SWAT recharge coverage provided by Leta et al. (2017).

The accuracy of the modeled stream arcs was quite low, and the calibration results were unsatisfactory (**Table 4**). Thus, stream arcs were ignored for model calibration. Future effort should eventually rework this aspect of the model. Although stream arcs were ignored in calibration, they still provided useful information once other calibration methods were implemented. Specifically, head levels in the model were reasonably well-calibrated and errors fell within acceptable limits (**Table 7** and **Figure 24**), although a large error at one mid-valley point (beyond station 7) resulted in estimated value above observed head by over 30 m (**Figure 25**). With satisfactory head level calibration, stream arcs could still potentially provide accurate stream flow estimates through MODFLOW for the upper and lower reaches of the Faga`alu Stream, as has been applied in **Tables 8** and **9**. The modeled results were further strengthened by comparing to reasonably matched stream discharge and SGD values that were determined during field measurements in 2014 (**Table 9**, Shuler, unpublished 2018). Estimated flow rates for stream arcs and coastal grid cells using MODFLOW closely matched the 2014 in-situ measurements (Shuler, unpublished 2018) that employed a radon survey and box model of Faga`alu Bay to determine SGD, and seepage runs to determine stream discharge. Relative error between measured (2014) and modeled (2016) discharge for the upper stream, lower stream, and coastal SGD were 11.2%, 1.4%, and 3.4%, respectively.

For better comparison of my model estimates with the 2014 direct measurements, the model results were reorganized in the following way. The MODFLOW grid cell overlying the stream mouth in my study was removed from the coastal SGD calculations and added to the

stream discharge calculations to reflect basal stream flow into the bay, rather than SGD. This grid cell was summed with the flow rates in stream arcs below station 2, representing the lower reach, while stream arcs from stations 2 through 7 defined the upper reach. Coastal SGD was thus recalculated without the flow rates of the above-mentioned stream mouth cell. This alternative method (to the one used in this paper) was used to match results of Shuler et al. (unpublished 2018) as shown in **Table 9**. Many of my modeled values lie within the uncertainty range of the 2014 measurements, and thus further reinforce the applicability of the hydrogeological model of Faga`alu produced by MODFLOW.

Table 9: Comparison of groundwater flow in Faga`alu watershed derived from different studies: 1) radon survey and box model of Faga`alu Bay along with seepage run measurements in Faga`alu Stream (Shuler, 2014), and 2) MODFLOW model-derived results based on this study. The MODFLOW numbers in this table are different from those listed in Table 7, as stream arcs were distributed differently for better comparison with methods used by the Shuler study (See Table notes below).

1	<u>2014 Survey</u> – Measured (Shuler)	<u>Flow (m³/d)</u>
	Stream (Upper Reach)	2368 ± 238
	Stream (Lower Reach)	1155 ± 117
	Coastal SGD	3030 ± 1152
2	<u>2016 Model</u> – Modeled (MODFLOW) (Welch)	
	Stream (Upper Reach)*	2022
	Stream (Lower Reach)**	1133
	Coastal SGD ***	3177

*The upper reach in this table was determined by the total stream flow in all arcs upstream of station 2. (In Table 7, the upper reach was represented by all arcs upstream of station 5 in order to capture the gaining and losing stream sections separately.)

**The lower reach in this table is described by the sum of flow from stream arcs ranging from station 2 down to the bay, plus the flow rate within the MODFLOW grid cell overlying the stream mouth. (In Table 7, the lower stream reach used stream arcs from stations 1-4, and without the added rate from the grid cell.)

***Coastal SGD listed here is the total SGD listed in Table 7 minus the estimated flow rate for the MODFLOW grid cell located over the stream mouth. (In Table 7, the total flow rate from all grid cells was included, not excluding any cells.)

Referring once again to **Table 8** (this study), the SGD fluxes of glyphosate and DDT were estimated to contribute 482 mg/d and 5519 mg/d, respectively, to the bay. The stream groundwater contribution via baseflow amounted to 89% and 91% in the upper reach, and 27% and 28% in the lower reach, respectively. The total stream fluxes (upper and lower reach) of glyphosate and DDT were 350 mg/d and 4560 mg/d respectively. This study provides evidence that contaminants travel through the groundwater aquifer in the Faga`alu watershed, and are discharged directly into the bay. The study focused only on the few pesticides that were selected based upon their probability of occurrence, and not based upon the severity of their effect on the coral reef. It would be valuable for a future study to focus on the most harmful pesticides from the perspective of the ecosystem. This current study suggests that other pesticides likely migrate through the groundwater aquifer, as well. Their fluxes through groundwater over the coastal boundary may present a contaminant load that poses a threat to coastal ecosystems, depending on their EPA-set toxicity levels.

4.2.2 MODFLOW discussion and modeling limitations

Although the modeling results seem to agree well with observations, there are uncertainties related to the information that is used in the model. Although properties are set to vary in between geologic formations, the extent of these formations is not exactly known, and they are treated as a homogenous material. In reality, it is expected that the Faga`alu substrate must contain irregularities, such as sedimentary layers and conduits, allowing preferential flow paths in its alluvial plain. It is likely to have a heterogeneous composition. Dike systems, which often occur in the basaltic mountain regions, likely exist in Faga`alu, yet the model did not take into account any such heterogeneities. The location of mountain springs was used for calibration of the model as the approximate head level for the aquifer. These springs could very well signify dike-impounded water, which is a common feature on other volcanic islands, such as those in Hawai`i (Takasaki 1985).

Another source of uncertainty that could account for differences that arose between the MODFLOW model and direct measurements is that this current study and the past seepage runs and radon surveys were performed at different times, separated by ~2 years. The MODFLOW model was calibrated with data collected in 2016, whereas the other used data from a 2014 survey. Baseflow levels may well have been different on the two dates due to the transient nature of recharge.

More precision in the MODFLOW model could also have been attained if the grid cell size was optimized to smaller dimensions for higher resolution in modeling water flow. Although the dimensions used (38 m x 30 m) produced a flow budget agreeable with the 2014 study (**Table 9**), the accuracy of SGD fluxes on the coast could be improved with a higher resolution cell grid. Finally, density-dependent flow was not simulated, which is important in coastal aquifers. Lack of appropriate data and complexities in modeling are factors that necessitated overlooking density-dependent flow.

4.2.3 MODPATH discussion and modeling limitations

True subsurface water flow includes dispersion and chemical reactions, which along with advection will affect contaminant transport through the subsurface. MODPATH, which only accounts for advective contaminant transport, was used to estimate flow paths to trace back the source of groundwater discharging into the stream and the bay at the well and push-point sampling sites. Thus, MODPATH is not able to predict the distribution of contaminants in the aquifer, but only the general path along flow lines. It can also provide average values for travel times along these paths. As it was chosen to set flow paths backward via advection, the lines produced represented possible source locations of pesticides found in the samples (**Figure 27**). Following path line identification, I inspected what land-use categories are intercepted by each flow path. A small agricultural land upstream of Faga`alu well #179, according to a recent land-use map (adapted from ‘Faga`alu land-use map’ 2012), was intersected by the modeled flow lines. Measurable concentrations of glyphosate and DDT were present at this location of

intersection, although both were present at very low levels. Flow paths with arrows, where each arrow on the path leading to the well represents ten years are shown in **Figure 27**. Although DDT may have had time to travel that distance since its application, glyphosate would likely not have taken this pathway. The half-life and period of application of glyphosate is much shorter than the temporal length of the flow path (represented by arrows) connecting the agricultural land to the well (~100-200 years).

Station 6 shows no connection in MODPATH to agricultural or populated areas. The undetectable levels of DDT at this station implied that MODPATH had made an accurate prediction. Glyphosate was present at station 6, however, and thus negated the potential of a MODPATH-agriculture connection. Although modeled paths do not always match an agriculture-to-sample conduit, MODPATH is still useful. According to the model, water moves very fast through the alluvial section of the valley where population centers are located, compared to the upper valley where it takes decades to make much progress. Pesticides are often applied to property owned by citizens in order to control pests, even in the absence of agricultural plots. The rapid flow rate predicted by the model (in the context of groundwater) estimates that contaminated water can make its way from the back of the alluvial plain to the ocean in roughly a decade. Such a transit time can be inferred by the one arrow on the longer flow path connected to station 1 (**Figure 27**). Contaminants could thus be transported to the bay following percolation into the water table in a relatively short time. This implies that fluxes of pesticides to the ocean derive from recent applications that occurred within the past decade or less. Another conclusion is that groundwater pesticide concentrations were not co-located to agricultural areas according to MODPATH, but in general were correlated with developed land-use. Developed land-use represents houses with yards and attached agricultural fields (personal observation), where small-scale pesticide applications are expected.

It should also be noted that these samples were collected through push-point samplers from less than one meter below ground. Depending where in the watershed these measurements

were taken, they may not have penetrated the water table (if pushed into a losing reach of the stream). If they instead intercepted lateral flow, or water percolating down from the surface, the concentrations measured may not correlate to the true groundwater signal. The coastal springs at the land-ocean interface, however, were tapping into the basal lens groundwater, and most stream sites sampled with push-points were at gaining locations, so it is less likely that lateral flow was sampled at these sites. A final note about the agricultural shapefile used (adapted from 'Faga`alu land-use map' 2012), is that it is difficult to precisely define and pinpoint all agricultural sources in the valley, as they are not organized in typical crop fields. This will be discussed further in the MT3DMS discussion.

4.2.4 MT3DMS discussion and modeling limitations

Instead of using sampling points to trace particle paths back to possible contaminant routes, as was the method used in MODPATH, polygonal areas were used in MT3DMS as the source to trace advective-dispersive contaminant flow. MT3DMS thus, is superior to MODPATH, because it estimates transient contaminant concentrations at various aquifer locations. Accuracy of model estimates can greatly suffer due to the lack of reliable estimates of dispersivity, however, which is the parameter controlling the dispersion process. A recent land-use map was used to create agricultural polygons to trace where contaminants, such as pesticides, may flow over time. For simplicity, chemical transformations of the pesticides in the aquifer were neglected. The MT3DMS simulations were run for 25 years for contaminant transport away from agricultural sources.

Most of the sampling sites were well within the contamination range reported by the model, with the exception of the uppermost waterfall site (station 7). Concentrations of moving contaminants are seen to build up and spread slowly in the aquifer, eventually arriving at the sites sampled in this study, as seen in **Figure 29**. Estimated concentration percentages from the breakthrough curves (**Figure 29**), do not directly correlate with concentrations found at the sampling sites relative to each other. This may necessitate additional modeling efforts in the

future, with additional data. Glyphosate is the only one of the tested pesticides that could follow the full ten year dispersive path modeled from source to endpoint, since DDT, although present, has not been applied to a source region for decades. The other two, imidacloprid and azoxystrobin, were not present in the watershed. Aside from the anomalous glyphosate concentration on top of the waterfall, dispersal patterns seen in **Figure 28** seem fairly justifiable.

Errors in the MT3DMS model can be attributed to a number of possible factors, generally related to the use of an inappropriate conceptual model or to the use of a coarse grid, or time steps, leading to numerical errors. As stated by Konikow (2010), prediction errors are often inevitable, as conceptual weaknesses and flaws exist in the underlying theory and classical governing equation of this model. On the northern coastline of the bay, a small group of cells displayed higher end values compared to the maximum concentration expected (3000 ppm compared to 100 ppm), which is likely a result of numerical model errors. It is likely also that inaccuracies in the conceptual model may lead to these overshoot errors, giving concentrations with values greater than the concentration at the source. Despite localized deviations present in these few cells, the overall dispersion trend in the greater part of the grid follows realistic and expected paths. The erroneous cells are therefore omitted in the analysis of groundwater dispersion, as over 95% of the grid cells follow expected trends. Also, as previously mentioned, the scattered backyard agricultural style found in Faga`alu makes it difficult to designate all cultivation in the valley. Agriculture in Faga`alu is more scattered, from backyards to hidden groves, instead of continuous fields. Much of the produce is tree-farm (i.e. banana and coconut) agriculture rather than conventional crops, which makes it difficult to obtain a full scope of possible pesticide application locations from ground observations or by satellite imagery. The map provided from which the GIS shapefile was produced was a recent estimation of land and tree agriculture (adapted from 'Faga`alu land-use map' 2012), but still may contain inaccuracies. In addition, as mentioned previously, the homogeneous structure assigned to the aquifer via

MODFLOW is not a true representation of the configuration below the surface. Dispersion patterns modeled in MT3DMS thus may not fully agree with certain field measurements.

4.2.5 General modeling limitations and recommended future efforts

Modeling can be a useful tool in analyzing measured data for better understanding of flow and transport processes. It can be used for predicting future aquifer responses and proposing management actions to deal with certain problems, such as pesticide contamination as in my case. However, modeling is always hindered by the quantity and quality of field data needed for model calibration. In many cases, development of a detailed model may not be justified if appropriate information does not exist. Simplified models can be acceptable by providing critical and important information guiding future data collection and more detailed modeling efforts.

The current modeling effort was intended to obtain possible source locations of pesticide application and travel times via MODPATH, and advective-dispersive contaminant concentrations and fluxes via MT3DMS. Accuracy of such results depends upon reliability of predictions of the water flow model MODFLOW, specifically regarding water levels at various locations and water fluxes to receiving bodies. Such bodies include the ocean and the stream, where pesticide fluxes are estimated by utilizing the predicted water fluxes and measured pesticide concentrations.

MODFLOW accuracy depends upon assumptions included in the conceptual model (see Section 2.3.2), and the quantity and quality of the observations used for calibration. For the conceptual model, the main assumptions were related to assigning a no-flow aquifer boundary along ridge lines, treating various geological zones as homogenous units, and considering stream arcs as drains that only receive water from the aquifer. Water level observations included a single well, and were supplemented by mountain springs, where atmospheric pressure was assumed. Uncertainties regarding such assumptions include the potential existence of perched water tables. In addition, the model was unable to accurately predict stream flow arcs, which thus were not included in calibration. Finally, observations and other data were not completely synchronized,

nor consistent with the simulations. This includes, for example, the use of average recharge rates which are not necessarily representative of the simulation period.

Despite these uncertainties, I believe that the model has reasonably calibrated water level data and has provided reasonable potential contaminant source locations though this method of calibration. The models used provide certain insights into transient advective-dispersive patterns of pesticides in the aquifer. Future enhancements can certainly improve upon these results. For example, MODFLOW calibration was manually computed in this study, but using the Parameter Estimation (PEST) calibration technique (a non-linear inverse modeling code) may yield better calibrated results, and thus more reliable estimates for multi-calibration data, including stream flows. PEST includes an option to allow heterogeneities to be considered within various geological units (Dixon 2016), which could not be done manually. Also, setting the Faga`alu Stream as a “stream” coverage in MODFLOW, rather than as a “drain” coverage as was done in this model, may produce more accurate results. Addressing salinity variation in the coastal portion of the aquifer is another addition that could provide more realistic outcomes in model estimations.

New data that can improve upon current results include additional stream discharge measurements, and more reliable head level information. Physically surveying for spring locations, rather than relying on literature sources, would give more helpful calibration data in the model as well. Future studies may be able to improve upon my modeling techniques, employing some of the above-mentioned suggestions.

5. Conclusions

As the people of American Samoa rely heavily on groundwater for their water supply, its contamination by pesticides from agricultural applications has become an increasingly concerning issue. This study investigated the concentrations of selected pesticides in groundwater and streams across Tutuila, as well as in a focused study in Faga'alua. The focused study quantified water fluxes through surface and groundwater pathways and the role of these two trajectories in the distribution of pesticides. Of the four pesticides studied across Tutuila, imidacloprid and DDT/DDE showed significant variance between surface and groundwater concentrations, with higher levels in groundwater than in surface water. Azoxystrobin was not present at all, and glyphosate showed no notable difference in concentrations between sample-type. Groundwater is thus just as, if not more important as surface water in its role of distributing water-soluble pesticides across Tutuila. Island-wide study reveals that certain highly developed areas have higher pesticide concentrations than undeveloped areas. Glyphosate showed elevated concentrations in Pago Pago and Faga'alua watersheds and the Tafuna Plain, while the presence of imidacloprid was most evident on the most densely populated Tafuna Plain. The higher concentrations in developed rather than rural areas, reflect the abundant practice of backyard agriculture and personal pesticide use on the island, rather than large-scale farming operations. DDT was the only pesticide in this study that showed an even distribution across the island, which can be explained by its mode of application via airplane spraying from the mid-20th Century. The presence of DDT on Tutuila was notable in its persistence in the waters many decades after its last application. All pesticides were found at levels orders of magnitude below limits set by the EPA as toxic to humans, however, their chronic effect on local aquatic species may still be of concern.

At the watershed level, looking at the focus site of Faga`alu, glyphosate concentrations in the stream correlate to gaining and losing sections of the stream, which were identified using seepage runs and radon concentrations. Both the measured glyphosate in stream bank groundwater and the results from the hydrological model support this correlation. Measurements were taken at baseflow conditions during the dry season, where higher concentrations of glyphosate were observed in gaining sections of the stream. The model of groundwater flow and corresponding pesticide fluxes through the Faga`alu aquifer demonstrated the importance of groundwater in the movement of these pesticides through the watershed to the coast. Most locations where glyphosate was detected could be traced back via groundwater flow path analysis to developed areas, but this remains a difficult task as there are no well-defined agricultural regions. Glyphosate concentrations were found to be higher in coastal springs than at others sites. Groundwater flow paths and rates were analyzed using the hydrologic model, revealing the coastal plain to be flushed within a decade. Recent applications in the developed region of Faga`alu would thus be flushed relatively quickly and discharged to the bay via SGD. Significant quantities of both glyphosate (963 g/d) and DDT (10,083 g/d) are discharged into the bay via the stream and SGD. According to the calculations, SGD is just as important as stream discharge in pesticide distribution, as each is responsible for approximately half of the pesticide load to the bay. But, as much of the stream discharge originates as groundwater-derived baseflow, groundwater is shown to be the primary mover of both water flow and pesticide flux into the stream, and therefore through the watershed, as well. Contaminant fluxes via surface water play a relatively diminished role during dry season in comparison to subsurface flow, according to the model. As the Faga`alu watershed is a priority watershed of the United States Coral Reef Task Force (USCRTF), the contribution of submarine groundwater discharge to the bay is also of concern for the health of the offshore coral reef community.

This study shows that a considerable quantity of pesticide is being transported via SGD across the land-ocean interface, in an amount that exceeds total riverine fluxes. As many studies

have focused primarily on the surface runoff contribution of pesticides, this study exhibits that groundwater fluxes should not be overlooked in the holistic representation of a watershed.

Groundwater in the dry season, according to the model, plays a larger role in the distribution of pesticides than do surface contributions. These results may not pertain to every type of watershed on a global scale, as this study specifically represents a coastal alluvial valley of a small volcanic island, but they do indicate the importance of groundwater, which is often overlooked in similar studies. The methodology used and the outcomes discovered from this study will be beneficial to future research with common objectives on small tropical islands of similar geologic origin.

APPENDIX A

Table A: A full list of sample sites on Tutuila from August 2016, with location, pesticide concentrations, and radon levels for all sites where they were measured.

Name	Sample Type	Latitude	Longitude	Glyphosate (ppb)	DDT (ppb)	Imidacloprid (ppb)	Radon (dpm/L)
Moa-93-11	Well	-14.34348	-170.76787	0.074	2.05	0.087	42
Ili-84-11	Well	-14.34597	-170.74276	0.159	1.672	0.1	123
Mmi-89-11	Well	-14.31754	-170.73821	0.082	2.072	0.137	283
Taf-33-11	Well	-14.32436	-170.73219	< 0.075	2.753	0.096	170
FG-S-12	Stream	-14.29137	-170.68379	0.076	0.839	< 0.075	122
FG-PZ-12	G.W.	-14.29137	-170.68379	0.091	1.219	< 0.075	587
FG-S-52	Stream	-14.2915	-170.68479	0.057	1.844	< 0.075	85
FG-S-72	Stream	-14.29074	-170.68668	0.091	1.382	< 0.075	19
FG-PZ-72	G.W.	-14.29074	-170.68668	0.074	1.313	< 0.075	77
FG-T-82	Tributary	-14.29044	-170.68707	0.048	1.742	< 0.075	11
FG-S-92	Stream	-14.29006	-170.68778	0.142	0.839	< 0.075	19
FG-T-92	Tributary	-14.29002	-170.68791	0.143	1.726	< 0.075	80
FG-9.22	Stream	-14.2897	-170.68926	0.232	< 0.625	< 0.075	15
FG-S-102	Stream	-14.28878	-170.69109	0.196	1.722	< 0.075	34
FG-S-102-DUP	Stream	-14.28878	-170.69109	0.112	1.041	< 0.075	
FG-PZ-102	G.W.	-14.28878	-170.69109	0.176	< 0.625	< 0.075	56
FG-S-112	Stream	-14.28813	-170.69337	0.164	2.026	< 0.075	29
Pala-S-1	Stream	-14.31768	-170.71676	0.183	1.629	< 0.075	58
Pala-PZ-1	G.W.	-14.31768	-170.71676	0.169	1.486	< 0.075	2
Pala-S-2	Stream	-14.31775	-170.71776	0	1.378	< 0.075	9

Pala-S-3	Stream	-14.31775	-170.72132	0.061	1.78	< 0.075	9
Pala-S-3-Dup	Stream	-14.31775	-170.72132	0.097	1.397	< 0.075	
Pala-S-4	Stream	-14.3154	-170.72373	0.162	1.262	< 0.075	18
Pala-PZ-4	G.W.	-14.3154	-170.72373	0.124	1.568	< 0.075	15
Pala-S-5	Stream	-14.31272	-170.72536	0	1.348	< 0.075	51
Pala-S-6	Stream	-14.30908	-170.72758	0.09	1.13	0.142	6
Pala-G-1	Tributary	-14.31111	-170.72738	0	2.168	0.078	1701
FG-S-HF-5	Stream	-14.2915	-170.68479	0.24	0.692	0.087	
FG-S-HF-11	Stream	-14.28813	-170.69337	0.118	2.091	< 0.075	
FG-S-HF-9	Stream	-14.29006	-170.68778	0.104	1.808	< 0.075	
ILI-167-P	Well	-14.34178	-170.74714	< 0.075	1.889	0.115	
MOA-91-P	Well	-14.34232	-170.76744	0.144	1.889	0.097	
MOA-83-P	Well	-14.336	-170.76941	< 0.075	2.376	0.104	
MOA-168-P	Well	-14.33358	-170.77082	0	2.76	0.105	
MOA-169-P	Well	-14.33337	-170.77319	0	2.957	< 0.075	
MOA-70-P	Well	-14.33971	-170.77473	0.056	2.67	0.149	
PAV-177-P	Well	-14.33637	-170.75013	0	2.338	0.087	
ASU-128-P	Well	-14.30996	-170.7721	< 0.075			
PUA-119-P	Well	-14.34596	-170.76707	0	3.076	0.095	
PAV-178-P	Well	-14.3365	-170.75485	0.078	2.387	0.087	
PAV-178-P-DUP	Well	-14.3365	-170.75485	0.162	2.391	0.148	
MES-85-P	Well	-14.3258	-170.74657	0.042	2.33	0.133	
MMI-67-P	Well	-14.31895	-170.73769	0.063	2.586	0.128	
TAF-81-P	Well	-14.32065	-170.73203	< 0.075	2.586	0.116	261
TAF-72-P	Well	-14.32154	-170.73219	0.193	2.884	0.15	
TAF-77-P	Well	-14.32273	-170.73214	< 0.075	2.703	0.107	
TAF-66-P	Well	-14.32455	-170.73248	0.136	2.856	0.132	

TAF-66-P-DUP	Well	-14.32455	-170.73248	0.148	3.717	0.172	
TAF-61-P	Well	-14.32686	-170.73554	0.127	2.76	0.07	
TAF-60-P	Well	-14.32604	-170.73451	0.137	3.37	0.108	
TAF-172-P	Well	-14.33531	-170.74393	0.171	3.577	0.102	
TAF-171-P	Well	-14.33373	-170.74288	0	3.156	0.117	
FALU-179-P	Well	-14.29104	-170.68895	0.156	0.876	< 0.075	334
FALU-179-P-DUP	Well	-14.29104	-170.68895				399
PALA-CSP-2-2	C.S.	-14.31969	-170.71535	0.184	1.369	0.105	141
PAGO-101-P	Well	-14.28003	-170.6938	0.051	1.658	0.124	
PAGO-163-P	Well	-14.27419	-170.70697	0.1	1.348	0.125	1300
FSA-143-P	Well	-14.29271	-170.72527	0			
PAGO-165-P	Well	-14.2797	-170.70648	0	1.824	0.055	317
PAGO-107-P	Well	-14.27862	-170.70548	0.128	1.756	0.121	
PAGO-105-P	Well	-14.2777	-170.7052	0.135	1.585	0.083	
AUA-97-P	Well	-14.2687	-170.66118	0.077	2.719	0.125	
VATI-180-P	Well	-14.25476	-170.66857	< 0.075			1170
VATI-180-P-DUP	Well	-14.25476	-170.66857	< 0.075			964
VATI-CSP-B	C.S.	-14.25116	-170.67168	0.103	2.647	0.078	572
VATI-CSP-A	C.S.	-14.24872	-170.67531	< 0.075			272
AFO-176-P	Well	-14.26778	-170.65048	< 0.075			
FTA-164-P	Well	-14.26756	-170.61795	< 0.075			
MAF-242-P	Well	-14.26088	-170.63721	< 0.075			
MAF-242-P-DUP	Well	-14.26088	-170.63721	< 0.075			
MAF-241-P	Well	-14.25994	-170.63665	< 0.075			
AOA-152-P	Well	-14.26459	-170.58577	0.189			
AOA-151-P	Well	-14.26502	-170.58598	0			
ALO-161-P	Well	-14.26244	-170.56889	0			

TULA-104-P	Well	-14.25284	-170.56952	0.101			
FLI-182-P	Well	-14.31177	-170.82471	< 0.075			
Malota-S-P	Stream	-14.26885	-170.61638	< 0.075			27
Failolo-S-P	Stream	-14.3293	-170.82467	< 0.075			
Dikesp-S-P	Stream	-14.33178	-170.81741	< 0.075			
Leone-S-P	Stream	-14.32982	-170.78184	0	1.991	< 0.075	13
Pav-S-P	Stream	-14.33625	-170.75594	0.082	2.183	0.143	
Mes-S-P	Stream	-14.32021	-170.74225	0.1	1.944	0.08	
Nuuuli-S-P	Stream	-14.3106	-170.71025	0.102	2.989	0.073	
Fa-nea-S-P	Stream	-14.30508	-170.69089	< 0.075	2.511	0.085	
Utulei-S-P	Stream	-14.3051	-170.69088	0.133	2.784	0.124	59
Fagasa-S-P-A	Stream	-14.28599	-170.72055	0.161	2.586	0.138	
Vati-S-P-A	Stream	-14.25093	-170.67553	< 0.075			29
Vati-S-P-B	Stream	-14.25239	-170.67273	< 0.075			23
Afono-S-P	Stream	-14.25946	-170.65156	< 0.075			
Afono-S-P-Dup	Stream	-14.25946	-170.65156	< 0.075			
Aua-S-P	Stream	-14.26891	-170.66329	0.128	2.406	0.088	
Fta-S-P	Stream	-14.26885	-170.61638	< 0.075			111
Fta-S-P-Dup	Stream	-14.26885	-170.61638	< 0.075			
Lover-S-P	Stream	-14.28595	-170.64464	< 0.075			
Pago-S-1	Stream	-14.28814	-170.70694	< 0.075	2.122	0.097	31
Pago-PZ-1	G.W.	-14.28814	-170.70694	0	2.153	< 0.075	31
Pago-S-4	Stream	-14.27383	-170.7026	0.096	1.514	0.095	86
Pago-PZ-4	G.W.	-14.27383	-170.7026	0.165	1.187	< 0.075	59
Pago-S-3	Stream	-14.27677	-170.70515	0.223	1.568	0.087	28
Pago-S-3-DUP	Stream	-14.27677	-170.70515	0.108	1.759	0.112	18
Pago-S-2	Stream	-14.28019	-170.70831	0.144	1.459	0.000	15

Leo-CSP-P	C.S.	-14.34022	-170.78565	0.118	1.713	0.085	60
OA-CSP-A1	C.S.	-14.25314	-170.64247	< 0.075			112
OA-CSP-B	C.S.	-14.25264	-170.64337	0.047	2.78	0.109	111
OA-S-1	Stream	-14.25457	-170.64335	< 0.075			23
OA-CSP-A2	C.S.	-14.25314	-170.64247	< 0.075			131
Falu-CSP-S-P	C.S.	-14.29294	-170.68039	0.301	1.509	< 0.075	32
Falu-CSP-N-P	C.S.	-14.28879	-170.68079	0.154	2.068	< 0.075	91

**C.S. = Coastal Springs, G.W. = Groundwater Push-Point Samples*

< 0.xxx = Below detection limits

Table B: Field measurements of water quality parameters using a multiparameter sonde (YSI 6820 V2-2) across Tutuila in August 2016. Sample identifications match those listed in Table A.

Name	Temperature (C)	Conductivity (mS/cm)	Dissolved Oxygen (mg/L)
Moa-93-11	26.12	0.480	6.95
Ili-84-11	25.98	1.687	5.96
Mmi-89-11	24.87	0.286	6.26
Taf-33-11	25.51	1.156	6.08
FG-S-12	24.77	0.29	7.04
FG-PZ-12	25.49	2.316	0.57
FG-S-52	25.05	0.222	7.98
FG-S-72	25.55	0.184	8.15
FG-PZ-72	25.91	0.195	2.2
FG-T-82	27.24	0.238	6.98
FG-S-92	25.39	0.173	7.84
FG-T-92	25.86	0.208	3.65
FG-9.22	25.04	0.171	7.91
FG-S-102	24.51	0.169	7.92
FG-PZ-102	24.85	0.169	6.12
FG-S-112	23.98	0.159	7.86
Pala-S-1	25.58	6.387	6.41
Pala-PZ-1	26.95	27.67	0.31
Pala-S-2	25.42	0.163	9
Pala-S-3	25.16	0.164	7.57
Pala-S-4	24.84	0.16	4.65
Pala-PZ-4	25.07	0.185	0.72
Pala-S-5	24.52	0.154	6.61
Pala-S-6	23.49	0.137	8.31
Pala-G-1	23.9	1.34	7.81
FG-S-HF-5			
FG-S-HF-11			
FG-S-HF-9			
ILI-167-P	25.7	0.643	7.11
MOA-91-P	26.68	0.337	6.42
MOA-83-P	24.95	0.2	7.74
MOA-168-P	24.5	0.269	7.19
MOA-169-P	24.54	0.278	7.22
MOA-70-P	25.61	0.342	6.64
PAV-177-P	25.51	0.937	7.15
ASU-128-P	24.6	0.12	6.42
PUA-119-P	25.58	1.599	4.53
PAV-178-P	24.41	0.276	7.33
MES-85-P	25.07	0.249	7.48

MMI-67-P	25.14	0.219	5.57
TAF-81-P	25.09	0.428	5.66
TAF-72-P	25.12	0.598	6.03
TAF-77-P	25.03	1.632	5.06
TAF-66-P	25.27	1.107	5.88
TAF-66-P-DUP	25.27	1.107	5.88
TAF-61-P	25.26	1.243	5.98
TAF-60-P	25.32	1.187	6.47
TAF-172-P	25.35	1.4	7.21
TAF-171-P	25.22	1.192	7.44
FALU-179-P	25.91	2.62	0.47
PALA-CSP-2-2	26.48	9.913	4.73
PAGO-101-P	25.01	0.24	7.18
PAGO-163-P	26.23	3.307	4
FSA-143-P	24.65	0.17	6.69
PAGO-165-P	25.5	0.269	6.7
PAGO-107-P	25.71	0.452	4.92
PAGO-105-P	25.82	2.66	10.26
AUA-97-P	26.22	4.487	9.2
VATI-180-P	25.49	0.219	4.91
VATI-CSP-B	26.5	0.945	0.77
VATI-CSP-A	26.83	11.2	1.31
AFO-176-P	25.95	0.235	6.13
FTA-164-P	26.51	2.625	3.55
MAF-242-P	25.66	0.213	4.43
MAF-241-P	26.14	0.244	3.65
AOA-152-P	26.27	1.239	2.91
AOA-151-P	28.28	0.515	2.96
ALO-161-P	26.32	10.35	1.92
TULA-104-P	27.1	0.353	1.36
FLI-182-P			
Malota-S-P	23.3	0.119	8.13
Failolo-S-P	23.25	0.137	8.26
Dikesp-S-P	24.16	2.1	7.58
Leone-S-P	23.25	0.131	8.28
Pav-S-P			
Mes-S-P	23.88	0.129	8.13
Nuuuli-S-P	25.04	0.167	7
Fa-nea-S-P	24.52	0.234	5.96
Utulei-S-P	31.5	0.259	6.79
Fagasa-S-P-A	26.31	0.164	7.37
Vati-S-P-A	28.63	0.418	6.47
Vati-S-P-B	24.88	0.147	5.61

Afono-S-P	27.25	0.16	7.28
Aua-S-P	25.48	0.314	6.07
Fta-S-P	26.85	1.469	4.14
Lover-S-P			
Pago-S-1	24.81	0.117	7.91
Pago-PZ-1	24.6	0.173	7.47
Pago-S-4	29.02	0.355	6.17
Pago-PZ-4	28.03	0.366	3.42
Pago-S-3	27.77	0.188	9.21
Pago-S-2	25.18	0.168	8.07
Leo-CSP-P	25.84	7.088	5.49
OA-CSP-A1	25.96	35.99	4.57
OA-CSP-B	28.12	42.41	4.8
OA-S-1	25.41	0.246	6.97
OA-CSP-A2	25.66	26.17	4.08
Falu-CSP-S-P		43.76	3.17
Falu-CSP-N-P	27.33	23.4	3.99

APPENDIX B: Supplemental Material

A note about the glyphosate test laboratory analysis:

1. While performing the ELISA analysis, the published analytical procedure (Abraxis LLC *Glyphosate* n.d.) was inadvertently modified for a number of samples. Out of the 111 samples run using the procedure, an over-diluted 'Wash Buffer' solution was used for samples numbered 47 through 111, at a 1:10 instead of recommended 1:5 ratio. As much of the competitive reaction between the water samples and enzyme conjugate had already taken place by this point, the misstep with the over-diluted wash buffer was likely inconsequential for the results of the analysis, as the buffer serves merely to rinse the wells before adding the color solution. 2. The amount of antibody solution provided with the kit was insufficient for all samples, and a solution which expired 8 months prior was used. This may or may not have had effect on the results of the final five of 111 samples in the kit. Fortunately all of the Faga`alu samples were prioritized and placed within the first twenty slots, and thus were not affected by either of these methodological aberrations. 3. Since Faga`alu was the focus of this study, and all samples from Faga`alu were properly analyzed for glyphosate, the watershed results are not impacted by the above mentioned errors in the testing process. However, certain island-wide samples may come under this scrutiny if investigated further.

Additional Illustrations

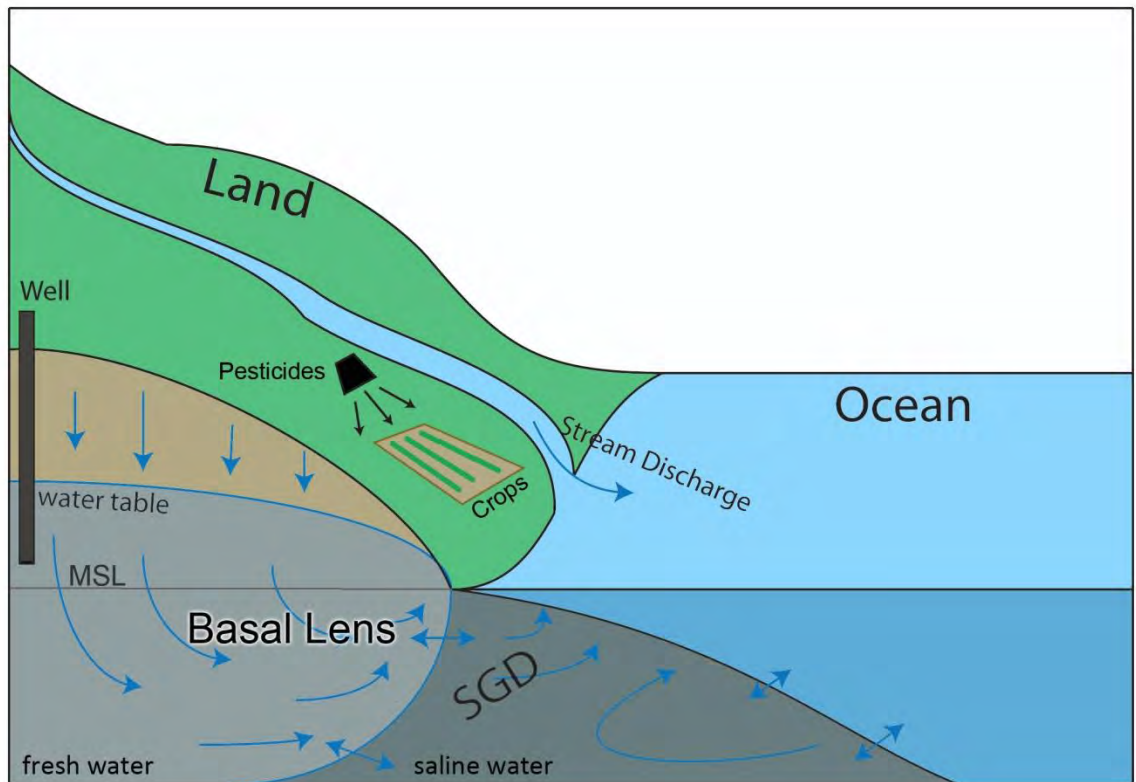


Figure 30: Illustration of a coastal island aquifer, with visual images of terms used often throughout this study, such as: 1) basal lens, 2) submarine groundwater discharge (SGD), 3) the water table, and 4) stream discharge.

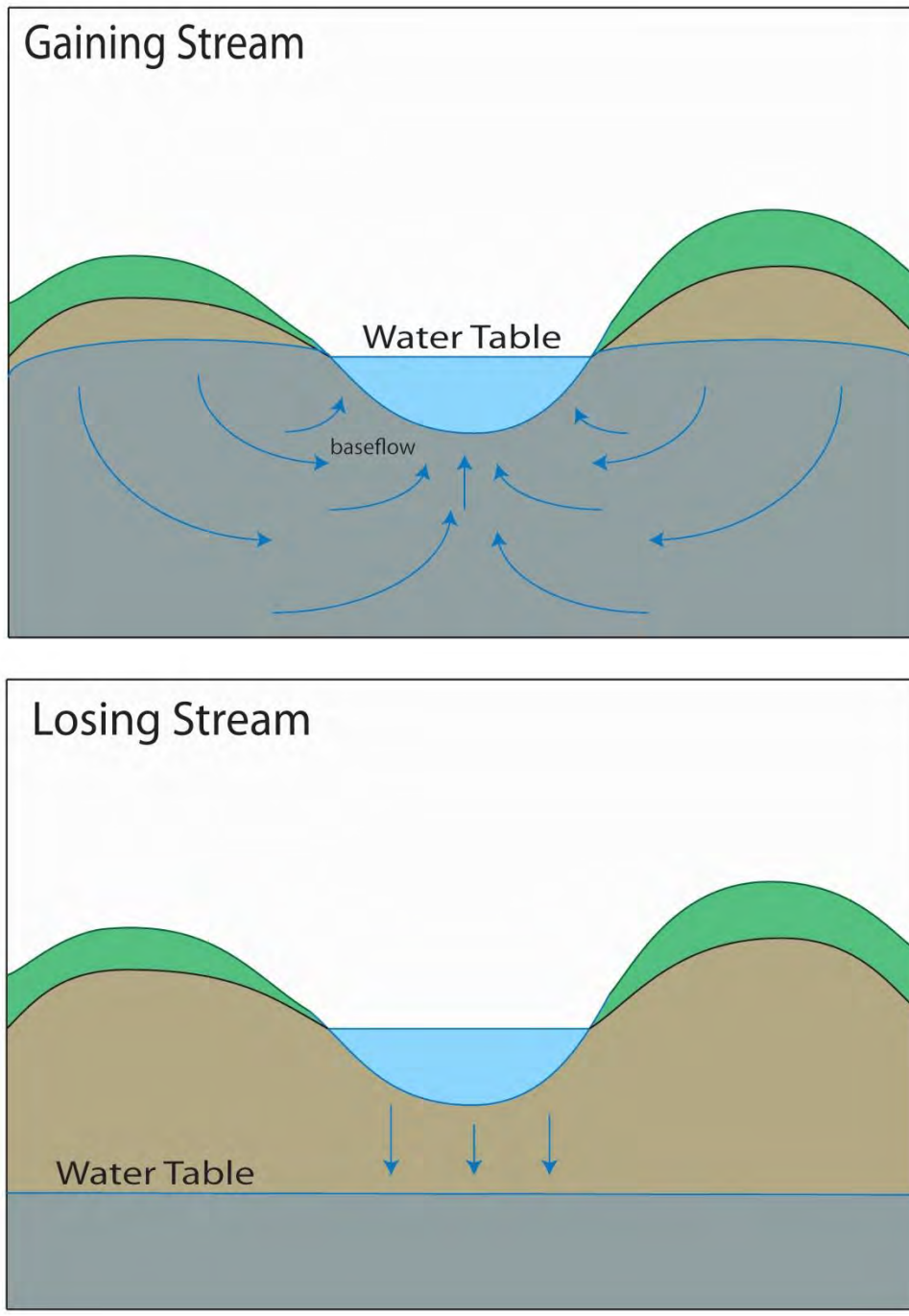


Figure 31: (Top) A gaining section of a stream is where the water table is level with the stream surface, and thus groundwater-derived baseflow is feeding the stream, thus increasing its flow rate. (Bottom) A losing stream is where the water table has fallen below the stream level, and water percolates downward from the stream bed to the lower water table, decreasing the stream flow rates.

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