# Ambient and Soil-Gas Assessment of Geothermal Hydrogen Sulfide (H<sub>2</sub>S) and Methane (CH<sub>4</sub>) in Clearlake, CA

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## ABSTRACT

Geothermal gases are present in ambient air around volcanoes because of increased nearby tectonic plate movements. At high levels many of these gases are toxic and become public health hazards. In Clearlake, CA, a city roughly 35 km away from an active volcano, citizens have expressed concern regarding geothermal hydrogen sulfide (H<sub>2</sub>S) and methane (CH<sub>4</sub>) venting. In response, I worked with the California Department of Public Health (CDPH) and Lake County Department of Public Health (LADPH) to conduct an ambient gas CH<sub>4</sub> and H<sub>2</sub>S assessment of a residential neighborhood. I used soil-gas data in the same study site and examined the correlation between soil-gas and ground-level measurements. In ground-level open air, the average H<sub>2</sub>S concentration ranged around 1-3 parts per billion (ppb), and CH<sub>4</sub> concentrations were under the instrument's detection imit. Ground-level enclosed spaces had higher average gas concentrations and larger variability, with an H<sub>2</sub>S range of 0-100,000ppb, and a CH<sub>4</sub> range of 0-500 % Lower Explosive Limit (%LEL). To compare ground level data with soil-gas data, I used ArcMap's ordinary kriging tool to estimate the ambient air and soil concentrations at the same spatial points and used the "extract values to point from raster" tool to compare the measured values with the corresponding estimated value. Positive correlations between soil-gas H<sub>2</sub>S and CH<sub>4</sub> measurements and non-zero ground-level enclosed-spaces H<sub>2</sub>S and CH4 measurements were found (H<sub>2</sub>S R-squared .618, P-value 5.23e-6, and CH<sub>4</sub> R-squared .2462 and Pvalue .01515), meaning that non-zero enclosed space measurement could indicate high soil-gas concentrations.

## **KEYWORDS**

Geothermal gas, gas venting, volcanic gases, kriging, public health, Lake County

#### INTRODUCTION

Geothermal gases are present in ambient air around active volcanoes due to the increased tectonic plate movement (Longo et al. 2010). Under normal outdoor conditions, volcanic gas emissions pose little threat to human health since they are quickly dispersed in open air. However, at higher levels some of these gases are toxic, and could become public health hazards (Shusterman 2001). Two of the most common geothermal gases are: hydrogen sulfide (H<sub>2</sub>S) and methane (CH<sub>4</sub>). Commonly measured in parts per million or parts per billion molecules (ppm or ppb), hydrogen sulfide is a corrosive gas that can cause acute eye and lung irritation at 50 ppm, and pulmonary edema at 100ppm (Guidotti 1996). At levels between 500-700ppm, H<sub>2</sub>S can cause coma within minutes and death within hours (Hawthorn 1970, Hansell 2004). Chronic exposure to low levels of H<sub>2</sub>S has been associated to damage the respiratory and nervous systems, and humans can detect this gas's "rotten-egg" smell at levels as low as 3 ppb (Reiffenstein et al., 1992, Legator et al. 2001, Bates et al. 2002). In accordance with these findings, the California Air Resources Board has set a H<sub>2</sub>S 1-hour exposure standard at .03 ppm, or 30 ppb (California EPA 2009). Another geothermal gas that is often present is methane. Methane is odorless, colorless, and at high levels can cause asphyxiation through oxygen displacement. Methane is also a fire hazard, and at concentrations of 5%-15% by volume the entire body of air becomes flammable (EPA Advisory 2005). Because of this, methane concentration levels are often measured in percent Lower Explosion Limit (%LEL), with 100% LEL equivalent to 5% CH<sub>4</sub> by volume.

The city of Clearlake, California is an example of a town located within 20 miles of an active volcano and experiencing geothermal gas emissions. The town is also near the world's largest geothermal complex (Lake County), Clearlake citizens have reported bubbling rain puddles and unusual rusting patterns, in addition to odor complaints. Moreover, Clearlake records have shown that gas accumulation inside buildings led to the demolition of a residential home in 2005, and the closure of the City's Family Resource Center in 2009 (CDPH, unpublished data 2012). Clearlake is the most densely populated city in the County of Lake, and presents the highest public health risk if emissions were at unsafe levels (US Census, 2011). To address these concerns, Lake County Health Department has taken preliminary study samples of indoor air, installed an outdoor hydrogen sulfide scrubber, and set up a real-time gas analysis

device to record gas and meteorological data. Previous collaborations between the California Department of Public Health (CDPH) and United States Geological Survey (USGS) have actively sampled and found areas in the open air with H<sub>2</sub>S reaching over 20ppb . Active sampling involves direct air intake by an instrument to immediately interpret and display the concentration of the airborne substance. Active sampling determines a concentration; however, it does not address the rate of emissions of these gases. One method that could potentially assess the emission rates at different locations is analyzing underground gases with a method called soil-gas sampling. Soil-gas sampling is done after digging and sealing a hole below ground, and taking the measurement from the sealed hole after equilibrium has been reached (Finlayson 1992).

To compare two sets of data in one study site, Geographic Information Science (GIS) is a tool to assist with spatial analysis. ArcMap 10.1 ((ESRI, Redding, CA), is a software equipped with tools such as Kriging and "Extract Values to Point from Raster" to create two sets of matching points at specific locations. Kriging techniques have been widely used in soil science and topography that use weighted sums of adjacent points to interpolate the values in-between known points, creating a surface of estimations (Lin et al. 2002). Ordinary kriging assumes that the first moment of the variables is constant (Cressie 1988). With these two tools in ArcMap 10.1, soil-gas data can be compared with the ground level data in the same testing site to calculate any correlation between soil-gas and ground level datasets.

Even though Lake County has taken a few active samples to assess the geothermal venting situation, there is still little knowledge on the current levels of geothermal gases on-site (Barreau et al., 2013). The city discovered three locations where development should avoided due to high gas emission levels, but there may be more and the average concentrations of  $H_2S$  and  $CH_4$  gasses in open space are unknown. Finally, it is still unclear whether active sampling in open air could accurately assess which areas have higher emission potential than others.

## **Objectives**

I used a handheld sampling instrument to take H<sub>2</sub>S and CH<sub>4</sub> measurements around Burns Valley residential neighborhood in Clearlake, and geospatially compared the data with soil-gas concentrations in the same study site to assess the following:

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- The average ambient concentration of H<sub>2</sub>S and CH<sub>4</sub> in the neighborhood
- Areas with high H<sub>2</sub>S and CH<sub>4</sub> concentrations
- The correlation between ground-level gas concentrations and below ground gas concentrations

## **METHODS**

## Study site

I conducted my study at a residential neighborhood in the City of Clearlake, California (Fig. 1). Located roughly 35 kilometers east of an active volcano called Mt. Konocti, Clearlake is the largest city in Lake County with a population of approximately 15,000 people (US Census, 2011). The specific study site is located in the western area of the city, adjacent to the lake. With dimensions of roughly 460 meters by 400 meters, the study site is centered on the intersection of Division St and Uhl Ave, at 38.95880948 N and 122.64647419 W. The northeast section of the study site consists of a public park, police station, and public works station; the mid-west area is Burns Valley Elementary School with an outdoor grassy playground, and the south and east areas are residential streets (Fig. 2, Fig. 3).



**Figure 1.1 and 1.2. Location of City of Clearlake and Mt Konocti.** Figure 1 illustrates the location of the Lake County with respect to other urban centers. Figure 1.2 depicts the locations of the volcano and the city with respect to the lake.



Figure 2. Map outline of sampling site marked, solid black line. Left side of this area is the lake, the site includes Burns Valley Elementary School. The broken line represents the boundary of a previous study looking at ambient  $H_2S$  levels.

The site was selected because of past gas accumulation occurrences and frequency of odor complaints in the area (Dr. Karen Tait, personal communication 2012). Previously, CDPH has completed preliminary field testing in the park area outlined by the broken line, and determined the presence of geothermal venting spots (Unpublished data, CDPH). For my study, I expanded the previous testing site to include the southern residential streets, and two streets east of the school to better assess community public health risks.



**Figure 3. Map of Burns Valley Neighborhood with the selected sampling streets numbered.** The streets I chose to sample are: Pearl Street (1), Robinson Ave (2), Uhl Ave (3), Evans St (4), Thomas St (5), Pine St (6), Olive St (7), and Locust St (8).

## **Collecting sample points**

Once determined, I marked roughly one location every 50 feet along the chosen streets. I began counting the points starting at Division St because Division St intersects all the other chosen streets, thus providing a convenient and consistent starting point. During marking, I recorded the GPS coordinates of each point using TRIMBLE Military Grade GPS (Trimble, Sunnyvale, California). At each sampling location I searched the immediate surrounding public areas for any points with a high probability of geothermal gas accumulation. These areas usually all under the categories below:

- Known locations of high emission (vents) from previous studies and community observations (Figure 4.1)
- Utility vaults & water meter boxes: because of their enclosed nature and accessibility to underground gases—which makes good testing areas to see if geothermal venting is in the area (Figure 4.2)
- drains: because of their low altitude and ability to shelter wind from all directions (Figure 4.3)

- culverts and pipes: because of their ability to partially shelter wind, and their low altitude (Figure 4.4 & 4.5)
- dirt and unpaved surfaces: because it is assumed to be relatively more difficult for gases to seep through thick concrete slabs (Figure 4.6)



**Figure 4. Different spots of interest**: 1.) Previously known spots 2.) water meters & utility vaults 3.) drains 4.) culverts 5.) pipes 6.) unpaved surfaces

With these options in mind, I marked 17 sample points from Pearl Avenue, 12 sample points from Robinson Ave, 9 from Uhl Ave, 8 from Evans Ave, 7 from Thomas Ave, 18 from Pine St, 16 from Olive St, 15 from Locus St, and 10 from the park area (Figure 4, below). Out of these chosen points, 70 locations have no mearbu enclosed spaces, hence in these spots I took open air measurements 3-inches above ground. The remaining 38 points had enclosed spaces of interest nearby, thus allowing measurements to be taken directly from the enclosed space.



**Figure 5. Locations of sample points (5.1), open-air points, (5.2) enclosed points:** Figure 5 marks all the selected sampling locations. If the location does not have any enclosed nearby spaces, I took an open air sample from 3in above ground (Figure 4.1). The points with an enclosed area mentioned above were sampled by sticking the device directly inside the enclosed space (Figure 4.2).

# **Taking samples**

For each sampling location, I used the Jerome 631-X (Arizona Instruments, Chandler, AZ) to measure H<sub>2</sub>S to the accuracy of 1ppb. To test for methane, I used the RKI Eagle (RKI Instruments, Union City, California), which has a lower methane detection limit of 1% LEL,

which is .05% by volume, and additionally also measures  $H_2S$  concentrations up to 100ppm. After five consecutive sampling days, I collected 3-4 measurements at each location, which totaled to be 356 sample points, and a little over three complete sets of data.

To take each sample, I lowered the handheld devices so the intake nozzle was 3 inches above the ground for all open air points. For water meters, utility vaults, and drains, I inserted the nozzle 1-inch into any small holes (see figure 3.2), and about 5 inches into any larger openings (See Figure 3.3). Then, the handheld devices presented a measurement after 30-60 seconds, which I recorded onto a data sheet with information regarding sampling time and location description. Sixty-nine open air points were used for data analysis after removing one outlier, and a total of 38 enclosed locations were sampled.

#### Soil-gas measurements

For soil-gas analysis, I used data provided from the Department of Public Health, which performed the soil gas testing in the same neighborhood, but at different sampling locations (Unpublished data, EBA Engineering 2012). For each soil-gas measurement, a 1-inch diameter hole was dug 3 feet below ground, and a Teflon tube was inserted through a rubber stopper. From this Teflon tube the testing devices were inserted to retrieve air from below ground, thus reading the CH<sub>4</sub> and H<sub>2</sub>S measurement at each location. Sixteen locations were sampled to assess the soil gas distribution for H<sub>2</sub>S and CH<sub>4</sub>, as well as the ambient air H<sub>2</sub>S concentrations at the same 16 locations 3 inches above ground.



**Figure 5: All Soil-Gas Sample Points:** EBA Engineering Company conducted soil-gas analysis and open-air H<sub>2</sub>S testing at these locations.

#### Data input and kriging using Geographic Information Science

To compare the surface-level samples with the soil-gas dataset, I plotted the points into ArcMap 10.1 (ESRI, Redding, CA), and created interpolated surfaces using the ordinary kriging tool. Then, I used the surfaces to estimate corresponding soil gas measurements to match each ground level sample, as well as use the ground-level interpolated surfaces to extract ground-level estimations at each sampled soil-gas location. For the surface level points, I plotted the points using the GPS coordinate system with latitude and longitude degrees, and entered the averaged H<sub>2</sub>S and CH<sub>4</sub> measurement in the metadata file. I then separated the data into two categories: one set of data for open air (Figure 5.1), and the other for enclosed spaces (Figure 5.2). To input the soil-gas values, I manually plotted the points using estimation by looking at a map containing the soil-gas sample points.

Using the ordinary kriging method in the ArcMap 10.1 toolbox, I created six different surfaces. The interpolated surface with the highest variability was made from the  $H_2S$  values in enclosed spaces, while for ground-level open-air  $H_2S$  values were least varied. To compare these points, I used the "Extract values to points from raster" function of ArcMap, which enabled me to pull a value from the surface at a given location. I then extracted values for roughly 100

ground-level locations from the soil-gas surface and extracted roughly 16 values for soil-gas locations from the ground level surfaces. This gave me paired datasets with a soil-gas concentration for each sampled ground level concentration. Below is a list of the six interpolated surfaces:

- H<sub>2</sub>S ground-level open air
- H<sub>2</sub>S ground level open air from soil-gas sampling
- H<sub>2</sub>S ground level in enclosed space
- H<sub>2</sub>S below ground from soil-gas sampling
- CH<sub>4</sub> ground level in enclosed spaces
- CH<sub>4</sub> below ground from soil-gas sampling

#### **Regression and data comparison**

I entered the sampled H<sub>2</sub>S and CH<sub>4</sub> values and the corresponding extracted values from the interpolated surfaces, and ran a linear regression on R and R Commander(R Program, Vienna, Austria, and Fox et al. 2009). I ran linear regression models to compare the open-air H<sub>2</sub>S values to soil-gas H<sub>2</sub>S, enclosed space H<sub>2</sub>S values to soil-gas H<sub>2</sub>S, and enclosed space CH<sub>4</sub> values to soil-gas CH<sub>4</sub>. The same processes were repeated for methane. After the initial round of linear regression analysis, I removed the zeros from ground-level H<sub>2</sub>S and CH<sub>4</sub> points, and ran the regression model again to look at the relationship between the non-zero ground-level values that includes both measured and estimated points, and their correlation with soil-gas values.

#### RESULTS

#### **Ground-level sampling**

#### Open air

Ground level open air samples revealed a continuous presence of low  $H_2S$ . A total of 70 locations were sampled, with each location was sampled three times. Removing the outliers, the  $H_2S$  open-air had an average of 1.4 ppb, median of 1.5 ppb, and ranged between 0.33 ppb to 2.67

ppb. As seen below, one outlier occurred at the intersection between Division St and Robinson Street, with an average  $H_2S$  concentration of 72 ppb. For  $CH_4$ , no levels that were above the 1% LEL detection limit of the RKI Eagle were noted.



**Figure 6: Open-Air Average measurements at each point**. A total of 70 locations had three samples averaged. In further analysis the outlier valued at 72ppb is removed.

## Enclosed spaces

There was higher variability in the concentrations gathered from enclosed spaces than concentrations gathered from open air. Some points consistently measured below detection limit (0ppb, 0%LEL), while other locations contained H<sub>2</sub>S concentrations that reached the RKI Eagle's upper detection limit of 100ppm. The average H<sub>2</sub>S amount of all enclosed spaces was 4,659 ppb. After removing the points that measured under detectable limit for both H<sub>2</sub>S and CH<sub>4</sub>, I found that the 17 non-zero points' H<sub>2</sub>S value averaged 10,415 ppb, the median concentration was 1.34ppb. The minimum H<sub>2</sub>S concentration was 0ppb (kept in dataset due to higher methane concentrations), and the maximum was 100 ppm.

For methane, the average concentration of the entire dataset of 38 enclosed points was 30%LEL. However, the 17 non-zero points had an average CH<sub>4</sub> gas concentrations of 68% LEL. The median concentration was 7.25% LEL, with the minimum measuring 0% LEL to the maximum of 460% LEL.



Figure 7.1: Averaged H2S point-concentrations in enclosed spaces. The highest values are north of Division St and Robinson Ave intersection, and above Olympic Drive and Uhl Avenue, measuring over 10,000ppb



**Figure 7.2.** Averaged CH<sub>4</sub> point-concentrations in enclosed spaces. The highest value was 460% LEL, at the intersection of Olympic Dr and Uhl Ave, the two points above Division St and Robinson Ave measured 355% and 50% LEL, and the point on Olive St measured 217% LEL.

## Soil-gas measurements

All points had a detected value in either surface (3-in)  $H_2S$ , or below-ground  $H_2S$  or  $CH_4$  measurements. Ground-level open air measurements averaged 6.5 ppb of  $H_2S$  with the median of 6.5 ppb, and had a range between a low of 2 ppb and 12 ppb. For soil-gas  $H_2S$  three feet below ground, the values averaged 4900 ppb, with the median of 8.5 ppb and a range between 2ppb and 50,000 ppb. Soil-gas methane measurements averaged 36% LEL with a median of 2% LEL, with all points between the minimum of 0% to the upper detection limit of 100% LEL.





**Figure 8.1-8.3: Soil gas point measurements**: 8.1) ambient ground-level H2S, 8.2) soil-gas H2S measurements 3ft below-ground, 8.3) Soil-gas CH4 measurements 3ft below ground

# **Kriging using Geographic Information Science**

The interpolated fields revealed some similarities between spatial variability in  $H_2S$  and  $CH_4$  concentrations.  $H_2S$  and  $CH_4$  measurements in enclosed spaces seem to appear most similar, followed by the three points of high  $H_2S$  and  $CH_4$  concentrations in soil-gas measurements. These surfaces are used to extract corresponding values for match soil-gas or ground-level locations.

Table 1: Interpolated maps of H<sub>2</sub>S and CH<sub>4</sub> measurements. The interpolated fields give a visual of where the higher concentrations are relative to other measurements. These surfaces are later used for estimate values at matching points between soil-gas and ground-level measurements.



## **Linear Regression Analysis**

Linear regression analysis of the soil-gas interpolated data and the ambient air interpolated data revealed a weak positive correlation between ground-level H<sub>2</sub>S concentration in enclosed spaces and corresponding soil-gas measurements. No significant correlation existed between the ground level open-air H<sub>2</sub>S measurements and soil-gas locations, nor with ground-level enclosed spaces and soil-gas methane concentrations.

 Table 2: Regressions of measured and estimated points:
 Summary statistics describe the relationships between various soil-gas and ground level measurements

Test Type	Soil-gas vs open air H2S	Soil-gas vs enclosed space H <sub>2</sub> S	Soil-gas vs enclosed space CH <sub>4</sub>
Scatter- plot			
Coefficient	1.2806	.41332	-0.06071
Standard- Error	1.976	0.9187	1.316
<b>F-Value</b>	1.514	10.65	0.3714
Adjusted R- Squared	0.008348	0.1983	-0.01557
P-value	0.2234	0.002336	0.5457

## Removal of non-detect values in enclosed spaces

Removal of the non-detectable points in the enclosed-spaces changed the relationship of the datasets. Linear regression with the altered datasets reavealed a significant positive correlation between non-zero enclosed spaces values and soil-gas values for both  $H_2S$  and  $CH_4$ . The correlation between the two datasets is stronger with the  $H_2S$  measurements, but both have a p-value of less than .05.

Table 3: Regression of measured and estimated points. After removing all the non-detect values from the enclosed-location, relationships are found with both  $H_2S$  and  $CH_4$  values in enclosed spaces with soil-gas measurements.

Test Type	Soil-gas vs enclosed space H <sub>2</sub> S (zeros removed)	Soil-Gas vs enclosed space CH <sub>4</sub> (zeros removed)	
Scatter- plot	$ \begin{array}{c}                                     $	$\left(\begin{array}{c} & & & \\ &$	
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Coefficient	0.6776	0.4357	
Standard- Error	0.6932	1.247	
<b>F-Value</b>	36.65	7.206	
Adjusted R- Squared	0.6184	0.2462	
P-value	5.229e-06	0.01515	

## DISCUSSION

The goal of this study was to assess the H<sub>2</sub>S and CH<sub>4</sub> concentrations in Burns Valley School District of Clearlake, California, and to calculate the correlations between the collected ground-level samples and the underground gas concentrations in the same area. The ambient air H<sub>2</sub>S concentration in Clearlake, CA ranged between 1-3ppb, which was below the concentrations which have been associated with human health effects (Bates et al. 2013). CH<sub>4</sub> in the ambient air was also lower than the measurement instruments' detection limit of 1% Lower Explosive Limit (%LEL). Spatial analysis comparing the measured non-zero surface level points with soil-gas concentrations revealed that there is a positive correlation between enclosed-spaces non-zero H<sub>2</sub>S and CH<sub>4</sub> values with the corresponding soil-gas values, with p-values being 5.229e-06 for H<sub>2</sub>S and .01515 for CH<sub>4</sub> values.

#### Study site field measurements

The open air measurements found a constant low ambient concentration of  $H_2S$  between 1-3ppb, and detected no methane above the detection limit of 1 % LEL. To my knowledge, this type of outdoor volcanic gas assessment has only been done in two cities: City of Clearlake, CA, and Rotorua, New Zealand (Bates et al. 2002, and Horwell et al. 2005). Clearlake has a lower overall ambient concentration of  $H_2S$  than Rotorua, and less concentration variability, which might be attributed to Clearlake's smaller observation area. One difference between the two study methods is that I took gas samples from Clearlake using repeated trials with a handheld active sampler, while Rotorua was measured with devices fixed in place that sampled across two weeks, and provided an average concentration across that time.

Gas concentrations in enclosed spaces were higher and more varied than open air concentrations—ranging from under detection limit, which is <1ppb for H<sub>2</sub>S and <1% LEL for CH<sub>4</sub>, to H<sub>2</sub>S reaching the maximum detection limit at 100ppm, and methane reaching 460% LEL. An unexpected discovery from this process was the variability between adjacent water vaults because there were no distinguishable physical features differentiating the enclosed spaces containing high amounts of H<sub>2</sub>S and CH<sub>4</sub> from those with non-detectable levels. This suggests that enclosed spaces such as water vaults could be subject to H<sub>2</sub>S and CH<sub>4</sub> accumulation, and workers maintaining water vaults and underground systems should take appropriate precautions.

## **Public health risks**

Although there have not been studies regarding long-term exposure to hydrogen sulfide at levels between 1-3ppb, there is presently little reason to believe that such concentrations pose a public health danger. Some areas where the geothermal gases could potentially be a danger to public health are the intersection on Uhl St and Olympic Dr, areas within the Division Ave and Austin St, and areas close to the intersection of Division St and Robinson Ave. These spots have been discovered to have H<sub>2</sub>S concentrations that were 50-200,000 times the ambient amount and methane that were above the explosive limit. Consideration could be given to remedial measures, such as changing the location of a bus stop, and alerting nearby property owners (Guidotti, 1996).

Areas of low ambient measurements should not be discounted as completely innocuous. They can still pose human health risks if either  $H_2S$  or  $CH_4$  gases enter an enclosed area and accumulate to higher concentrations, which is a phenomenon called vapor intrusion. Vapor intrusion is when gases enter into a building through the cracks of a building's base, and occurs most frequently with slab-on-grade foundations because the concrete slab pushes pressure down onto the soil and the cracks provide a direct channel for the gases to enter the enclosed space (Healy et al, 2004 and Durand, 2005). In Clearlake, vapor intrusion had been discovered for one of the former public service buildings (unpublished data, Lake County Department of Public Health 2009). The building has now been shut down due to the high accumulated indoor concentration of hydrogen sulfide. Risks of vapor intrusion could be assessed by soil-gas data, and the soil-gas  $H_2S$  measurements suggest that areas within 50 meters of Pine St, and 50 meters within the intersection of Robinson Ave and Baylis Ave should be carefully evaluated before conducting any infrastructure projects due to the higher chances of vapor intrusion from the soil-gas directly below.

One other aspect of the geothermal venting in Clearlake could prove to be a public health danger is inside enclosed spaces such as water vaults and drains. We found that inside some vaults  $H_2S$  and  $CH_4$  concentrations were high enough to have human health impacts, which suggests that other sections of the underground water system could also accumulate geothermal gases, which could affect people working underground. Moreover, if a burning object is dropped in areas with methane concentrations above 100% LEL, fire or explosion could occur.

## Data input, Kriging, and Comparisons

This is the first study that compares gas concentrations from two different sampling methods. There is a positive correlation between non-zero ground-level enclosed spaces measurements and soil-gas measurements of  $H_2S$  and  $CH_4$  concentrations, with p-values of 5.229e-06 and .01515, respectively. This suggests that taking active air samples in enclosed spaces could potentially indicate areas of high soil-gas concentrations. It should be noted that the results have false-negatives where zeros for enclosed spaces corresponded to non-zero soil-gas measurements, but there were no false-positive points that reveal high enclosed-spaces concentrations corresponding to low soil-gas measurements. Additionally, due to its low cost and

simple procedures, active sampling can be used to assess ambient air conditions by measuring H<sub>2</sub>S levels in open air, in addition to potentially suggesting areas of high soil concentrations.

#### Limitations

Even though this study assessed the geothermal gas concentration in the open air of Burns Valley Neighborhood in Clearlake, CA, and a comparison was made between soil-gas measurements and those at ground level, there were still factors this assessment did not address. For example, with each sample point being measured roughly three times over a course of five days, any variability that would occur in longer time-frames such as weeks, months, or seasons would not be accounted for. So far it can be said that the current average ambient open-air concentration is 1-3ppb during the daytime, in the summer season.

Another factor limiting the comparison between soil-gas samples and ground-level samples is the difference in time of sampling. The soil-gas sampling was done 14 days after I collected ground-level samples, so any conclusions derived from comparing these two data sets must assume that there were no changes in emission characteristics between ground-level measurements and the soil-gas collection period. It was also not possible to take into account the changing meteorological conditions such as temperature, wind speed, wind direction, and air pressure of each measurement taken in both the field study and the soil-gas collection.

Finally, the nature of interpolation adds another element of variability, since the half the points used for comparison were based on constructed surfaces instead of actual measurements. Taking into account that there were only 16 soil-gas points, the accuracy of the interpolated surface can be called into question, especially when the surface is used to interpolate values for over 100 ground level locations. The errors of these surfaces would have a dramatic effect on the correlation of the extracted points.

#### **Future research**

In terms of public health, re-visiting the study site to conduct a more extensive soil-gas collection should be done to determine areas of high concentrations of underground  $H_2S$  or  $CH_4$ , to better determine proper and safe building placement. In addition, another session gathering the

ground level measurements during the winter would be useful as well due to potential differences in climate and groundwater level affecting emissions characteristics. Another method of taking weather variability into account is to use a passive sampling method, such as performed in Rotorua. Passive samplers provide a concentration averaged over the course of 1-3 weeks.

Other than making this study more robust by taking into account seasonal variations and adding more soil-gas sample points, to better understand the geothermal emissions it would be useful to research the city's water system infrastructure. Out of all ground level-points I have sampled, the most variability came from water-vault and water meters. Understanding the water system may help to explain the wide gas variations between vaults that are physically next to each other, and possibly allow us to trace the gasses to an identifiable source.

#### Conclusion

In terms of public health, the ambient measurements of H<sub>2</sub>S and CH<sub>4</sub> have established that outdoor areas of Clearlake, CA are generally safe. The weak correlation between different measurement types suggests that active sampling may be used to both determine the ambient open air H<sub>2</sub>S concentrations, as well as suggest possible soil-gas H<sub>2</sub>S and CH<sub>4</sub> concentrations. Soil-gas measurements found areas of high H<sub>2</sub>S and CH<sub>4</sub> areas that should probably not have infrastructure developments built on them near areas between Austin St and Division St, and Evans Street.

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