HYDROGEN SULFIDE EMISSIONS OF GEOTHERMAL DEVELOPMENT IN HAWAI'I

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We certify that we have read this thesis and that in our opinion it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science

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Abstract

Geothermal energy is a renewable source of energy that has been developed worldwide and on the Island of Hawai'i. Future geothermal developments are proposed for the State of Hawai'i, but first environmental impacts of such development must be fully evaluated. Hydrogen sulfide gas is the main emission of concern to the environment and human health, and has had a history of being a severe health concern during previous geothermal developments. Data from the State of Hawaii Department of Health air quality monitors adjacent to Puna Geothermal Ventures plant were acquired and analyzed. The observed concentrations of hydrogen sulfide are below the EPA and Department of Health limits, but the effectiveness of the monitoring system currently in place has been questioned and reviewed. For future developments, a more comprehensive and effective system must be developed to monitor and, if necessary, reduce hydrogen sulfide emissions.

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PREFACE

Energy independence is a very prominent problem for the State of Hawai'i, which imports the majority of its energy in the form of foreign oil. Renewable energy has found a niche here, and wind farms and solar panels have integrated into the grid and have started a trend to create an economy with energy independence. I have always been interested in conserving energy and renewable sources of energy, such as wind, solar, wave, and geothermal. It is only natural that Hawai'i uses a combination of all of these renewable sources to move towards an energy independent state. Hawai'i Island is home to some of the most famous volcanos in the world, and their underlying heat has the potential to move us significantly closer to our energy goals through the use of geothermal energy.

It is important to focus on developing renewable energy that does not contaminate or affect the surrounding people and local environment. Renewable energy that has minimal environmental impact should be the clear goal set for the State of Hawai'i's energy future. Geothermal energy has the potential to fill this need for our state but it must be first shown that its benefits outweigh its environmental impacts, such as hydrogen sulfide emissions, the topic of this thesis.

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CHAPTER 1. INTRODUCTION

The State of Hawai'i is taking large steps to move the economy off fossil fuel combustion to reduce carbon dioxide emissions by integrating more renewable energy into the electricity mix. Geothermal energy is an economical and environmentally beneficial alternative to fossil fuels (Kagel, 2008) and approximately one fifth of the power on Hawai'i Island, roughly 38 Megawatts, already comes from geothermal (Boyd 2002). The State is also using wind and solar as alternative energy sources but geothermal has been shown to have the largest potential for the future (GeothermEx, 2000).

Geothermal energy has an extensive background in Hawai'i and has been developed in the district of Puna on the island of Hawai'i. Much research has been done, on the feasibility of geothermal electricity production, the environmental impacts of such development, and the characteristics of the existing reservoir. The geothermal reservoir in the Kilauea East Rift Zone is a high temperature resource and has production capabilities, which lead to the Puna Geothermal Venture plant (Murray, 1995). Hydrogen sulfide emissions from past, current, and future geothermal developments, pose potential human health and environmental risks that need to be fully understood and evaluated.

Geothermal energy production utilizes the heat of the earth by extracting hot fluids from underground geothermal reservoirs associated with specific geologic features such as rift zones (GeothermEx, 2005). Water is conductively heated by magma that comes into contact with the geothermal fluids through rock pores and fractures (Kagel et al, 2005). These fluids are pumped up to the surface where a series of physical processes take place, including a drop in pressure, which creates steam that drives a turbine to

generate electricity. Geothermal electricity production is considered a firm, renewable source of energy because the heat will not run out on human time scales (Thomas, 1979). The geothermal fluids are a mix of saltwater intrusion as well as meteoric sources. The multiple sources of water help to avoid issues such as subsidence, as happened at the Wairakei geothermal field in New Zealand (Allis 2000).

Geothermal energy can be a clean, reliable source of base load power compared to intermittent renewable energy technologies such as wind farms and solar panels, which only produce power when the wind blows and the sun shines, respectively. Additionally, in comparison with fossil fuel power plants and other renewable energy types, geothermal power plants use a smaller amount of land to create a reliable source of electricity (Fridleifsson 2001). The cost of the electricity produced is another advantage for geothermal energy, as most of the cost is in the drilling and initial developmental stages. Many reports, such as the UN World Energy Assessment Report, show that geothermal energy is generally cheaper to produce than wind, biomass, or solar photovoltaic (Fridleifsson 2001).

The main environmental issue associated with geothermal development here in Hawai'i is the release of hydrogen sulfide gas. Hydrogen sulfide, H_2S , is a colorless gas with a strong odor of rotten eggs and is commonly associated with volcanos and sewer systems as it is a byproduct of decaying organic matter in the presence of sulfate (EPA 2013), and low temperature volcanic emissions. Direct inhalation of high concentrations of hydrogen sulfide can cause death to humans and animals in a matter of minutes. The effect of long-term exposure to hydrogen sulfide at low but varying levels is less understood but it is believed to cause chronic health issues such as cardiovascular and

respiratory problems (Bates, 2002), but more recent research from New Zealand has drawn no such conclusions (Bates et al. 2013).

CHAPTER 2. BACKGROUND

2.1 Geothermal Energy and Hawai'i

The Hawai'i Geothermal Resources Assessment Program was initiated in 1978, and highlighted 20 potential geothermal resource areas across the state based on geological, geochemical, and geophysical data (Boyd et al, 2002). The potential for each of these sites was described by depth and temperature parameters, and probabilities were given for finding low, moderate, and high temperature geothermal reservoirs capable of electricity production (Thomas et al. 1979). Figure 1 depicts the geothermal areas identified in Hawai'i County.

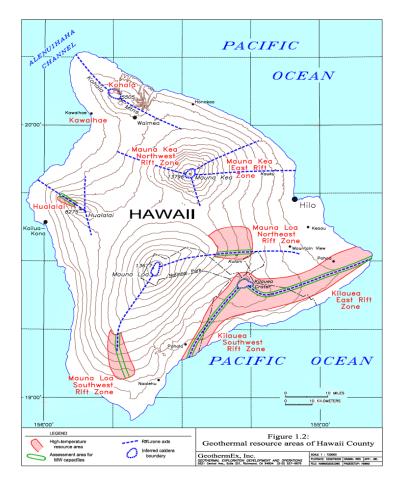


Figure 1. Map of Estimated Geothermal Reservoirs of Hawai'i County. (GeothermEx, 2000)

Notice the large geothermal resource in the Kilauea Rift Zone depicted in Figure 1. This geothermal reservoir gets its heat from the underlying volcanic activity powered by the magma plume of the Pacific hot spot (Gardner et al., 1995). These areas are positioned over a 70 million year old active hot spot in the Earth's crust and are the home of active volcanos such as Kilauea on the island of Hawai'i (Thomas et al. 1979). The Kapoho Geothermal reservoir in the lower Kilauea East Rift Zone has an estimated potential of 500 to 700 Megawatts (Gardner et al., 1995).

2.1.2 History of HGP and PGV

The discovery of the Hawaiian geothermal reservoirs, specifically the discovery of the Kapoho Reservoir in the Kilauea East Rift Zone, led to the creation of the Hawai'i Geothermal Project, ("HGP"). The first successful geothermal well (HGP-A) was drilled in 1976, and soon thereafter concerns about hydrogen sulfide and health arose (DOH, 1984). At the time of the initial geothermal development, very little was understood about the long-term low-level exposure to hydrogen sulfide that was going to take place. The State of Hawaii Department of Health found that in the areas adjacent to the Puna geothermal plant, the rates of acute and chronic respiratory health conditions were higher than for Hawai'i County and Statewide, but were thought to possibly have to do with natural volcanic emissions such as Vog (DOH, 1984).

2.2 Geothermal Emissions

Geothermal power plants have much lower emissions of greenhouse gases compared to equivalent fossil fuel power plants (Bourcier et al, 2005). As there is no combustion in geothermal energy production, there are very few associated greenhouse gases produced.

Table 1 by Kagel et al. (2005), lists the generalized emissions of nitrogen oxides, sulfur dioxide, carbon dioxide, and particulate matter from geothermal power plant direct emissions compared to those of fossil fuel plants.

lbs per megawatt hour:	Nitrogen Oxides	Sulfur Dioxide	Carbon Dioxide	Particulate Matter
Coal	4.31	10.39	2191	2.23
Coal, life cycle emissions	7.38	14.8	not available	20.3
Oil	4	12	1672	not available
Natural Gas	2.96	0.22	1212	0.14
EPA Listed Average of all U.S. Power Plants ⁹⁶	2.96	6.04	1392.5	not available
Geothermal (flash)	0	0.35	60	0
Geothermal (binary and flash/binary)	0	0	0	negligible
Geothermal (Geysers steam)	.00104	.000215	88.8	negligible

Table 1. Summary of average air emissions of geothermal and equivalent fossil fuel plants in pounds per megawatt hour. (Kagel et al. 2005)

The low levels of emissions from geothermal power plants shown in Table 1 result in better ecosystem and air quality in proximity to the power plants relative to what would be produced by fossil fuel power plants. Greenhouse gas emissions are not the major concern for geothermal developments but great concern is given to another gas, hydrogen sulfide.

2.3 History of Hydrogen Sulfide Emissions

2.3.1 Puna

During human geothermal development activities in the Kilauea East Rift Zone ("KERZ"), there were many planned and unplanned venting events. These events were concentrated in the drilling phase of development and lead to the release of large amounts of gases to the atmosphere, including hydrogen sulfide (Thomas, 1987). The hazards of these emissions caused evacuations of nearby residents of Puna, as well as ecosystem impacts from a lowering of rain pH downwind of the power plant (Ingoglia 1991). The main hazard during these events is hydrogen sulfide because it is very toxic to human health but also sulfur dioxide and sulfuric acid in the atmosphere, which are byproducts of hydrogen sulfide (Kagel 2005). During times of normal energy production, hydrogen sulfide emissions depend on the technology utilized (see Table 1), as well as the characteristics of the reservoir. However, at the Puna Geothermal Ventures (PGV) Well, the concentration of hydrogen sulfide in the geothermal fluid is four times greater than found at the average geothermal plant, but the geysers geothermal field in California has been found to have similar concentrations to PGV (Monnons, 1980). This is approximately 900 parts per million by weight of hydrogen sulfide in the geothermal fluid.

Atmospheric emissions from HGP-A and PGV, whether planned or unplanned, have caused moderate amounts of toxic hydrogen sulfide as well as (volatile) heavy metals to be released to the atmosphere. For example, during a 31-hour uncontrolled blow out resulting from inadequacies from the PGV drilling plan, roughly 2247 pounds of hydrogen sulfide were estimated to be released to the atmosphere (EPA 2000). This type

of incident would lead to very high concentrations downwind of the plant and can be very hazardous to the surrounding environment and communities.

The source of hydrogen sulfide in the geothermal reservoirs of Hawai'i is unknown but is likely to come from high temperature sea-water basalt interactions, instead of microbial respiration of organic matter using sulfate as the electron acceptor as would occur in low temperature geothermal reservoirs (Vetter et al., 2010). The source of the hydrogen sulfide can not be known for certain as sulfur is dissolved in the magmatic intrusions and can be mobilized in the fluids but also is expected to precipitate out of seawater before encountering the temperature where it is reduced by hydrogen. New Zealand's geothermal reservoirs have little sea water intrusions but have high natural hydrogen sulfide emissions, leaving the source still mainly unknown.

Technologies developed in the West Coast of the United States have proven to decrease emissions of hydrogen sulfide as much as 99.9 percent by turning the hydrogen sulfide into elemental sulfur, which can be used as a fertilizer and soil amendment (Nagel et al., 1999). These technologies are not yet used in Hawai'i, but may be utilized by future geothermal development to manage environmental hazards and create beneficial by-products if applicable.

2.3.2 New Zealand

Hydrogen sulfide has caused significant issues in other parts of the world where geothermal energy is utilized. On the north island of New Zealand, geothermal energy has been developed at Rotorua as well as other areas (Siegel and Siegel, 1984). The development has been done very close to nearby towns and high levels of hydrogen

sulfide have been reported in the populated areas. Time series data have been lacking in these areas and the most concern in these areas has been attributed to large peaks in emissions (Siegel et al, 1980). Health effects and other damage related to hydrogen sulfide were not a large concern of the residents after consistent testing was done (Siegel, 1985), but some health effects have started to turn up from chronic exposure (Bates, 2002). Residents live with relatively high levels of hydrogen sulfide, often above 30 ppb, but accept this as a small price to pay for the renewable energy being produced. (Siegel and Siegel, 1984).

2.4 Hydrogen Sulfide Environmental and Health Impacts

Hydrogen sulfide is a colorless, highly toxic gas that is denser than air (Rotorua OSH 1999). As previously discussed, gas emissions containing hydrogen sulfide are vented to the atmosphere during geothermal well drilling and production. Due to the density differences between hydrogen sulfide and air, on calm days hydrogen sulfide can pool up in low lying areas and cause large ecological respiratory hazards, along with sulfuric acid formation (Allis, 2000). Hydrogen sulfide has a short residence time in the atmosphere of less than 24 hours, and is converted to sulfur dioxide and sulfuric acid, which have their own environmental hazards such as low pH precipitation, known as acid rain (Kagel et al., 2005).

Hydrogen sulfide is a toxic gas to almost all life, and can be detected by humans through smell in concentrations as low as 1 part per million in air. At higher concentrations, 100-150 ppm, it is especially dangerous because it can paralyze the olfactory nerve causing no smell to be detected even though dangerous concentrations are

present (Rotorua OSH, 1999). Hydrogen sulfide is more toxic than carbon monoxide, and almost equivalent in toxicity to hydrogen cyanide, which is used in criminal executions (Kagel et al., 2005). Hydrogen sulfide is taken directly into the lungs during respiration, where it enters into the blood stream.

The human body, analogous to many animals, rapidly oxidizes the compound once in the blood stream to protect itself from the harmful effects. When the concentrations of hydrogen sulfide build up in the blood, the nerve centers in the brain that control breathing are paralyzed and asphyxiation occurs (EPA 2003).

The EPA has shown that the absorption of hydrogen sulfide at concentrations greater than 2000 ppm can be fatal within a minute to humans and animals by absorption through the lungs (EPA 2003). Studies have also showed that it is possible to absorb the chemical through ingestion but it is only moderately water-soluble and thus mostly a hazard in its gaseous phase. If absorbed into the body, the hydrogen sulfide is primarily released through urine. The EPA describes the toxicity of low levels of hydrogen sulfide as,

"Lower levels have been associated with lung function deficit and eye, nose, and throat irritation. However, little is known of the concentration-response relationship at low levels of chronic exposure" (EPA 2003)

The Environemental Protection Agency (EPA) Minimum Risk Levels for Ammonia and Hydrogen Sulfide are presented in Table 2.

Substance	Acute Exposure (1-14 days)	Intermediate Exposure (15-364 days)	Chronic Exposure (365 days and longer)
Ammonia	500 ppb	(None listed)	300 ррь
Hydrogen Sulfide	70 ррb	30 ррь	(None listed)

Table 2. EPA Minimum Risk Level for Ammonia and Hydrogen Sulfide (EPA 2013)

This table not only shows the estimated minimum level to be at risk for a intermediate amount of time, but also reinforces that even the EPA does not have a limit for chronic exposure to hydrogen sulfide.

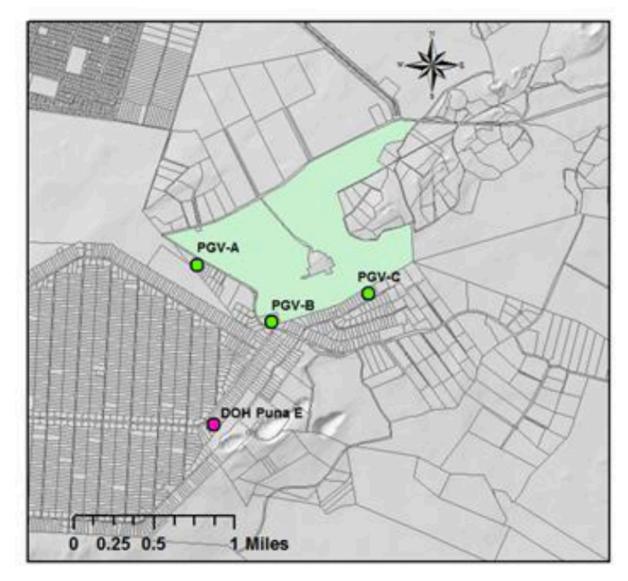
It is clear that volcanic emissions have caused many health problems in Hawai'i and New Zealand, with the focus on respiratory and cardiovascular diseases. It is unclear how much of this is directly related to emission of geothermal energy production due to the fact that long term studies are difficult and that most subjects with chronic exposure are usually located in areas of natural volcanic pollutions. Despite the fact that direct long term effects of hydrogen sulfide exposure are not certain, monitoring the emissions is the first step in solving the problem and future prevention. The modern way to monitor hydrogen sulfide is with calibrated gas detectors that have been implemented around nearly all geothermal power plants to reduce environmental impacts and hazards to human health.

2.5 Monitoring Hydrogen Sulfide Emissions

Controlling the amount of hydrogen sulfide emissions has been a struggle for the HGP-A and PGV in the past. Groups opposed to geothermal energy development have cited the impact of hydrogen sulfide emissions as reason to stop geothermal development (Boyd 2002). In Hawai'i, there were instances where fluids were released straight to the atmosphere with no environmental mitigation during well blowouts (GeothermEx, 2000).

The State Department of Health has been monitoring the air pollution from the Puna Geothermal Ventures (PGV) plant since 1993 through their Clean Air Branch (DOH, 2013). This is actually mandated by state and federal law so that clean air standards can be maintained and enforced. The ambient air quality standard of hydrogen sulfide is 25 parts per billion (ppb) in any one-hour period (DOH 2013).

Because hydrogen sulfide emission can be such so dangerous, it is important to know that installed gas monitors are really recording all the emissions and that they are in the correct locations to provide representative data for the site. The wind direction is highly variable and only careful examination of the data will show if the monitors are indeed effective in monitoring the hydrogen sulfide emissions. Shown next is a site location map of the three stations whose data are used in this thesis. In the center of the green is the location of the plant.



PUNA AIR QUALITY MONITORING STATION LOCATIONS

Figure 2. Map of the Puna Geothermal Ventures plant (center of green zone) and the Department of Health monitors, A, B, and C.

The locations and distance of the three monitoring stations to the source is important because of the small-scale wind patterns and rapid dispersion of the gas. With the monitoring design shown in Figure 2, if winds were coming from the south, or west, it is very likely that any hydrogen sulfide would not be detected by any of the monitors. These monitors are very important as they warn the surrounding communities when there are high levels of hydrogen sulfide. The response to a situation like this is evacuations of nearby residents (Boyd 2002). This has happened many times in the past but with proper prevention included in development, the sensors should be simply a confirmation that the communities are safe rather than an evacuation alert system.

CHAPTER 3. METHODS

3.1 Data Collection

Hourly time series of hydrogen sulfide concentrations adjacent to the geothermal development in Puna have been recorded and made available by Puna Geothermal Ventures as well as the Hawai'i State Department of Health. The location of these monitors can be clearly seen with respect to the geothermal plant in figure 2. Included in the data are hourly hydrogen sulfide concentrations in parts per billion (ppb), wind direction in degrees, wind speed in meters per second (m se c^{-1}), temperature in degrees Celsius, humidity and precipitation in millimeters (mm).

The hydrogen sulfide concentrations and wind direction at each of the monitors were acquired for the years 2005, 2007, 2008, 2009, 2010, 2011, and 2012. The data for year 2006 were unavailable due to unknown reasons. The data set has some missing values, but more importantly, the hydrogen sulfide concentrations include a significant number of negative values, which suggests equipment calibration issues or instrumental drift. This problem occurs in all the monitors and during all the years so it is a persistent issue with the data.

3.2 Hydrogen Sulfide Data

The data were obtained in Excel 2012 format and imported into Matlab 2012a for analysis. Some alterations needed to be made to the hydrogen sulfide concentration data. First, missing data were changed to the value of the mean concentration in that particular year. The original method was to replace any missing values with a zero, but that would lead to a less accurate, and lower total calculated amount of emissions. On average there

were 400 missing values for each year, which contain 8760 values in total with 2008, and 2012 as leap year exceptions with 8784 data points. Therefore roughly five percent of the hydrogen sulfide data were filled in with the mean concentration for missing values. The missing data points are likely from regular maintenance and calibration procedures where the instruments were off line for a specific amount of time.

Second, corrections for negative values which likely derived from instrumental drift, had to be made. There are two options for treating the negative values; the first is to designate the most negative value as an arbitrary zero, since a negative concentration is impossible, and correct all the other data equivalent to the most negative value in the data. The second option, which is the method I used, is to consider the negative values to arbitrarily represent a zero concentration of hydrogen sulfide and average all the positive values with both recorded zeroes and zeroed negative values.

Once the data were corrected to be all positive and continuous, a boxcar average of hydrogen sulfide concentrations in ppb was calculated. The boxcar average is done over a two-week time span, with a value given for individual hour increments. As an example, the average for January 1st at 1 am would be the average of the next 2 weeks, or 360 data points. This smoothes the data so that hydrogen sulfide emissions can be viewed over longer time scales and the monitors compared efficiently.

The maximum single hour concentrations detected from each station per year have also been retrieved and listed in table 3, on page 32. These incidents are important to analyze because hydrogen sulfide is most toxic at high concentrations and the box car averages throughout the year will not likely reflect large events that do occur (Ingoglia, 1991).

3.3 Wind Data

The wind direction data are given in degrees of the compass, where 0 is North, 90 is East, 180 is South, and 270 is West. There are many fewer missing data points in the wind directions data compared to the hydrogen sulfide concentrations, but all missing data points were filled in with the mean direction of each year. This correction shifted the data to show a false extra dominant wind direction, which must be taken into account when discussing the wind rose plots. Once the data were continuous, they were processed in Matlab and changed into radians to create a wind rose graph. This graph shows the units of time, hours in this case, that the wind is coming from a certain direction based on the length of the vector at each point around the compass.

Wind rose plots were made for each monitor were made so that the variations in the small scale wind patterns can be observed in the differences of the plots. This can also help in deciding if the monitors are stationed in effective places around the geothermal plant and are actually recording the plant emissions. The three monitors are positioned to the south and west of the plant, catching the emissions blown by the north easterly trade winds. These are the predominant winds of the area but the topography and weather pattern changes can lead to variability in the wind direction. A combination of the hydrogen sulfide data and the wind direction should give an accurate understanding if the monitors are recording all the emissions or if improvements should be made to their positioning in order to better characterize the emissions from the plant.

Correlation plots were also made to examine if the different monitors were recording similar values at the same times. Note that the correlation plots used the hourly

data for the hydrogen sulfide concentrations not the boxcar averages. It is expected that the wind data will be highly correlated, but not identical, as there are local wind effects and variations associated with local topographic features. Hydrogen sulfide readings are not expected to be correlated as there could be a range of conditions from static winds to heavy trades. During high wind conditions, Station A for example might be recording a high concentration of hydrogen sulfide as it is downwind from the plant, while station C would record less, assuming the only emission of this gas is directly from the plant and not from a nearby natural source. These correlation plots will also help to analyze the effectiveness of the stations, and help determine if additional monitoring stations should be installed for the protection of the surrounding environment and communities.

CHAPTER 4. RESULTS

4.1 Hydrogen Sulfide Data

The hydrogen sulfide 2-week average concentrations for all three stations are shown in the following plots. Note that in all plots, monitor A is the black line, monitor B is the red line, and monitor C is the blue line.

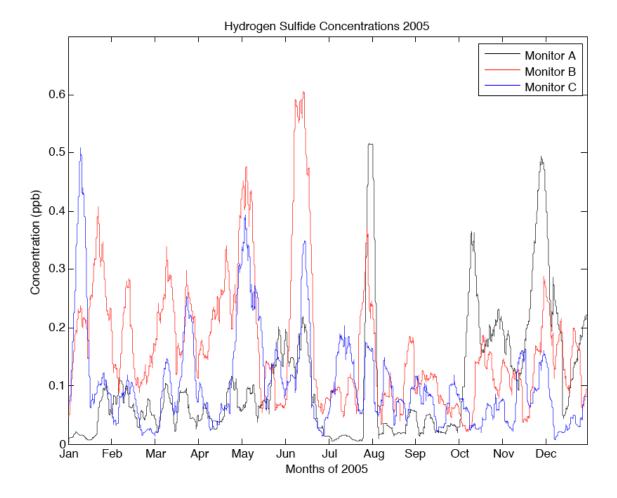


Figure 3. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2005.

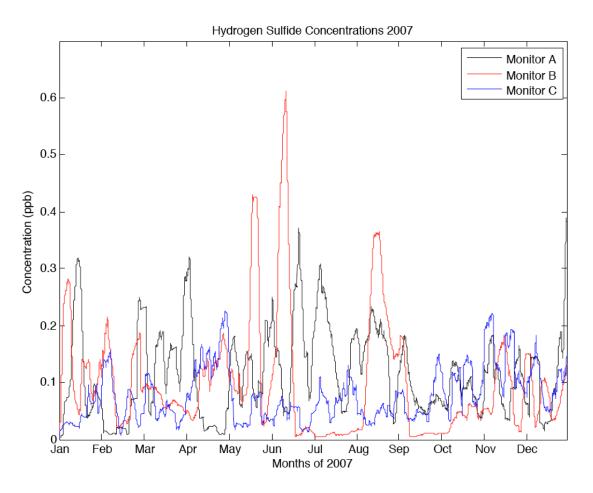


Figure 4. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2007.

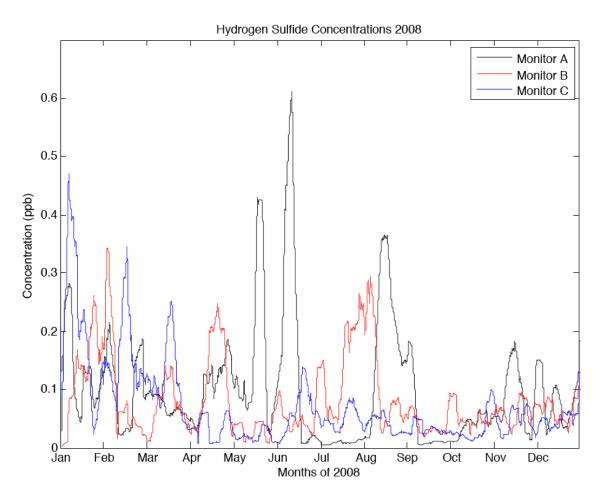


Figure 5. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2008.

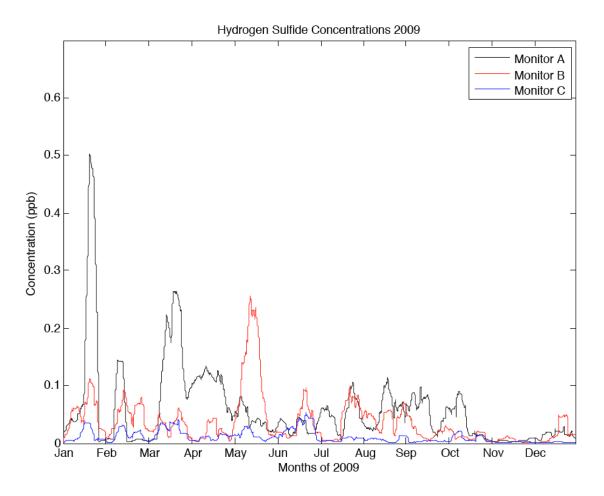


Figure 6. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2009.

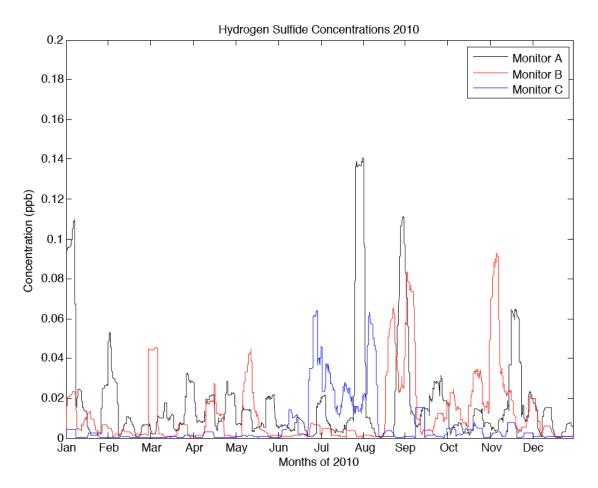


Figure 7. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2010.

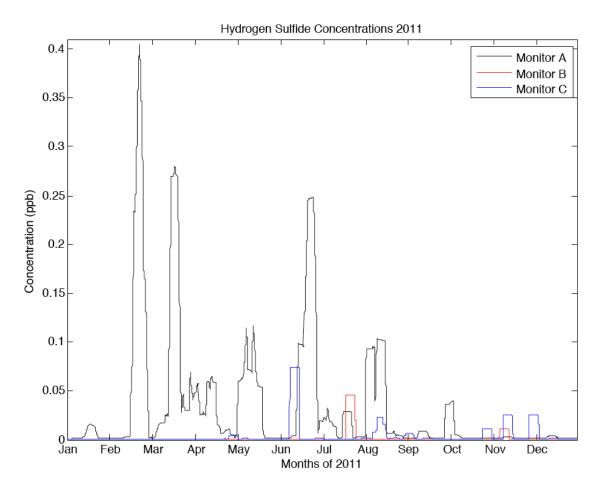


Figure 8. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2011.

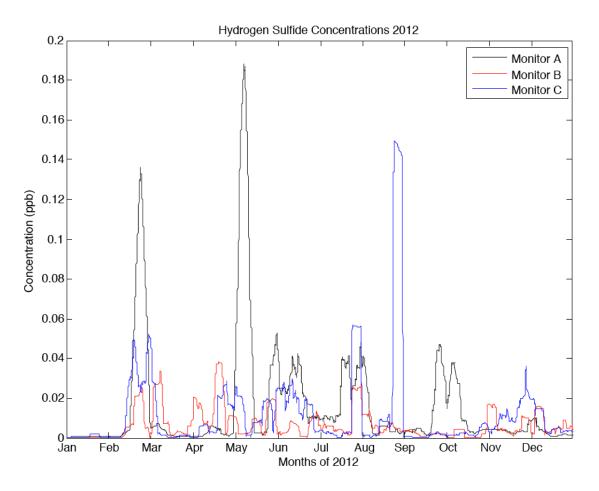


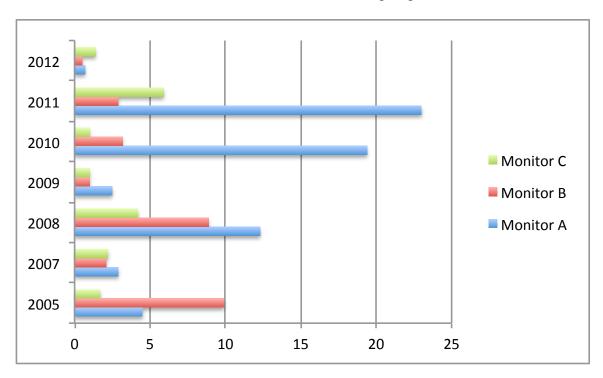
Figure 9. Hydrogen Sulfide Concentrations for Monitors A, B, and C in 2012.

Table 3 shows the single maximum hourly concentration from the raw data recorded at each monitor in the study.

Station	2005	2007	2008	2009	2010	2011	2012
A	4.5	2.9	12.3	2.5	19.4	23.0	0.7
В	9.9	2.1	8.9	1.0	3.2	2.9	0.5
С	1.7	2.2	4.2	1.0	1.0	5.9	1.4

Table 3. Maximum recorded hourly concentration by the monitoring stations around Puna Geothermal Ventures in parts per billion (ppb).

Figure 10 plots the single maximum-recorded concentrations shown in table 3.



Maximum Concentrations Recorded in part per billion.

Figure 10. Maximum Hydrogen Sulfide Concentrations Recorded during the period of study.

Correlations plots for all three monitors were prepared for the year 2005. Hydrogen sulfide concentration correlations can be seen in figures 11-13, and wind direction correlations can be seen in figures 15-17.

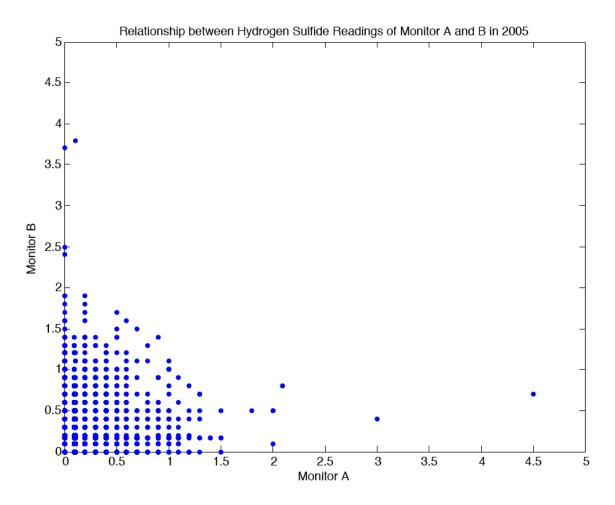


Figure 11. Correlation between the Raw Hydrogen Sulfide Concentrations (ppb) measured at Stations A, and B in 2005.

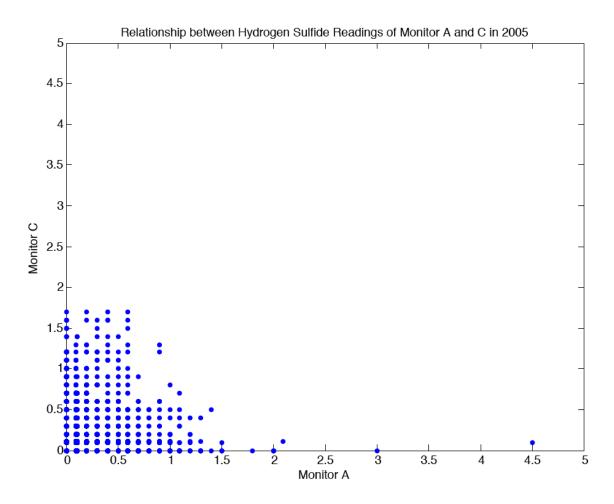


Figure 12. Correlation between the Raw Hydrogen Sulfide Concentrations (ppb) measured at Stations A, and C in 2005.

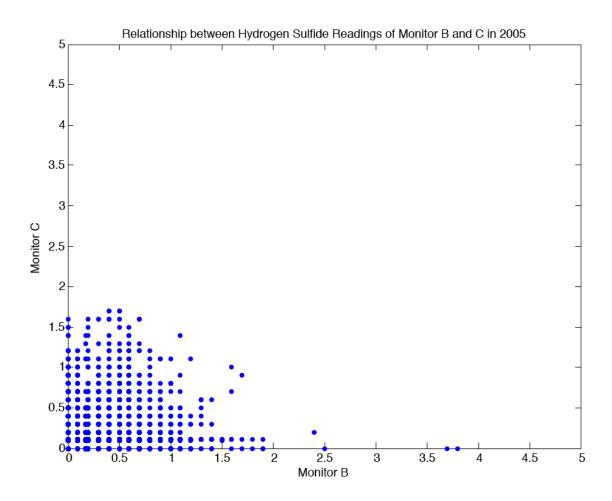


Figure 13. Correlation between the Raw Hydrogen Sulfide Concentrations (ppb) measured at Stations B, and C in 2005.

Figure 14 shows the wind rose plots from monitors A, B, and C in for the years of 2005-2012. They have been overlaid on the map of PGV in order to better illustrate their individual wind direction patterns.

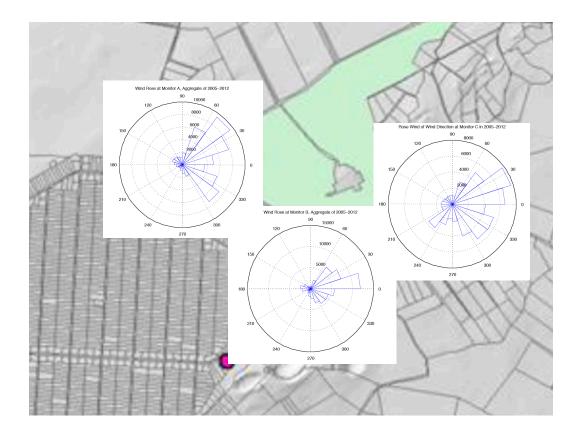
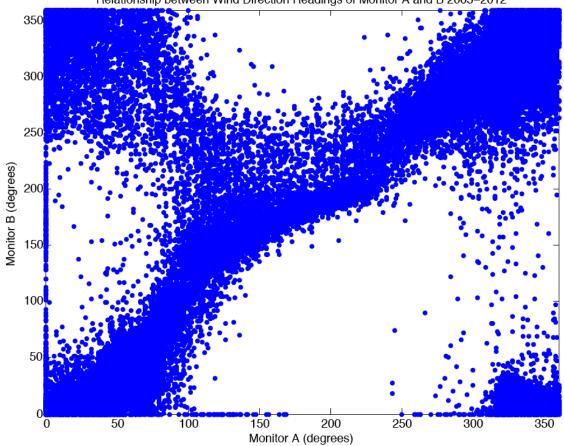


Figure 14. Wind rose plots from monitors A, B, and C in for the year in their actual locations in relevance to the Puna Geothermal Plant (the blue star) during the period of study. The inner circles represent the number of hours the wind was blowing from that direction during the years 2005-2012.



Relationship between Wind Direction Readings of Monitor A and B 2005–2012

Figure 15. Correlation between the Wind Directions measured at Stations A, and B in the period of study. A perfect correlation of the two monitors would show a slope of one on the graph. Clumps of data in top left and bottom right corner explained in discussion on page 46.

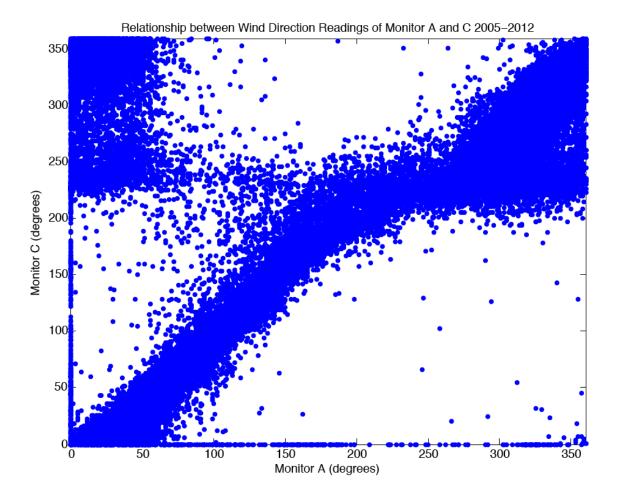


Figure 16. Correlation between the Wind Directions measured at Stations A, and C in the period of study.

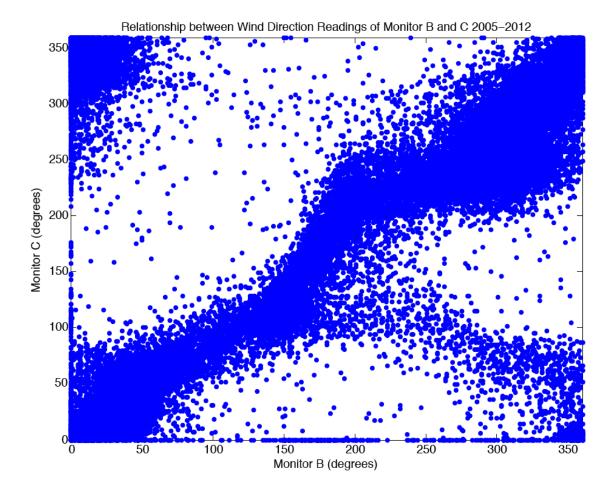


Figure 17. Correlation between the Wind Directions measured at Stations B, and C in the period of study.

CHAPTER 5. DISCUSSION

The hydrogen sulfide emissions recorded by the monitors, A, B, and C in Puna have large variations, but the two week averages show a more continuous representation of the data. The maximum concentrations shown in table 3 are, for the most part an order of magnitude greater than the (boxcar) averaged concentrations shown in figures 3-9. This indicates that during normal production at the plant, the emissions are generally low, but can be significantly higher during single emission events; such events are not accurately shown in the plots of two-week averages. This being said, the concentrations measured by the monitoring stations are well below the dangerous levels mandated by the EPA and other risk assessments (EPA 2003), even below the Department of Health's own standard of 25 ppb (DOH 2013). The highest value recorded in the seven years was 23.0 ppb at station A in 2011, and the second highest was 19.4 ppb also at station A in 2010. The highest box car average value for the study period was 0.7 ppb, which is considered to be a very low level of pollutant according to the EPA and compared to the geothermal emissions of hydrogen sulfide in New Zealand (DOH 1984).

The utilization of two-week boxcar averages with the hydrogen sulfide concentrations allowed for comparison with findings from research done by Bates, 2013. The 2-week averaged hydrogen sulfide concentrations observed in Rotorua, New Zealand were much higher than observed in Puna, averaging annually at 20.3 ppb, with a single monitor high of 63.9 ppb (Bates et al. 2013.) Even with these high concentrations of hydrogen sulfide observed in residential and commercial areas in Rotorua compared to in Puna, there was not an observed increase in respiratory problems such as asthma. Additionally, research on hydrogen sulfide in the body has shown that it's an important

signaling molecule for smooth muscle relation and reduced inflammation, which both contribute to protecting against asthma affects. This research gives a background on the concentrations observed in Puna, and the concentrations present in Rotorua are much higher than Puna without observed health effects (Bates et al. 2013).

The yearly maximum concentrations of hydrogen sulfide measured are not consistent across the three monitors and in fact, can vary greatly in some years. It is also important to note that monitor A recorded the highest concentration in five consecutive years, and the second highest in the remaining 2 years, as seen in table 3. The position of the individual monitors in relation to the plant, well field, and pipelines is the most obvious reason for these differences: and monitor A is directly west of the plant, making it catch the majority of the emissions during normal trade wind events. Monitor B is to the southwest, so it also catches the emissions when the winds are normal trades, but monitor C is located to the south east, and would theoretically not be exposed to much of the emissions directly from the plant during normal wind conditions. It is important to note the monitors A & B are closer to the well field source of the plant and could explain why those two monitors tend to have higher average concentrations.

It is clear from the results that the averaged concentrations decrease with every year of the period of study. Within the time frame of this study, emissions were greatest during the years 2005-2008, while during the years 2009-2012 there was a significant decrease in the averaged emissions. Geothermal production during the period of study was consistent, however, therefore the changes in concentrations of hydrogen sulfide as time progressed are likely due to natural emission variability. Pu'u O'o Crater could be a natural source of hydrogen sulfide in the area, as it is roughly 25 miles to the south west

of the monitors. It has been shown that when the vent at Halema'uma'u opened in 2008, the emissions from Pu'u O'o began to decrease which could explain the decreasing trend seen in the hydrogen sulfide emissions.

The correlation plots from the three monitors and their hydrogen sulfide readings seen in figures 11-13 confirm the assumption that they would not be directly correlated. As seen in figure 11, monitor A can be registering a concentrations of 4.5 ppb while at the same time, monitor B, which is less than a mile away, is only registering a concentration of 0.7 ppb. The trend of one monitor reading high while another reads low is seen throughout all three of the hydrogen sulfide correlation plots and leads to a conclusion that additional monitoring stations may be needed to better evaluate the air quality in the area. However, it is uneconomical and unrealistic to have monitoring completing surrounding the plant to observe all the hydrogen sulfide emissions. Instead, the monitors are theoretically strategically placed to detect the wind along the most probable wind trajectory (DOH, 2013)

In previous research with fewer data, correlations have been drawn between the hydrogen sulfide concentrations and wind direction of a single station. In this analysis, it is possible to see what the hydrogen sulfide concentrations are at times where the monitor is upwind, or downwind from the PGV plant. A conclusion of the previous research was that there were other sources of hydrogen sulfide than just the geothermal plant because the monitors were still registering average concentrations even when upwind from the plant. This method of correlations was not utilized in the current study, but is an avenue of further research in understanding the natural and anthropogenic hydrogen sulfide emissions in the Puna area.

The wind rose plots in figure 14 confirm the expected results that the dominant winds are from the north east. However, all three monitors also show a definite south east wind direction about half as often as the north easterlies. Following the trajectory of a south east wind blowing over the PGV plant shows that any emissions from the plant itself during times the wind is from this direction would pass to the north west of the plant and not observed by the monitoring stations. However, the well field of the plant is stationed slightly to the east of the main plant, meaning that during south east winds, monitor A would be in the direct trajectory for emissions from well fields. The combination of these reasons could be one explanation as to why monitor A recorded the highest concentrations in five consecutive years.

The one thing to note is that in the wind roses of monitors B and C, there are very rarely winds from the south west, commonly known as Kona Winds. Such a change of wind direction is usually associated with a considerable decrease in wind speed. Hydrogen sulfide is the most dangerous volcanic gas emitted to the environment and is most likely to affect human populations when the wind is light and the gas it is able to sink and pool in low areas due to its greater density than air (Rotorua Health Service 1999). The only monitor that would be exposed to the hydrogen sulfide during such events like this would be monitor C, but it is only to the east of the PGV plant, and any wind with a southerly component would allow the emissions to go undetected. This could be dangerous for the local population because if there was a large release of hydrogen sulfide during periods of Kona wind, it is possible that the gas could go largely undetected, and pool in low lying residential areas, such as Leilani Estates, a residential development to the west of PGV.

Correlations plots between the wind direction at the three stations shown in figures 15-17 confirms the assumption that they are indeed correlated. The general 1-1 slope of the three plots means that the monitors are generally recording winds from the same direction at the same time. The small differences in the plots are likely to be from the topographical differences of the area, and small scale wind patterns that affect the direction at each station. Note that the clumps of data points in the top left and bottom right corners of figures 15-17 are due to the circular data method. Simply, a wind that is from 359 degree at one station, and only a few degrees to the north and east in direction will appear uncorrelated and cause the data clumps in the corners, whereas most data falls near the 1-1 slope.

In Rotorua, New Zealand, people are exposed often to regular concentrations of hydrogen sulfide exceeding 143 ppb, and a maximum in a residential area was measured at 1,000 ppb, or 1 parts per million (ppm) (Bates 2002). At such levels, there is some evidence that adverse health effects are common. Neurological effects, cardiovascular and respiratory diseases have been noted to occur at higher frequencies in populations chronically exposed hydrogen sulfide emissions such as those observed in Rotorua (Bates 2002). More recent studies by Bates, in 2013, have questioned the previous finding and state that it these health concerns are possible, but not observed in Rotorua (Bates et al. 2013).

Similarly to Rotorua, residents of Puna have been noted to have higher rates of respiratory conditions than throughout the rest of the island, and even state-wide but a direct connection between hydrogen sulfide and the respiratory problems has not been unequivocally made in Puna specifically, but are more associated with natural volcanic

emissions (DOH 1984). The much lower levels of hydrogen sulfide emissions occurring in Puna compared to Rotorua could explain why direct connections have not been observed, but the threat is still believed to be there. Concentrations recorded in Puna however, are consistently below the state, and EPA standards for minimum risk levels, lending some reassurance that the PGV plant is not posing a large danger to the population.

Although there is no evidence that the population should express concern over hydrogen sulfide emissions from the PGV plant, the effectiveness of the monitoring system needs to be reviewed because hydrogen sulfide is such a dangerous pollutant. The data retrieved from the monitors had many missing values, approximately 5% for the hydrogen sulfide concentrations, and many of the other values were negative. The negative values were assumed to reflect instrumental drift, and were set to zero, but if the calibrations of the monitors is incorrect, then the rest of the data is somewhat questionable and needs to be reviewed. As noted previously, some of the missing values can be attributed to maintenance and calibration procedures. It is possible that through the manipulation of the data, and from the corrections for missing and negative values, the averages I obtained were lower than they really, assuming the negative values are not from instrumental drift but from faulty calibration. This is not such a concern at this stage because the averages obtained were still less than 1 ppb and the lowest negative values recorded were more positive than -1.0 ppb.

It is also important to determine the inherent error in the monitoring instruments themselves in addition to ensuring their calibrations are correct. In the Hawai'i State Department of health's 1984 research into the impact of hydrogen sulfide on health in

Puna and the Leilani Estates, their instruments for measuring monitoring the hydrogen sulfide had an accuracy of plus or minus 2 ppb. The range of error for the Department of Health monitors used in this study were unfortunately not given but if the concentrations being measured are numerically within the range of error for the instrument, the accuracy of the data would be under question.

CHAPTER 6. CONCLSUSIONS

Geothermal power production may have a bright future in Hawai'i, and with the governmentally influenced changes towards a sustainable energy mix this future may not be to far away. The geothermal reservoirs that have been discovered on the island of Hawai'i, and potentially on Maui, are some of the hottest in the world and have some of the highest potential for power production (GeothermEx, 2005). The production of these resources, however, is not without environmental impacts such as gaseous emissions during drilling and production, and contamination of groundwater aquifers during brine re-injection. Biogeochemical processes in the geothermal reservoirs create potentially dangerous gases such as hydrogen sulfide, which can subsequently transform to other harmful gases, such as sulfur dioxide and sulfuric acid in the atmosphere; the latter can cause a lowering of the pH of precipitation (Kagel 2005).

There have been many attempts to link geothermal emissions to the health conditions of the nearby residents of Puna, but due to the consistently low emissions and little known nature of the toxic gas in the body at low concentrations, a solid connection has yet to be made. During venting, or well blowouts at the plant, large amounts of hydrogen sulfide are sometimes released to the air unabated and can cause widespread panic in nearby residents and lead to evacuations. Even though the nature of these events is dramatic and large amounts of hydrogen sulfide are released, it is difficult to assess the threat these sporadic (and acute) events cause to public health. Many times, research has concluded that further surveys and reports are needed to address the adverse health effects associated with geothermal development in Hawai'i, and few have come to a definitive conclusion (State of Hawai'i 1984).

Monitoring the consistent hydrogen sulfide release of previous developments, such as PGV in Puna, can lead to improvements in the future that can help lead Hawai'i to a more sustainable and energy-independent independent future, while mitigating the environmental and health hazards of such development. As shown in the current study, the emissions recorded at the PGV plant are well below the minimum risk levels of the EPA and State of Hawai'i Department of Health. However, the locations and accuracy of the monitors are potentially questionable, as evidenced by analysis of the wind patterns and because of missing data not from calibration procedures. Placing additional monitors to the north of the PGV plant, combined with more regular calibrations and verification of the accuracy of the monitors, could better assist the Puna community in protecting themselves from potentially dangerous emissions of hydrogen sulfide.

It is clear that there are emissions of hydrogen sulfide in the area, whether these are natural or anthropogenic, and each of the monitors is clearly independent from one another in monitoring these emissions. Therefore, the accuracy of such a monitoring system depends on the number of stations that are set up, and their location with respect to the plant and dominant wind patterns. The three Department of Health monitors, A,B, and C, are doing their job of monitoring the air quality surrounding the plant and well field, but during certain wind conditions, such as southerly winds, the real concentrations of hydrogen sulfide might be undetected due to the locations of the monitors. This can have serious implications for the surrounding communities and environment if no warning is given.

Before more geothermal energy can be developed in Hawai'i, the potential environmental impacts must be addressed more carefully and mitigated. There are many

successful geothermal power plants such as the one in Geyser California where hydrogen sulfide is abated through chemical processes (Nagel et al. 1999). These abatement processes have issues of their own as large quantities of chemicals are brought in for the abatement. Geothermal plants designed to cause minimal environmental impacts should be role models for Hawaiian geothermal development. The potential has been shown, the risks have been assessed, and the technology is currently available for a large development of geothermal resources in Hawai'i, specifically of the Kapoho geothermal reservoir in the Kilauea East Rift Zone. With an environmentally sensitive approach, geothermal development could help to boost Hawai'i's economy and lead to a sustainable self-sufficient energy future without compromising the air quality and health of neighboring communities, ecosystems, and aquifers.

BIBLIOGRAPHY

Alexandra, Vetter, Andrea Vieth, Kai Mangelsdorf, Stephanie Lerm, and Mashal Alawi. *Biogeochemical Characterisation of Geothermally Used Groundwater in Germany*. Publication. Neubrandenburg: German Research Centre for Geosciences, 2010.

Allis, Rick G. *Review of Subsidence at Wairakei Field, New Zealand. Geothermics* 29.4-5 (2000): 455-78.

Assessment of Energy Reserves and Costs of Geothermal Resources in Hawai'i. Richmond, California: GeothermEx, 2005.

Michael, Bates N. "Investigation of Health Effects of Hydrogen Sulfide from a Geothermal Source." *Archives of EnvironmenHealth* 57.5 (2002): 405-11.

Bates, M.N., et al., Associations of ambient hydrogen sulfide exposure with self-reported asthma and asthma symptoms. Environ. Res. (2013), http://dx.doi.org/10.1016/j.envres.2013.02.002i

Bourcier, W. L., M. Lin, and G. Nix. *Recovery of Minerals and Metals from Geothermal Fluids*. Lawrence Livermore National Laboratoy, 2005.

Boyd, Tonya L., Donald Thomas, and Andrea T. Gill. *Hawai'i and Geothermal What Has Been Happening*. Geo-Heat Center Bulletin, 2002.

Department of Health, Clean Air Branch. *Regulating Geothermal Air Emission*. DOH, 2013.

Fridleifsson, Ingvar B. "Geothermal Energy for the Benefit of the People." *Renewable and Sustainable Energy Reviews* 5.3 (2001): 299-312.

Gardner, Murray C., James R. McNitt, Chrisopher W. Klein, and Dean Nakano. *History and Results of Surface Exploration in the Kilauea East Rift Zone*. Richmond, California: GeothermEx, 1995.

Ingoglia, Mark J. *Review of Emergency Plan and Response to the 12 June 1991 Uncontrolled Venting of the Puna Geothermal Ventures (PGV) KS8 Geothermal Well.* Issue brief. Honolulu: State of Hawai'i: Hazard Evaluation and Emergency, 1991.

Kagel, Alyssa. *The State of Geothermal Technology Part II: Surface Technology*. Washington D.C.: Geothermal Energy Association for the U.S. Department of Energy, 2008.

Kagel, Alyssa, Diana Bates, and Karl Gawell. *A Guide to Geothermal Energy and the Environment*. Washington D.C.: Geothermal Energy Association, 2005.

Legator, Marvin S., and Debra L. Morris. "Health Effects from Chronic Low-Level Exposure to Hydrogen Sulfide." *Archives of Environmental Health* 56.2: 123-31.

Nagel, Gary J. *Controlling H2S Emissions in Geothermal Power Plants*. Rep. 17th ed. Vol. Bulletin of Hydrology. 1999.

Ouali, Salima. "The Exploitation of Hydrogen Sulfide for Hydrogen Production in Geothermal Areas." *Eslevier* 36 (2011): 4103-109. *Science Direct*. Web. 1 Nov. 2013.

Siegel, S. M., and B. Z. Siegel. *Geothermal. The Environment. Impact: Air-Quality Data.* Vol. 4. Honolulu: Hawai'i Energy Resource Overviews, 1980.

Siegel, S. M., and B. Z. Siegel. *Geothermal Hydrogen Sulfide and Health in Rotorua, New Zealand*. Publication.: Hawai'i Natural Energy Intitute, 1984.

Siegel, Standford M. *Hydrogen Sulfide and Health in New Zealand Final Report*. Hawai'i Natural Energy Intitute, 1985.

State of Hawai'i, and Department of Health. "A Study of the Health Status of a Population Exposed to Low Levels of Hydrogen Sulfide (and Other Efluents) in Puna, Hawai'i." (1984).

The ABC's of Hydrogen Sulphide in Geothermal Bores. Rotorua Occupational Safety and Health Service, 1999.

Thomas, Donald M. *Geothermal Resource Assessment for Hawai'i*. Tech. Vol. 3. Honolulu: Hawai'i Institute of Geophysics, 1979. Geothermal Resources Council.

Thomas, Donald M. *The Geochemistry of the HGP-A Geothermal Well: A Review and an Update*. Vol. 11. Honolulu: Hawai'i Institute of Geophysics, 1987. Geothermal Resources Council.

Update of the Statewide Geothermal Resource Assessment of Hawai'i. Richmond, California: GeothermEx, 2000.

US Environmental Protection Agency. *Toxicology Review of Hydrogen Sulfide*. Publication. Washington, D.C.: Integrated Risk Information System, 2003.

Kelley, Donham, and Peter Thorne. *Chapter 8. Exposure Limits Related to Air Quality and Risk Assessment.*