Near Field Fate of Atmospheric Hydrogen Sulfide from two Geothermal Power Plants

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Dissertation submitted in partial fulfillment of a
Philosophiae Doctor degree in Environmental Engineering

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Abstract

Knowledge of the distribution of chemicals in the atmosphere and their interaction with the environment is fundamental in assessing their environmental impact. This includes analysis of environmental factors that influence the atmospheric concentration of chemicals, their distribution and depletion, in order to be able to assess the need for mitigating their emission. Hydrogen sulfide (H_2S) gas emission to the atmosphere usually increases following the development of a geothermal area. The gas is toxic in very high concentrations (above 700,000 $\mu g/m^3$ can be fatal) but can become an odor nuisance at low concentrations. Two geothermal power plants, the Nesjavellir and Hellisheidi Power Plants, are within 30 km from the city of Reykjavik in southwest Iceland. Geothermal power production has been expanding in the area and odor complaints have increased after the Hellisheidi Power Plant started production in 2006. In 2010 a health limit was set in Iceland by the Ministry for the Environment and Natural Resources at 50 $\mu g/m^3$ for a running 24-hour average. The aim of this research was to evaluate the near field distribution and the fate of H_2S from the two power plants. The results showed that H_2S concentration increases in more stable air, lower wind speeds (1.5-4 m/s) and lower temperatures (<3°C). Plumes of H_2S were observed to be guided in mountainous terrain and exhibited self-similarity, indicating repeated plume patterns. Plumes were narrower over smoother terrain, such as a lake. Spatial variability in the wind field was observed when the two plumes converged and when the plume path shifted considerably over a mountain ridge. Oxidation by the OH radical was identified to be the largest near field sink of H_2S, followed by uptake in Lake Thingvallavatn. Washout in precipitation was found to be the smallest sink as H_2S is unreactive in the low pH of precipitation in the area. Although the H_2S was estimated to be depleted by a few hundred tons per year in the study area the sinks are insignificant compared to the emissions from the power plants.

Útdráttur

Þekking á dreifingu efna í andrúmsloftinu og samspili þeirra við umhverfið er grundvallaratriði við mat á umhverfisáhrifum þeirra. Þetta felur í sér greiningu á þeim umhverfisþáttum sem hafa áhrif á styrk efnanna í andrúmsloftinu, dreifingu þeirra og eyðingu, til að geta metið hvort þörf sé á mótvægisaðgerðum. Þegar jarðhitasvæði eru virkjuð eykst yfirleitt losun brennisteinsvetnis (H_2S). Gasið er eitrað í miklum styrk (getur verið banvænt við 700,000 $\mu g/m^3$) en lykt þess getur valdið óþægindum við lágan styrk. Innan við 30 km frá höfuðborg Íslands, Reykjavík eru tvær jarðvarmavirkjanir þ.e. Nesjavalla- og Hellisheiðarvirkjun. Orkuframleiðsla á þessu svæði hefur aukist á síðastliðnum árum og hafa kvartanir vegna lyktar óþæginda aukist síðan Hellisheiðarvirkjun tók til starfa árið 2006. Árið 2010 setti Umhverfisráðuneytið reglugerð um styrk brennisteinsvetnis í andrúmslofti, heilsuverndarmörk voru sett fyrir 24-stunda hlaupandi meðaltal, 50 $\mu g/m^3$. Markmið þessarar rannsóknar var að meta dreifingu og heildar örlög brennisteinsvetnis allt að 35 km frá virkjununum. Niðurstöðurnar sýndu að H_2S styrkur eykst með stöðugra lofti, hægari vindi (1,5 - 4 m/s) og lækkandi hitastigi (< 3 °C). Mælingar sýndu að strókar brennisteinsvetnis fylgja landslagi í fjalllendi og endurtekin mynstur sáust í dreifingu þeirra. Strókarnir voru grennri yfir sléttara landslagi s.s. yfir stöðuvatni. Sýnt var fram á áhrif staðbundins breytileika í vindi þegar strókarnir tveir sköruðust og þegar strókar mældust beygja af upphaflegri leið yfir fjalllendi. Stærsti svelgur H_2S á svæðinu var oxun með OH radikal, næst stærstur var upptaka í Þingvallavatni. Útskolun með úrkomu reyndist vera minnsti svelgurinn þar sem H_2S er óhvarfgjarnt við lágt pH eins og í úrkomu. Þó að áætluð eyðing H_2S hafi verið verið nokkur hundruð tonn á ári er það óverulegt magn í samanburði við heildarlosun frá virkjununum.

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International reviewed journals

Olafsdottir, S., Gardarsson, S.M. 2013. Impacts of meteorological factors on hydrogen sulfide concentration downwind of geothermal power plants. Atmospheric Environment 77, 185-192. (Chapter 2). *Olafsdottir was responsible for data gathering, majority of the data analysis and majority of the writing of the manuscript.*

Olafsdottir, S., Gardarsson, S.M., Andradottir, H.O. 2014. Spatial distribution of hydrogen sulfide from two geothermal power plants in complex terrain. Atmospheric Environment 82, 60-70. (Chapter 3). *Olafsdottir was responsible for the measurements of atmospheric H_2S concentration, majority of the data analysis and majority of the writing of the manuscript.*

Olafsdottir, S., Gardarsson, S.M., Andradottir, H.O. Natural near field sinks of H_2S from two geothermal power plants. Submitted to Atmospheric Environment. (Chapter 4). *Olafsdottir was responsible for precipitation sampling for isotope measurements, data gathering, majority of the data analysis and majority of the writing of the manuscript.*

Conference papers and book chapters

Olafsdottir, S., Gardarsson, S.M., Armansson, H. 2010. Concentration of hydrogen sulfide from geothermal power plants in the vicinity of Reykjavik City, Iceland 2007-2009. Proceedings World Geothermal Congress 2010, Bali, Indonesia, 25–29 April. (Appendix D).

Andradottir, H.O., Gardarsson, S.M., Olafsdottir, S. 2010. Lárétt útbreiðsla gosstróka Eyjafjallajökuls metin frá gervihnattamyndum. Árbók VFÍ & TFÍ, bls. 239-248.

Olafsdottir, S., Gardarsson, S.M., Gustafsson, L., 2008. Measurements and modeling of hydrogen sulfide in Reykjavik City 2006 and 2007. Proceedings 19th International Symposium on Transport Phenomena 2008, Reykjavik, Iceland, 17-20 August. (Appendix E).

Presentations at conferences

Olafsdottir, S., Gardarsson, S.M., Andradottir, H.O. 2014. Near field fate of hydrogen sulfide from Nesjavellir and Hellisheidi Power Plants. Reykjavik Energy Science Project day, Reykjavik Energy Headquarters, March 14, 2014.

Olafsdottir, S., Gardarsson, S.M., Andradottir, H.O. 2013. Fate of hydrogen sulfide from Nesjavellir and Hellisheidi Power Plants. Landsvirkjun Energy Research Fund seminar, National Museum of Iceland, November 28, 2013.

Olafsdottir, S., Gardarsson, S.M., Andradottir, H.O. 2013. Fate of hydrogen sulfide from Nesjavellir and Hellisheidi Power Plants. Conference on the impacts of hydrogen sulfide on the environment, health and economy held by the Icelandic Environmental Scientist Society.

Olafsdottir, S., Gardarsson, S.M., Andradottir, H.O. 2013. Fate of hydrogen sulfide from Nesjavellir and Hellisheidi Power Plants. Seminar series on treatment and utilization of discharge from geothermal utilization held by GEORG: Geothermal Research Group.

Olafsdottir, S., Gardarsson, S.M., Armansson, H. 2010. Concentration of hydrogen sulfide from geothermal power plants in the vicinity of Reykjavik City, Iceland 2007-2009. Proceedings World Geothermal Congress 2010, Bali, Indonesia, 25–29 April, 2010.

Olafsdottir, S., Gardarsson, S.M. 2008. Hydrogen sulfide concentration in Reykjavik City 2006 and 2007. Proceedings Nordic climate solutions, Copenhagen, Denmark.

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1 Introduction

1.1 Motivation

It is essential to know the distribution and fate of a chemical to establish its effect on the environment. Knowing the factors that influence its concentration and its rate of depletion is key to discovering the extent of its effects. The environmental effects of hydrogen sulfide (H_2S) have not been defined in a broad context. With geothermal utilization growing due to an effort to decrease reliance on carbon based energy, emissions of H_2S are increasing worldwide. Furthermore, H_2S gas is produced as a byproduct in various industries, e.g. kraft pulp mills (Bordado and Gomes, 2003), wastewater treatment plants (Latos et al. 2011), coal gasification plants (Ko et al., 2006) and swine feeding operations (O'Shaughnessy and Altmaier, 2011). H_2S is a concern in areas near its sources. It is harmful to human health in high concentrations and its vigorous smell can become a nuisance at low concentrations, or above 7 $\mu g/m^3$ for half-hour averages (WHO, 2000). Different countries have set environmental guidelines or health limits based on the odor nuisance or possible health impacts (Bjornsson and Thorsteinsson, 2013).

Geothermal utilization has been increasing in Iceland during the last few decades and it is still increasing, as in many other countries that possess geothermal power. Two geothermal power plants are within 30 km of Iceland's capital of Reykjavik, the Nesjavellir and Hellisheidi Power Plants, and their production has been expanding. The increased emission of H_2S has resulted in increased public concern. Complaints of the odor have been more common and impacts on electrical equipment have also been reported. In 2010 a health limit was set in Iceland by the Ministry for the Environment and Natural Resources (2010) at 50 $\mu g/m^3$ for a running 24-hour average. This regulation requires the geothermal industry in Iceland to lower H_2S emissions (Gunnarsson, et al., 2013). The findings from research on H_2S distribution and identifications of its sinks will be beneficial in determining the effects of its emission, thus establishing the necessity of mitigation measures and determining what kind of mitigation measures would be the most effective.

1.2 Background

1.2.1 Study Area

The study area was within 35 km of the Nesjavellir (180 m a.s.l.) and Hellisheidi (260 m a.s.l.) Geothermal Power Plants in the Hengill volcanic system in Southwest Iceland. The power plants are 10 km apart, located on the north and south side of Mt. Hengill (805 m a.s.l.). Northeast of the mountain is Iceland's largest natural lake, Lake Thingvallavatn (83 km^2). The Nesjavellir Power Plant is located near the lake shore in a small valley, with ridges rising to the west and to the east. The Hellisheidi Power Plant is located at the southwest base of Mt. Hengill with Middalsheidi Heath to the west sloping towards the capital area which easternmost part is about 20 km from Mt. Hengill (Figure 1−1). The capital area consists of the city of Reykjavik and five neighboring towns. In the southern part of the study area are volcanic fissures with crater rows from eruptions that have taken place over the last 10,000

years (Gunnlaugsson et al., 2010). Small towns are located within the study area, away from the capital, as well as farms and summer houses. In 2013 over 222,000 inhabitants lived within the area or 69% of Iceland's inhabitants. Even so, most of the area is sparsely populated. There are recreational areas within the study area: the Mt. Hengill area has tracks for hiking and biking, a skiing area is in Mt. Blafjoll and Lake Thingvallavatn is known for both its beauty and its part in the nation's history. Local flora is characterized by moss, grass and small shrubs.
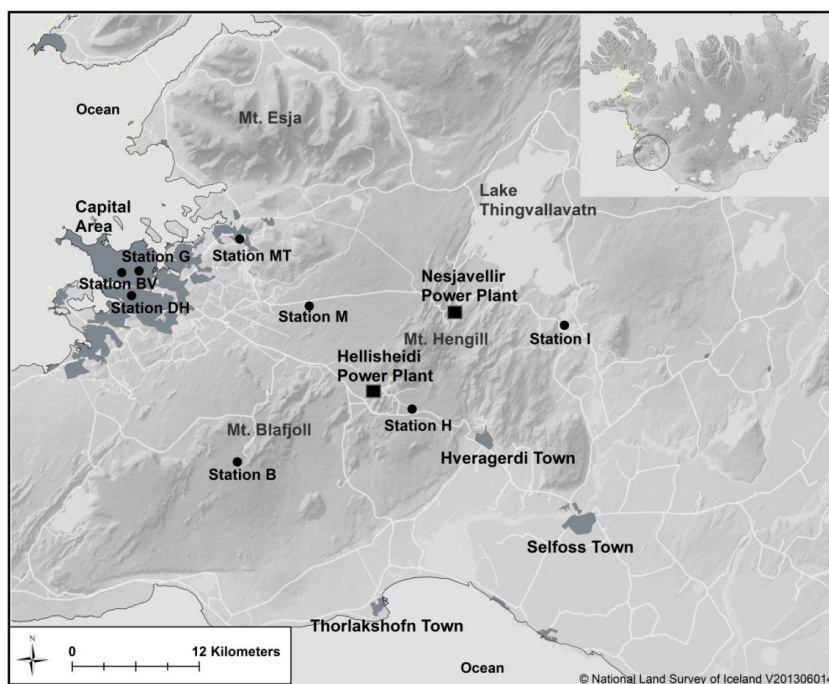
Figure 1–1. Study area, showing weather stations and other measuring stations used in the study, the capital area and local towns, and the Nesjavellir and Hellisheidi Power Plants. Roads are shown in white; lakes, rivers and ocean are in light gray.

1.2.2 The Geothermal Power Plants

Gaseous sulfuric compounds from geothermal areas exist in the form of hydrogen sulfide (H_2S). Following the development of a geothermal area, the H_2S is usually emitted at a higher rate into the environment than before development (Kristmannsdottir and Armannsson, 2003).

The Nesjavellir Power Plant (Figure 1–1 and Figure 1–2) is about 25 km from the easternmost part of the capital of Reykjavik and about 35 km from the city center. Hot water production started in 1990 and electricity production in 1998. With two enlargements, first in 2001 and then in 2005, the current production is 120 MW_e and 300 MW_{th}. The Hellisheidi Power Plant (Figure 1–1 and Figure 1–3) is about 18 km from the eastern-most part of Reykjavik City and about 28 km from the city center. Electricity production began in October 2006, at 90 MW, but in 2007 a 33 MW low-pressure turbine was installed. The electricity production has since

been expanded twice with two 45 MW turbines units in 2008 and 2011. The installed capacity is 303 MW_e and 133 MW_{th}. Further increase in hot water production is planned before 2020.

The gases in the fluids in the Nesjavellir and Hellisheidi geothermal fields are characterized by a relatively low concentration of CO_2 compared to other geothermal fields in Iceland. The concentration of gases in the steam is approximately 0.4% of which about 30% is H_2S (Gunnarsson et al., 2013). The amount and concentration of geothermal gases is estimated from the composition of the steam entering the turbines. A fraction of the gases is lost in the vacuum pumps of the condensers; therefore the composition is slightly overestimated (Gunnarsson et al., 2013). The gas is released at the top of the cooling towers of the power plants where the gas is vigorously mixed with the steam in four closely spaced outlets, with fans to accelerate emission. However, the gas was emitted from the top of the Hellisheidi Power Plant at first, but in 2007 the emission was moved to the cooling tower. As the power plants expanded production the emission of H_2S also increased; the yearly emission from 2006 to 2012 is shown in Figure 1–4. Note that emission from the Hellisheidi Power Plant in 2006 has been calculated from energy production data as a collecting system had not been installed.

Figure 1–2. The Nesjavellir Power Plant (photo by Gretar Ivarsson).

Figure 1–3. The Hellisheidi Power Plant (photo by Gretar Ivarsson).
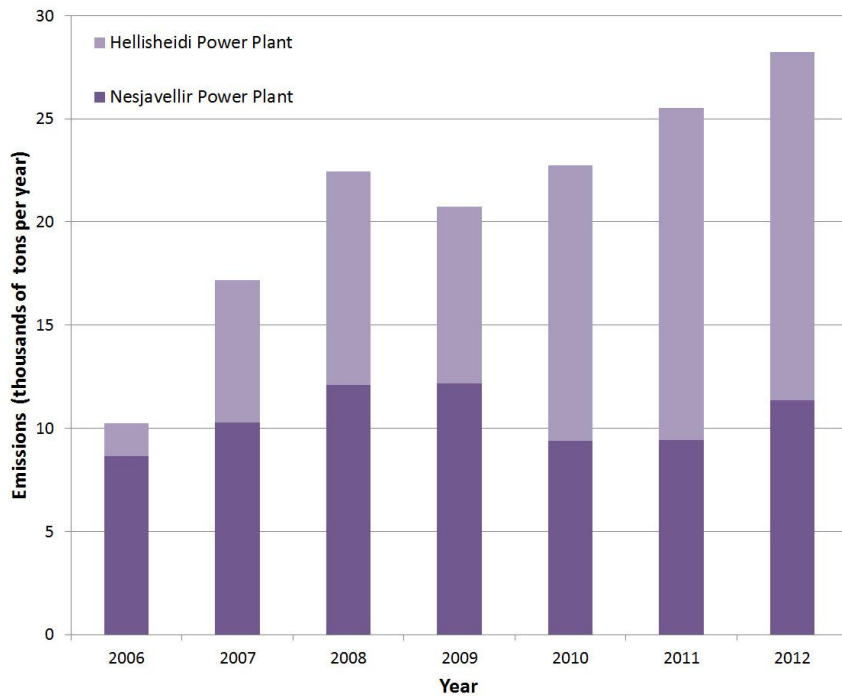
Figure 1–4. Emissions from Nesjavellir and Hellisheidi Power Plants from 2006-2012 (Thorarinsdottir and Sigurdardottir, 2013). Emission from the Hellisheidi Power Plant in 2006 was calculated from energy production.

1.2.3 Hydrogen Sulfide

Hydrogen sulfide (H_2S, CAS No. 7783-06-4) is a colorless flammable gas, with a molecular mass of 34.08 g/mol, which is about 18% heavier than dry air (US EPA, 2003). H_2S has a characteristic odor of rotten eggs with an odor threshold that varies depending on each individual. The geometric mean odor threshold is 11 µg/m^3 but odor nuisance can become a public problem with a concentration as low as 7 µg/m^3 for half-hour concentrations (WHO, 2000; 2003). Short-term inhalation exposure of high concentrations of H_2S causes health effects in many systems of the body and few breaths at 700,000 µg/m^3 can be fatal (WHO, 2013). Long-term, low-level health effects on the population of Rotorua City, New Zealand, have been extensively studied. Bates et al. (2002) found exposure-response trends particularly for nervous system diseases, but also for respiratory and cardiovascular diseases. However, in a more recent study, Bates et al. (2013) found no evidence of increased asthma risk. In fact, their results indicated reduced risk of asthma and its symptoms, though more research is needed to confirm such effect. Also in a recent study, Reed et al. (2014) studied a range of cognitive functions: attention, memory, psychomotor speed, fine motor function and mood, where no evidence was found of harmful effects of H_2S exposure. Carlsen et al. (2012) studied the associations of daily ambient levels of H_2S and other air pollutants to the use of drugs for obstructive pulmonary diseases in adults in Iceland's capital area. The results showed weak association between the dispensing of the drugs to the H_2S ambient air levels. It was reported that the weak association could be confounded by unevaluated variables and that further studies are needed.

In the atmosphere H_2S can be oxidized to SO_2 by the OH radical via the following reactions (Wallace and Hobbs, 2006),

$$H_2S + OH \rightarrow HS + H_2O \tag{1.1}$$

$$HS + O_3 \rightarrow HSO + O_2 \tag{1.2}$$

$$HS + NO_2 \rightarrow HSO + NO \tag{1.3}$$

$$HSO + O_3 \rightarrow HSO_2 + O_2 \tag{1.4}$$

$$HSO_2 + O_2 \rightarrow HO_2 + SO_2 \tag{1.5}$$
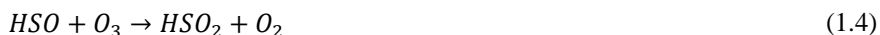
The hydrogen atom abstraction has also been reported to take place via the nitrate radical (Finlaysson-Pitts and Pitts, 2000),

$$H_2S + NO_3 \rightarrow HS + HNO_3 \tag{1.6}$$
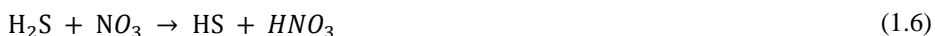
H_2S is a weak diprotic acid and dissociates via the following reactions (Arnorsson et al, 1982),
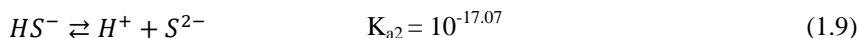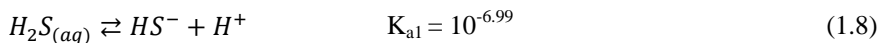
$$H_2S_{(g)} \rightleftarrows H_2S_{(aq)} \tag{1.7}$$

$$H_2S_{(aq)} \rightleftarrows HS^- + H^+ \qquad K_{a1} = 10^{-6.99} \tag{1.8}$$

$$HS^- \rightleftarrows H^+ + S^{2-} \qquad K_{a2} = 10^{-17.07} \tag{1.9}$$

where $H_2S_{(g)}$ and $H_2S_{(aq)}$ refer to H_2S in the gas and aqueous phase respectively, K_{a1} and K_{a2} are the first and second acid dissociation constants. The reactivity of aqueous H_2S is largely dependent on the pH of the solution. Ball and Liss (1983) reported that at pH 5 to 6, H_2S behaved like an unreactive gas of moderate solubility but as the water pH was raised the magnitude of H_2S dissolved increased.

1.2.4 Regulatory Environment in Iceland

The World Health Organization (WHO) gives air quality guidelines for public health protection. The guideline value given for H_2S is 150 μg/m^3 for 24-hour average (WHO, 2000). WHO also states that half-hour averages of 7 μg/m^3 will cause odor annoyance. Limits for H_2S concentration in the ambient air vary between countries (and states), both the limit value and its reference time. For example, India uses the guideline set by WHO (Bhawan and Nagar, 2000) but California has a 1-hour limit of 42 μg/m^3 (Collins and Lewis, 2000). A more thorough overview of different health limits can be found in Bjornsson and Thorsteinsson (2013).

In 2010, a regulation on hydrogen sulfide concentration in ambient air was published by the Ministry for the Environment and Natural Resources in Iceland (2010). A health limit was set at 50 μg/m^3 for a running 24-hour average, not to be exceeded more than five times per year until July 1, 2014, after which the limit should never be exceeded. A yearly average health limit was set at 5 μg/m^3. A concentration over 150 μg/m^3 for three hours or more should be reported and the public notified. After July 1, 2014, concentrations over 50 μg/m^3 for three hours or more shall be notified. Violations of the provisions of these regulations are subject to fines if they are committed intentionally or through gross negligence. In case of serious or repeated intentional violation the responsible party shall furthermore be liable to imprisonment for up to four years.

Occupational exposure of H_2S in Iceland is set by the Ministry of Welfare (2012) as 7 mg/m^3 (7,000 μg/m^3) for an 8-hour work day and 14 mg/m^3 (14,000 μg/m^3) for 15 minutes. Note that this unit is 1000 times larger than the ambient air health limit.

Table 1–1. Ambient air health and occupational limits in Iceland. Volume based on the temperature of 293 K and a pressure of 101.3 kPa.

Limit	Value (μg/m^3)	Reference time	Regulation no.
Health	50	24-h running average	514/2010
Health	5	1 year	514/2010
Occupational	7,000	8-h	1296/2012
Occupational	14,000	15 min	1296/2012

1.2.5 Status of H2S Emissions and Mitigating Measures in Iceland

Currently there are six geothermal power plants producing electricity in Iceland with a total of 661 MW produced and a total H_2S emission of about 36,400 tons per year. New power plants and enlargements of current power plants are underway with an estimated production increase of about 355 MW, increasing H_2S emissions by about 19,000 tons per year (Juliusson, 2013).

H_2S from geothermal power production has until now been emitted into the atmosphere unhindered. With increased H_2S concentration in the air in Reykjavik following the opening

of the Hellisheidi Power Plant mitigating measures came into more focus. Conventional proven industrial solutions for mitigating the emissions were shown to be unfavorable for Icelandic conditions, so more unconventional solutions were sought. Three experimental pilot scale projects have been in planning and operation since 2006 aimed at dissolving both CO_2 and H_2S gas in effluent waters and re-injecting them back into the ground. The aim is to sequester the dissolved gases in minerals in the basaltic bedrock. Industrial scale of the injection is planned for 2014 when about 15% of the H_2S gas from the Hellisheidi Power Plant will be dissolved in condensed water and re-injected into the geothermal system. Further development of the project will be planned based on the results of that injection (Gunnarsson et al., 2013).

1.3 Objectives

The objective of this doctoral research is to analyze the environmental factors that influence the atmospheric concentration and distribution of H_2S. The research is intended to reveal how meteorological and terrain factors influence the atmospheric concentration and distribution of H_2S and furthermore, to identify the near field sinks of H_2S from the Nesjavellir and Hellisheidi Power Plants in southwest Iceland. Extensive field measurements of atmospheric H_2S concentration were carried out up to a 30 km distance from the source as well as precipitation sampling. Comprehensive data collection was made together with analyses of the interaction of H_2S and the environment based on standard environmental processes to determine the depletion of H_2S from the atmosphere. The results will increase the understanding of the overall fate of atmospheric H_2S, which is important in evaluating its environmental impact and in assessing the need for mitigating its emission.

 The main research questions are:

1. How do meteorological factors affect the atmospheric H_2S concentration?

2. How is H_2S distribution affected by meteorological and terrain factors? How does modeled plume distribution compare to measurements?

3. What are the possible sinks of H_2S in natural conditions? To what extent is H_2S depleted from the atmosphere near field of the power plants?

1.4 Methods and data

1.4.1 Measurements

A 12-month measurement program was carried out in 2009 in order to determine the areal extent and strength of H_2S gas plumes in various weather conditions. H_2S measurements were performed along the major highways, at different spatial intervals between events, downstream of the plumes. Measurements were made for 3-4 days in a row each month for 1-3 hours each day. In total, measurements were conducted on 44 days (see dates and locations in Appendix A). Measurements were made with a handheld measuring instrument, Jerome 631-X (Arizona Instruments, USA) (Figure 1–5), which includes a thin gold film which undergoes an increase in electrical resistance proportional to the mass of H_2S present. The instrument has a detection range of 4-7100 $\mu g/m^3$ and a ± 4 $\mu g/m^3$ accuracy for the measurement range of this research. Two nearly instantaneous (~20 sec) measurements were

made at each location and the average concentration was converted using the conversion factor of 1 ppm = 1420 μg/m^3 H$_2$S (at 20° and 1 atm).
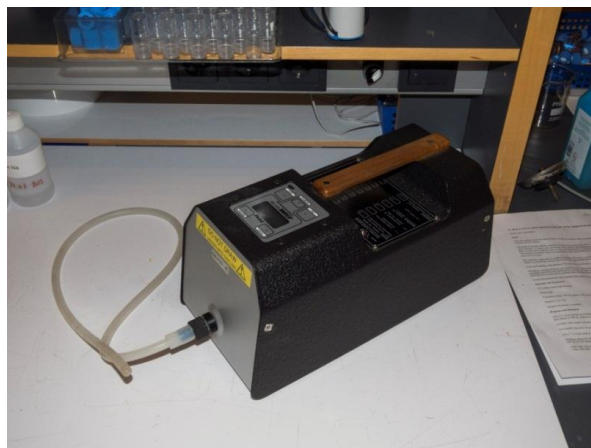
Figure 1–5. The Jerome 631-X measuring instrument.

Precipitation was collected at eight sample sites at about 10 to 30 km distance from the power plants over eight 24-hour periods in 2009. The sulfide and chloride content of the samples was measured at Iceland Geosurvey's chemical lab to analyze the sulfide content in the precipitation downwind from the power plants. The analyses did not find any increase. As some of the sampling sites were near a main road, SO$_2$ from exhaust is expected to have affected the results. It was therefore concluded that the sulfate measurements in precipitation did not give any conclusive results.

In 2010 isotope measurements were made in 9 precipitation samples taken in a line extending about 16 km northwest from the Hellisheidi Power Plant. As the sulfur content of the precipitation was low and a minimum amount was needed for the analysis, the sample size had to be large and 1 gallon bottles were therefore used for the collection. The bottles had to be out for a long time in order to be filled and ended up being out for about two months with some of them freezing in the ground with the samples. The long collection time and having some of the precipitation falling as snow resulted in large uncertainties in the measurements.

In 2010 isotope measurements were made in 6 soil samples taken at three sampling sites (top samples and at about 10 cm depth) in a line extending about 16 km northwest from the Hellisheidi Power Plant. The soil samples were damp but were dried before measurement; the isotope signal of the water was thus included in the bulk soil. The results did not show correlation with distance from the source. One of the sampling sites was located by a road and was likely affected by traffic exhaust. The results were determined to be inconclusive.

In addition to measurements specifically made for the research, data from various companies and agencies were used in the study, which have performed measurements of H$_2$S and other sulfur chemicals for various purposes unrelated to this study.

H$_2$S concentration data were obtained from airborne chemical measuring stations. Currently nine measuring stations measuring H$_2$S are operational in the study area. Four are in the capital area, one in the town of Hveragerdi, one movable station owned by the Environmental

Agency of Iceland and one at each power plant. In this research data were used from the Grensasvegur Measuring Station in Reykjavik (Station G, Figure 1–1 and Figure 1–6), provided by the Department of the Environment in the City of Reykjavik and the Environmental Agency of Iceland, the Mosfellsbaer Town Measuring Station (Station MT, Figure 1–1), data provided by the Environmental Agency of Iceland and the Kopavogur Town Measuring Station (Station DH, Figure 1–1), data provided by the Environmental and Health Protection Department of Hafnafjordur, Kopavogur and Gardabaer. Note that the Kopavogur Town Station is portable and data from more than one location were used for different analyses in the study.

Figure 1–6. The Grensasvegur Measuring Station

Measurements of various chemicals, including sulfur, have been made in precipitation and particulate matter at the Irafoss Hydropower Plant (Station I, Figure 1–1) since 1980. Samples are collected 24-hours at a time. Measurements were provided by the Icelandic Meteorological Office.

In 2008 measurements were made on the sulfur content of Woolly Fringe-moss (WF-moss, Racomitrium lanuginosum) in the vicinity of the Nesjavellir and Hellisheidi Power Plants by EFLA Consulting Engineers for Reykjavik Energy (Bragason and Yngvadottir, 2009). Comparison samples were taken at Mt. Blafjoll.

Measurements of total sulfur from Lake Thingvallavatn were provided by the Faculty of Earth Sciences at the University of Iceland (Eiriksdottir and Gislason, 2013).

Meteorological data from weather stations at the Bustadarvegur Station in Reykjavik (Station BV, Figure 1–1), Middalsheidi Heath (Station M, Figure 1–1), Skardsmyrarfjall Mountain, Hellisskard Pass, Mt. Blafjoll (Station B, Figure 1–1) and upper air data measured at Keflavik airport were obtained from the Icelandic Meteorological Office. Weather data from the Mosfellsbaer Town Measuring Station (Station MT) were obtained from the Environment Agency of Iceland and from Hellisheidi Heath (Station H, Figure 1–1) from the Icelandic Road Administration.

1.4.2 Models

The American Meteorological Society – Environmental Protection Agency Regulatory model (AERMOD) was used to calculate plume dispersion. AERMOD is a steady-state Gaussian plume model with a pre-processor, AERMET, for calculating boundary layer parameters using meteorological data (wind speed, wind direction, temperature, ceiling height and cloud cover) and surface characteristics (albedo, surface roughness and Bowen ratio). Air sounding (rawinsonde) is required in order to calculate the convective mixing height. Boundary layer parameters calculated are: friction velocity, Monin-Obukhov length, convective velocity scale, temperature scale, mixing height, and surface heat flux. These parameters are then passed to AERMOD which calculates vertical profiles of wind speed, lateral and vertical turbulent fluctuations, potential temperature gradient and potential temperature (US EPA, 2004a). The distribution in the stable boundary layer (SBL) differs from the distribution in the convective boundary layer (CBL) as the concentration distribution is assumed to be Gaussian in both the vertical and horizontal in the SBL but the vertical distribution is described with a bi-Gaussian probability density function in the CBL. AERMOD tracks any plume mass that penetrates into the elevated stable layer and, if appropriate, allows it to re-enter the boundary layer (US EPA, 2004a). Another pre-processor, AERMAP, uses gridded terrain data to create receptor grids and calculate a terrain height scale, which information is passed to AERMOD. In complex terrain AERMOD models the plume as either impacting and/or following the terrain. Multiple receptor networks in a single run are an option e.g. for a denser grid over a certain location. There is an option of using different types of sources, including point, volume and area sources. Emission rates can be constant or vary during the modeling period (US EPA, 2004b). Output options for AERMOD are: summaries of high values by receptor; summaries of overall maximum values and tables of concurrent values summarized by receptor for each day of data processed (US EPA, 2004b). The main limitations of the model are that the model does not take into account that H_2S is heavier than air, it does not take into account variable wind direction in space nor with a smaller time resolution than 1 hour, and it does not model changes in wind direction or plume direction because of terrain obstruction unless there is a temperature inversion lower than the topography.

The depletion of H_2S from the atmosphere was estimated by using an idealized box model approach. Neglecting spatial variability and differences in surface types, the H_2S concentration was assumed to be homogeneous in a volume with the horizontal area of a standard Gaussian plume (Figure 1–7), where the source was assumed to be at the center of mass of the combined emissions. The plume's horizontal and vertical dimensions were found by applying a Gaussian plume model in neutral air, over a 35 km distance. The plume was assumed to expand from the source to $4\sigma_y$, 6.57 km, yielding an areal extent of $1.14 \cdot 10^8$ m^2. The plume height was assumed to be represented by $2\sigma_z$ at 35 km or 544 m over the whole area. The mean wind speed at Station H was 7 m/s, yielding 83 minutes of traveling time out of the area, during which 4.5 tons of H_2S were discharged into the atmosphere on average in 2012. Assuming homogeneous distribution within the plume volume, this yielded a concentration of C_{air}=72 µg/m^3.
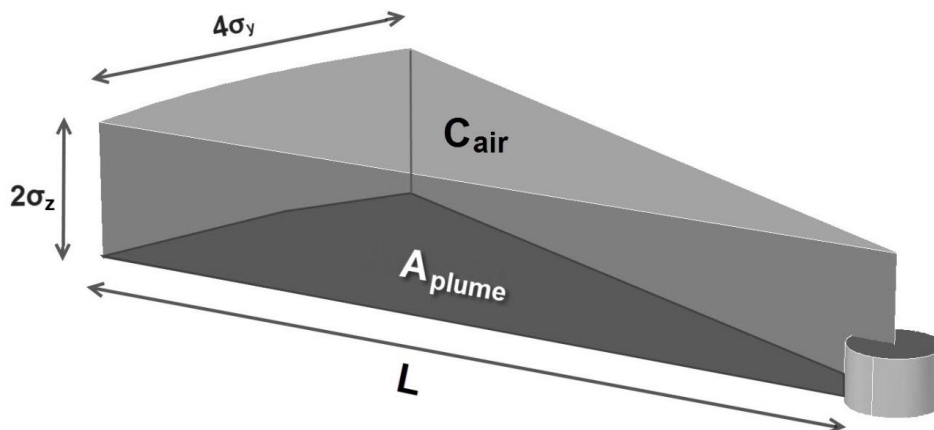
Figure 1–7. A schematic of the control box for the Gaussian plume.

1.5 Literature Review

Chapters 2-4 contain literature discussion corresponding to the subjects discussed in each of the chapters. This section contains additional brief discussion of the literature used and additional references that were used in the dissertation work but were not included in the articles, either due to length restrictions or that they were not directly relevant.

Atmospheric hydrogen sulfide can be a local problem surrounding its various sources. Measurements have been made surrounding geothermal and volcanic areas in Greece (D'Alessandro et al., 2008, Vasilakos et al., 2005), Italy (Aiuppa et al, 2007) and Iceland (Kristmannsdottir et al., 2000) also in association with geothermal power plants in Mexico (Peralta et al., 2013), Kenya (Marani et al., 2000) and Iceland (Thorsteinsson et al., 2013, Kristmannsdottir et al., 2000). Hydrogen sulfide has been studied at urban areas located on geothermal fields both in Taipei, Taiwan (Lin et al., 2010, Chen et al., 2003) and in Rotorua, New Zealand (Horwell et al., 2005). H_2S monitoring surrounding other sources have been made, e.g. at urban traffic sites in Greece (Kouridis et al., 2008) and Korea (Shon and Kim, 2006), at waste water treatment plants in Greece (Latos et al., 2011), at landfill areas in Korea (Song et al., 2007, Shon et al., 2005, Kim et al., 2006, Kim et al., 2005), and sewage treatment plants in Norway (Sostrand, 2000) and Kuwaid (Al-Shammiri, 2004).

The effects of meteorological factors on H_2S concentration have been studied to some extent. Thorsteinsson et al. (2013) found that high levels of H_2S pollution in Reykjavik occurred during a very limited range of weather conditions. It was indicated by Olafsdottir et al. (2010) that H_2S was more widely distributed in lower wind speeds. Decrease in H_2S concentration has been reported during and following precipitation (Kristmannsdottir et al., 2000, Thorsteinsson et al., 2013). However, Susaya et al. (2011) found that airborne H_2S showed positive correlations with relative humidity, dew point and rainfall. Oxidation of H_2S depends

on radiation and has been studied on numerous occasions (D'Alessandro et al., 2008, Shon et al., 2005, Shon and Kim, 2006, Spedding and Cope 1984).

Laboratory experiments regarding the reactions of hydrogen sulfide have been made both in the gas and water phase. The oxidation of H_2S by the OH radical was studied by Cox and Sandals (1974) who reported that it was a major loss process for H_2S in the atmosphere. Cox and Sheppard (1980) studied the rate constant for the oxidation. Dlugokencky and Howard (1988) studied the oxidation of H_2S with the NO_3 radical. Scaldaferri and Pimentel (2009) used chemical calculations to study the reactions of H_2S and NO_3 both in the gas and water phase.

The exchange of H_2S between water and air has been studied, both in the laboratory (Balls and Liss, 1983, Santos et al., 2012, Yongsiri et al., 2004) and by modeling (Blunden et al., 2008). The solubility of H_2S has been studied by Fernandez-Prini et al. (2003) and Lee and Mather (1977). H_2S is a weak diprotic acid and dissociates in water. Dissolved H_2S can be oxidized in the presence of absorbed oxygen to form elemental sulfur, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}, which kinetics have been studied by Chen and Morris (1972) and O'Brien and Birkner (1977) and in aerosols by Brown and Webster (1994).

The lifetime of H_2S in the atmosphere also has been studied. Pham et al. (1995) estimated the global lifetime of H_2S regarding the tropospheric sulfur cycle while Bottenheim and Strausz (1980) studied the lifetime in clean air at 55°N latitude where the main sink estimated was oxidation with OH radical. Watts (2000) studied the mass budgets of hydrogen sulfide with the oxidation being the only sink. Other sinks have been estimated in the vicinity of sources and in laboratory research. The impacts of H_2S on vegetation have been studied on various occasions (Bartiromo et al., 2012, Loppi et al., 2006, Tretiach and Ganis, 1999, Bussotti et al., 1997, Cope and Spedding, 1982). The capacity of soil for sorption of H_2S has been studied in laboratory experiments by Smith et al. (1974) and Cihacek and Bremner (1990). Dry deposition of H_2S has also been studied (Judeikis and Wren, 1977).

The AERMOD model has been used in air quality modeling for various occasions (Heckel and LeMasters, 2011, Venkatram et al., 2009, Zhang et al., 2008). It has been used by students in the United Nations University Geothermal Training Programme to model H_2S emissions in the study area (Khoirunissa, 2011, Pineda, 2007). Limitations of the model have been found regarding modeling concentrations in complex terrain over 5 km from the source (Seangkiatyuth et al., 2011), also the model has been reported to perform better in stable wind direction and speed (Peralta et al., 2013).

1.6 Organization of dissertation

The dissertation consists of six chapters.

- Chapter 1 describes the motivation of the research, gives the background of the study area, of hydrogen sulfide emission from the power plants, the characteristics of H_2S, the regulatory environment in Iceland and the status of H_2S mitigating measures in Iceland. Furthermore it describes the data collection for the research, shows a review of the literature on H_2S, describes the main objectives of the study and lists the research questions.

- Chapter 2 describes analysis of the impacts of meteorological factors on H_2S concentration in the city of Reykjavik (journal paper 1).

- Chapter 3 describes the measurements, and their analysis, of H_2S distribution around the geothermal power plants (journal paper 2).

- Chapter 4 presents the identification of H_2S sinks and their quantification (journal paper 3, submitted).

- Chapter 5 presents a summary of the overall fate of H_2S.

- Chapter 6, Conclusions, discusses and summarizes the main findings and provides recommendations for future research on the subject.

2 Impacts of meteorological factors on hydrogen sulfide concentration downwind of geothermal power plants

Abstract

Hydrogen sulfide (H_2S) concentration in the city of Reykjavik, downwind of geothermal power plants has been studied with respect to meteorological factors as the odor and other effects are starting to become a nuisance. The main sources of H_2S in Reykjavik City were the Nesjavellir and Hellisheidi Geothermal Power Plants, which are both less than 35 km east of the city. The H_2S concentration in Reykjavik was correlated with the H_2S emissions from the power plants but was also heavily influenced by weather conditions. The results showed that the H_2S concentration at the Grensasvegur Measuring Station was elevated when the wind direction was from 54° to 125°, especially when the wind direction was stable for several hours. The H_2S concentration in Reykjavik was highest when the wind speed in the city was between 1.5-4 m/s, and decreased rapidly with higher wind speeds. H_2S concentration showed correlation with the air temperature in the city below 3°C and the concentration rose as the temperature decreased, and the air became more stable and was highest when there was a temperature inversion. The quantitative effects of precipitation on H_2S concentration could not be determined in this study although the events with the highest H_2S concentration occurred when there was no precipitation. The results showed that favorable conditions for high H_2S events can be expected in Reykjavik 2-6 times per year and events with H_2S concentration exceeding 50 µg/m^3 might be expected on average about 2 times per year. The results also indicate that events with high H_2S concentration can be predicted by using a current weather forecast.

Keywords: Hydrogen sulfide; Geothermal emission; Wind; Temperature; Air stability

2.1 Introduction

Geothermal energy is a clean and sustainable energy source which is being increasingly developed as part of an effort to decrease reliance on carbon based energy in countries that have geothermal resources, including Iceland. Nevertheless, its development has some environmental impact, with chemical air pollution being one of the most important. Carbon dioxide and hydrogen sulfide are of primary concern, but methane, mercury, radon, ammonia and boron can also cause problems (Kristmannsdottir and Armannsson, 2003). Gaseous sulfuric compounds from geothermal areas exist in the form of hydrogen sulfide (H_2S).

Following the development of a geothermal area the H_2S is usually emitted at a higher rate into the environment than before development (Kristmannsdottir and Armannsson, 2003). Hydrogen sulfide has a characteristic smell and can be a malodor-nuisance at levels far below those that cause health hazards. A half-hour concentration of over 7 $\mu g/m^3$ is likely to be perceived as a nuisance among the persons exposed (WHO, 2000). At about 300,000 $\mu g/m^3$ the sense of smell is lost, and at 450,000 – 750,000 $\mu g/m^3$ pulmonary edema can occur, with the risk of death (WHO, 2000).

Geothermal utilization has been increasing in South West Iceland for the past two decades due to construction and operation of two geothermal power plants. Odor has become more of a nuisance in Reykjavik City since the second plant, Hellisheidi Power Plant, began production in 2006. A mean value of 50 $\mu g/m^3$ in a 24-hour period was set as health limit by the Ministry for the Environment and Natural Recourses in 2010 (Regulation no. 514/2010 for hydrogen sulfide concentration in atmosphere, 2010). This limit is not to be exceeded more than five times per year until June 1st, 2014, after which the health limit should not be exceeded. The World Health Organization (WHO, 2000) has published a guideline value of 150 $\mu g/m^3$ as the mean value for 24 hours.

Hydrogen sulfide can be an offensive odorant in urban areas and it can have various sources for example: traffic (Kourtidis et al., 2008), landfill sites (Kim et al, 2006, Kim et al., 2005), sewage treatment plants (Al-Shammiri, 2004, Sostrand et al., 2000), stormwater catch basins (Kabir et al. 2010) and fishery industrial complexes (Seo et al., 2011). It can also have natural sources such as lake sediments (Susaya et al., 2011b) or geothermal areas (Horwell et al., 2005, Kristmannsdottir et al., 2000). Natural emitting hydrogen sulfide can have a significant effect on urban air quality (Lin et al., 2010).

Research regarding H_2S concentration in the atmosphere and its dependence to weather indicate oxidation if conditions are favorable. The H_2S concentration has been reported to be lower during summer than winter both in naturally emitted sites such as the geothermal area of Sousaki, Greece (D'Alessandro et al., 2009) and in urban areas such as Thessaloniki, Greece (Kourtidis et al., 2008) where the main source was traffic, indicating oxidation. Researches regarding sulfur gas in the Nesjavellir area however have indicated that oxidation of H_2S to SO_2 within the area is at least slow if any (Kristmannsdottir et al., 2000, Edner et al., 1991). Thorsteinsson et al. (2012) and Susaya et al. (2011a) reported that H_2S concentration was higher at night than in the day time. Thorsteinsson et al. (2012) also found that levels of H_2S exceeding 50 $\mu g/m^3$ in Reykjavik occurred during a limited range of weather conditions. H_2S was found to be high during low temperatures and low wind conditions, correlated with high atmospheric pressure and often connected to the Greenland high, which typically results in slow wind. Kristmannsdottir et al. (2000) reported that H_2S concentration was low during precipitation. Susaya et al. (2011a) reported that the concentration of H_2S exhibited direct correlations with temperature, relative humidity, dew point and rainfall, while maintaining inverse correlations with pressure, wind speed and radiation in the city of Ansan, South Korea.

In the present paper the influence of different weather conditions on transport of hydrogen sulfide from geothermal power plants in the vicinity of Reykjavik on concentration in the city was analyzed. The analysis provides a base for predicting H_2S concentration for different weather conditions and thereby the likelihood of conditions that may exceed the regulatory requirement for H_2S concentration and also the possible effect of increased emission.

2.2 Methods

There are two geothermal power plants in the vicinity of the capital of Reykjavik. The Nesjavellir Power Plant is about 25 km from the easternmost part of the city and about 35 km from the city center. Hot water production started in 1990 and electricity production in 1998, with a current hot water production of 300 MW and electricity production of 120 MW. The Nesjavellir Power Plant is located at 97° (clockwise from North) from the Grensasvegur Measuring Station, as shown in Figure 2–1. The Hellisheidi Power Plant is about 18 km from the southeastern most part of Reykjavik and about 28 km from the city center. Production was begun in October 2006. At first electricity production amounted to 90 MW, but in 2007 a 33 MW low-pressure turbine was installed. In the fall of 2008 the electricity production was expanded with two 40-45 MW turbine units which in turn increased hydrogen sulfide emission. The combined H_2S emissions from these power plants are shown in Table 2–2. Note that emissions from the Hellisheidi Power Plant in 2006 have been calculated from energy production data as a collecting system had not been installed. The electricity production expanded further in 2011, from 213 MW to 303 MW, but the present data analysis extends only to the end of 2010. Geothermal gas was emitted from the top of the power plant at first, but in 2007 the emissions were moved to the cooling tower, which is more effective in dispersing the H_2S gas. The Hellisheidi Power Plant is located at 116° (clockwise from North) from the Grensasvegur Measuring Station, as shown in Figure 2–1.
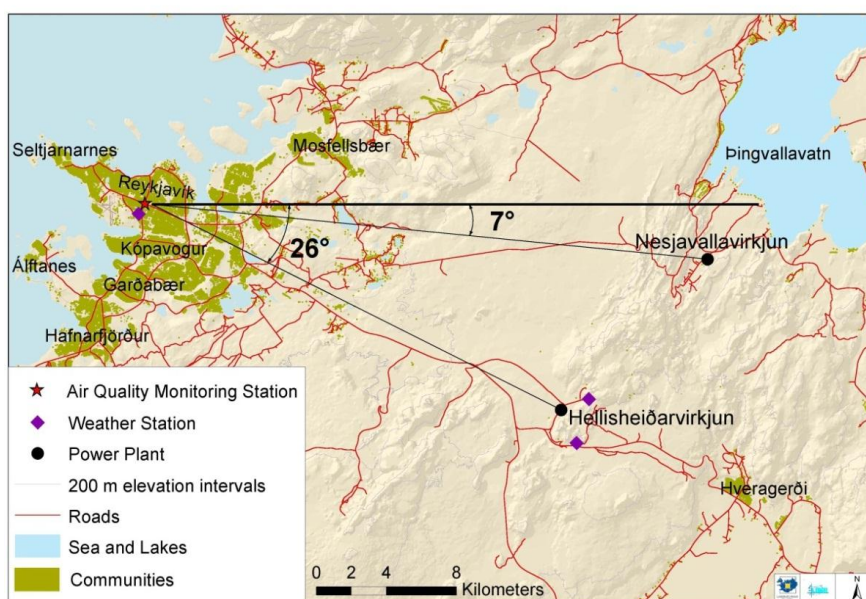
Figure 2–1. Map of the area showing Grensasvegur measuring station (★), Reykjavik Weather Station (◆), Skardsmyrarfjall Weather Station (◆), Hellisskard Pass Weather Station (◆), Hellisheidi Power Plant (●) and Nesjavellir Power Plant (●). A horizontal line, located in direction 90° clockwise from North from Grensasvegur measuring station (thick line), and lines from Grensasvegur measuring station towards Nesjavellir and Hellisheidi Power Plants (thin lines) located 7° and 26° respectively from horizontal.

A hydrogen sulfide measuring device was installed at the Grensasvegur Measuring Station in February 2006 by the Reykjavik Environmental Department. This location was chosen as

there was a measuring station that measured air pollutants, mainly from traffic. Since then other measuring devices have been installed to monitor the hydrogen sulfide in the atmosphere in the capital area but no other measuring device was installed before the Hellisheidi Power Plant started production. The hydrogen sulfide data used in this analysis are from the Grensasvegur Measuring Station in Reykjavik. The measurements were made with a HORIBA APSA-360A H_2S analyzer. The instrument uses ultra violet fluorescence method (UVF method) to measure 30-minute averages of SO_2 and has a built-in H_2S converter which oxidizes H_2S and other sulfur compounds to SO_2 for measurement. Since the device was first installed it has been calibrated and maintained at least once per year or when needed. The device was calibrated with 200 ppb SO_2 gas and checked with H_2S gas. In each calibration of the device there had been a slight drift, small at first but increasing somewhat over time; no records of the magnitude of the drift where made until 2010; therefore the data could not be fully corrected but based on calibration experience the actual span drift is about ±3% over 6 months. Accuracy of the calibration gas used, linearity uncertainty of the device, span and zero drift, add up to a maximum of 17% uncertainty. The measuring station was run by the municipality of Reykjavik until late 2009 when The Environment Agency of Iceland took over. In the ownership change the device was not calibrated when needed in June 2010 until October 29th 2010 and therefore the data from June 20th to October 29 were removed from the analysis.

There are gaps in the hydrogen sulfide data because of calibration and maintenance. The gaps have been from a few hours up to a few months, as listed in Table 2–1. Note that the measuring device was not installed until 2006 and the data used are from March 1st 2006.

Weather measurements used in this analysis are from The Icelandic Meteorological Office. Weather data used were measured at the Bustadarvegur Station in Reykjavik, at Skardsmyrarfjall Mountain and at the Hellisskard Pass (see Figure 2–1). Temperature measurements were 1 minute means and wind measurements were 10 minute means. Precipitation data showed accumulated precipitation over an hour in mm. Wind direction data were sampled at 10 min intervals and a running mean was taken for each measurement with 3 measurements before and 3 after each measurement. Wind direction can fluctuate considerably so a running mean was used to best represent the circumstances in the atmosphere for each event while the H_2S was moving from the source to the city of Reykjavik.

Table 2–1. Percent of hydrogen sulfide data missing from Grensasvegur Measuring Station for each quarter of the years 2006-2010.

Year	Q1 (%)	Q2 (%)	Q3 (%)	Q4 (%)
2006	66.7	0.2	0.8	1.5
2007	5.9	9.4	1.6	1.1
2008	4.1	64.0	62.7	5.8
2009	1.4	0.2	0.3	3.0
2010	5.8	17.2	100	35.8

2.3 Results and discussion

2.3.1 General concentration distribution

Table 2–2 summarizes the H_2S concentration in Reykjavik in 11 concentration increments. The first increment contains concentrations below the smell threshold, 7 µg/m^3, accounting for the majority of the measurements. As can be seen from the table the incidents dropped of quite rapidly as the concentration increased in all years. There is no distinct difference in the concentrations between the years and it does not seem to be correlated to the emission amounts. Relatively, the highest number of measurements with the lowest concentrations was in 2006 but that was only 10% more than in 2010 even though the total emission had more than doubled (note though that the emission data from the Hellisheidi Power Plant in 2006 was calculated from energy production and H_2S measurements could not be obtained from the power plant). Concentrations over 100 µg/m^3 were more common in 2009 and 2010 than in the other years even though the emissions were lower in 2009 than in 2008. The highest concentrations were measured in 2009. There were four measurements greater in 2007 and one in 2006 and 2008 than the greatest measurement in 2010 though concentration over a 100 µg/m^3 in general is more common in 2010 that in 2006-2008. The difference in concentration does not seem to have been correlated with an increase or decrease in emissions. This could partly have been because the cooling tower, where the gas exits, was not operational until 2007; before that the gas was emitted though the top of the power plant but the cooling tower is more effective in dispersing the H_2S gas.

Table 2–2 gives a general view of the frequency and magnitude of the hydrogen sulfide concentration in Reykjavik but it is important to realize that weather conditions significantly impact the concentration level. In the following subsection the data from 2006-2010 are analyzed with respect to weather conditions, that is, wind direction, wind speed, precipitation, temperature, air stability, and radiation.

Table 2–2. H₂S measurements from the Grensasvegur Measuring Station, 2006 - 2010, grouped by concentration.

H_2S ($\mu g/m^3$)	Incidences of measured H_2S (% of total)											Total H_2S emission* (tons/year)
	0-7	7-15	15-25	25-50	50-75	75-100	100-125	125-150	150-175	175-200	200-225	
2006	13563 (94.2%)	318 (2.2%)	165 (1.1%)	188 (1.3%)	98 (0.7%)	35 (0.2%)	18 (0.1%)	11 (0.1%)	5 (0.04%)	0 (0%)	0 (0%)	10153**
2007	14962 (89.4%)	969 (5.8%)	355 (2.1%)	287 (1.7%)	83 (0.5%)	43 (0.3%)	17 (0.1%)	9 (0.05%)	5 (0.03%)	2 (0.01%)	0 (0%)	17177
2008	10198 (88.2%)	621 (5.4%)	295 (2.6%)	306 (2.6%)	84 (0.7%)	33 (0.3%)	16 (0.1%)	13 (0.1%)	1 (0.01%)	1 (0.01%)	0 (0%)	22437
2009	15751 (91%)	717 (4.1)	361 (2.1%)	296 (1.7%)	94 (0.5%)	42 (0.2%)	31 (0.2%)	7 (0.04%)	4 (0.02%)	3 (0.02%)	2 (0.01%)	20756
2010	8858 (84.2%)	684 (6.5%)	393 (3.7%)	351 (3.3%)	123 (1.2%)	61 (0.6%)	33 (0.3%)	13 (0.1%)	3 (0.03%)	0 (0%)	0 (0%)	22724

* Arnalds and Sigurdardottir, 2011. **Calculated from energy production.

2.3.2 Wind direction

The downstream concentration of airborne hydrogen sulfide at a particular location will depend heavily on wind direction. The Nesjavellir and Hellisheidi Power Plants are located east of Reykjavik, at directions 97° and 116°, respectively, with east being 90°, as is marked in Figure 2–1. In Figure 2–2, the H_2S concentration at the Grensasvegur Measuring Station is shown as a function of wind direction at the Bustadarvegur Weather Station, where the 90 and 50 percentiles are marked with solid lines, calculated at 5°intervals. The figure shows that there is a strong correlation between concentration level and wind direction. As previously discussed, 7 µg/m^3 is the smell detection limit of H_2S as defined by WHO (WHO, 2000) and will be used as a reference value. Analysis of the data shows that the 90 percentile line exceeds 7 µg/m^3 between 54° and 125°, indicating the spread of the plume that reached the Grensasvegur Measuring Station from the Nesjavellir and Hellisheidi Power Plants. The middle of this range is at 89.5°, which is considerably more to the east than the mean direction to the power plants, 106.5°, indicating that topography pushes the plume to the north from the power plants as it moves toward Reykjavik. In the following analysis, easterly winds will be defined as winds between 54° and 125°.
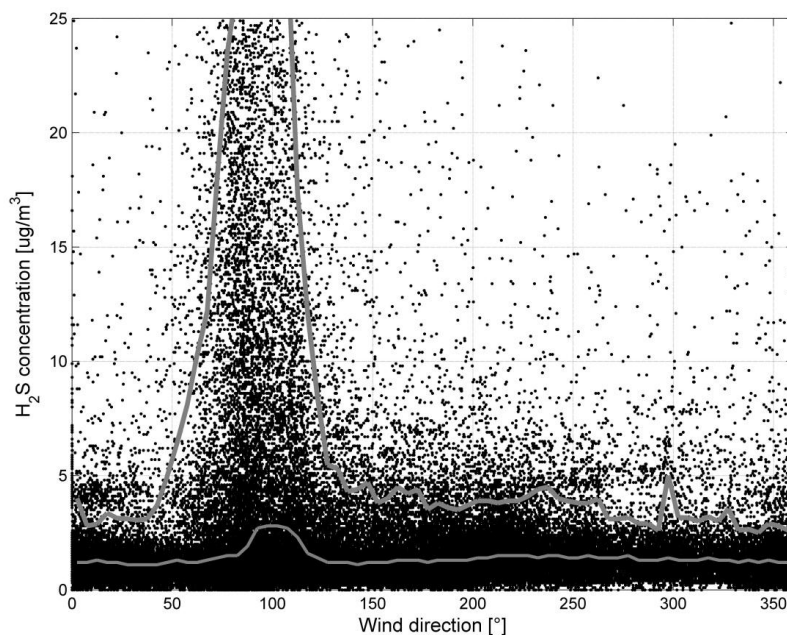
Figure 2–2. H_2S concentration at Grensasvegur Measuring Station plotted as a function of wind direction in Reykjavik from 2006 to 2010. The solid lines show 90 and 50 percentiles, calculated for 5° intervals.

2.3.3 Consecutive wind

In Figure 2–3 the mean concentration of hydrogen sulfide is shown as a function of consecutive hours of easterly winds in Reykjavik, referred to as an event in the subsequent discussion. The lines show the 50 and 90 percentile limits, calculated for five hour intervals. The 50 percentile line rises for events lasting from 2 to 13 hours and is then relatively steady between about 13 and 23 hours at about 6 μg/m^3. This indicates that events shorter than 10 hours tend to get reinforced as the number of consecutive hours of wind increases, up to about 20 hours. A similar trend is seen for the 90 percentiles. This indicates that the highest concentration can be expected in events extending between 10-20 hours, although sharp peaks can occur for shorter durations, as the figure shows. The 90 percentile line rises sharply at 48 hours due to one large event, measuring 82.4 μg/m3. For events lasting 52 hours or more there are no events with mean hydrogen sulfide concentration greater than 20 μg/m^3. The reason for low hydrogen sulfide concentrations in long events can be partly explained by other weather parameters having an effect on the concentration and not being as steady as the wind direction, e.g. low wind speeds are usually not observed for long events. One event lasted longer than 24 hours and exceeded the 24 hour health limit of 50 μg/m^3. Another event exceeded the health limit for 23 hours and one event lasted almost 50 hours and had a concentration just below the health limit.
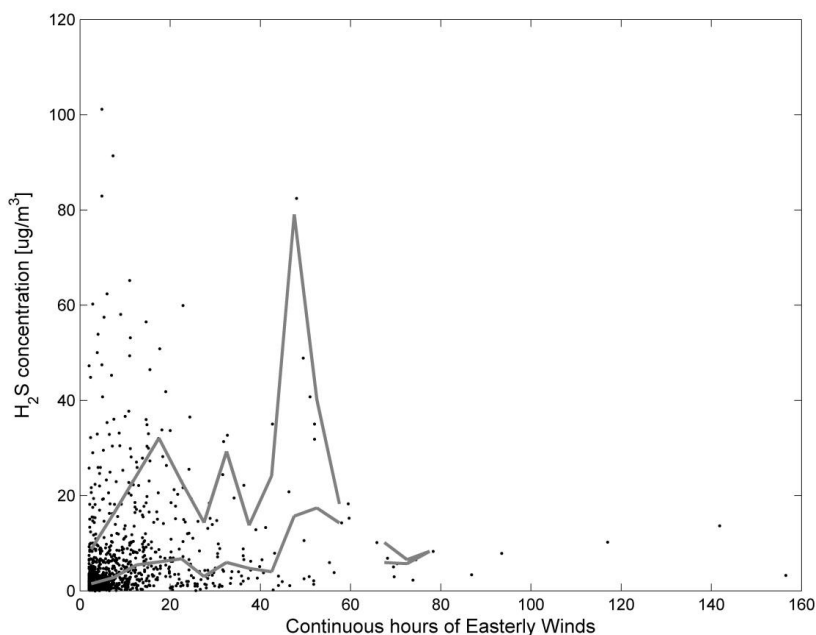
Figure 2–3. Mean concentration of hydrogen sulfide plotted as a function of consecutive hours of easterly winds in Reykjavik 2006 to 2010. The solid lines show 50 and 90 percentiles, calculated for five hour intervals.

2.3.4 Wind speed

In Figure 2–4, the mean concentration of hydrogen sulfide is plotted as a function of mean easterly wind speed for the same events of consecutive easterly winds as in Figure 2–3. The lines in the figure show 50, 90, and 95 percentile limits, calculated at 1 m/s intervals. The 50 percentile line is relatively steady and below 5 $\mu g/m^3$. The 90 percentile line starts off low for low wind speeds and reaches a maximum between 1.5-2.5 m/s at values exceeding 20 $\mu g/m^3$. The lower values for slower wind speeds reflect the fact that some wind is needed to transport the plume all the way to Reykjavik. The 90 percentile line drops off significantly and the 95 percentile line even more so at about 4 m/s. The 95 percentile line is significantly greater than the 90 percentile line for wind speeds lower than 4 m/s, indicating the tendency to large concentrations for the largest events. The reduction in number of large events with increasing wind speed indicates that it is unlikely to observe events with high mean H_2S concentrations when the mean wind speed is above about 4 m/s due to stronger dilution processes. Hence, the optimal wind speeds for high hydrogen sulfide concentration in Reykjavik are between approximately 1.5 and 4 m/s.
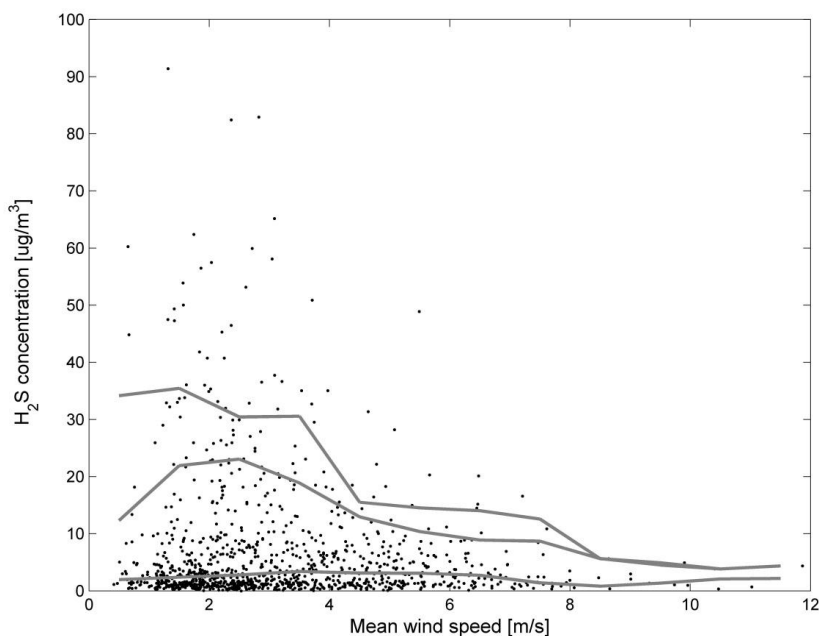
Figure 2–4. Mean concentration of hydrogen sulfide for events of consecutive easterly winds in Reykjavik plotted as a function of the mean wind speed in each event. The solid lines show 50, 90 and 95 percentile, calculated at 1 m/s intervals.

2.3.5 Temperature

In Figure 2–5 the mean concentration of hydrogen sulfide is plotted as a function of temperature for the same events of consecutive easterly winds as in Figure 2–3 and Figure 2–4. The lines in the figure show the 50 and 90 percentile lines, calculated at 2°C intervals. The 50 percentile line is relatively steady and below 5 μg/m3. The 90 percentile line is high for temperatures below zero, but drops off sharply as the temperature approaches zero. Above 3 °C the concentration seems to be independent of the temperature, where the 90 percentile line fluctuates around 10 μg/m^3. This indicates that the strong influence of temperature on H_2S concentration is likely due to air stability as air is more stable in colder weather. This is discussed in detail in Section 2.3.6.
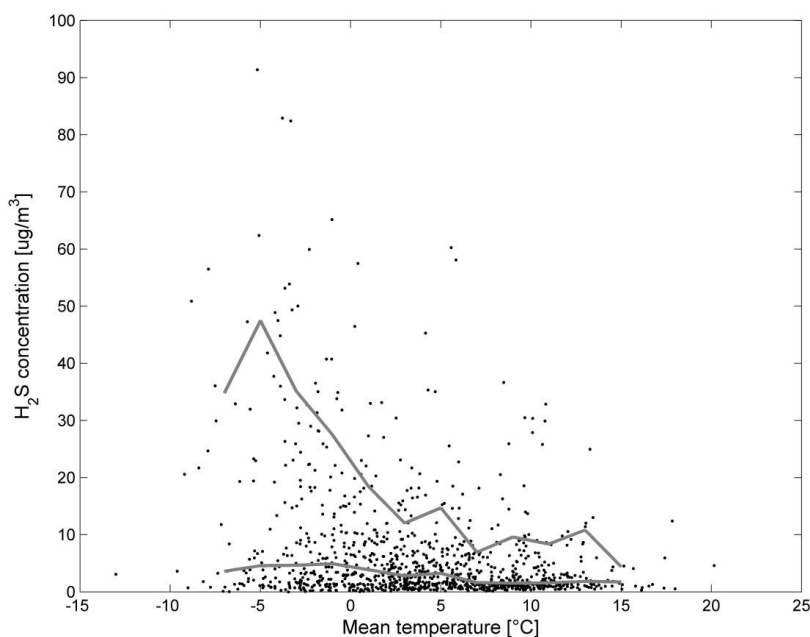
Figure 2–5. Mean concentration of hydrogen sulfide for events of consecutive easterly winds in Reykjavik plotted as a function of the mean temperature in each event. The solid lines show 50 and 90 percentiles, calculated at 2° C intervals.

2.3.6 Air stability

Two weather stations are located near the Hellisheidi Power Plant, that is, the Skardsmyrarfjall Mountain and the Hellisskard Pass stations, both marked in Figure 2–1. The height difference between the weather stations is 217 m, with Skardsmyrarfjall Mountain located higher; therefore the temperature difference between the two stations can be used as an indicator for air stability. In neutral air the temperature profile follows the adiabatic lapse rate leading to a temperature difference of about -2.2°C between the two stations.

In Figure 2–6 the mean concentration of hydrogen sulfide is plotted as a function of the mean temperature difference between Skardsmyrarfjall Mountain and Hellisskard Pass for the same

events of consecutive easterly winds as in Figure 2–3, Figure 2–4 and Figure 2–5. According to previous discussion, the horizontal axis can be divided into three zones: unstable air for a temperature difference smaller than -2.2 °C which marks neutral conditions; stable air for a temperature difference larger than about -2.2 °C; and inversion (very stable air) for a temperature difference larger than about zero. The lines in the figure show the 50 and 90 percentiles, calculated at 0.5°C intervals. The figure shows clearly that few events were recorded with a temperature difference smaller than -2.2°C, that is, with a temperature difference that indicates unstable air, thus indicating strong dilution processes. For these few events, both the 50 and 90 percentile lines show small H_2S values. For a temperature difference above -2.2°C, the air is stable and both the 50 and the 90 percentile lines rise steadily although the 50 percentile flattens at about -0.5°C. The 90 percentile line rises sharply with greater temperature differences, and the 50 percentile is at maximum value for a temperature difference above 1°C, both correlating strongly with the increasingly stable air. These results show clearly the importance of the air conditions for generation of high H_2S events. Due to the damping of vertical movement in stable air the chemicals are less diluted than in turbulent unstable air. A temperature inversion seals off the chemicals from above and the air flow becomes laminar. Due to the topography the cold air closest to the ground can easily slide down from the Hellisheidi Power Plant to the city of Reykjavik, causing elevated concentration.
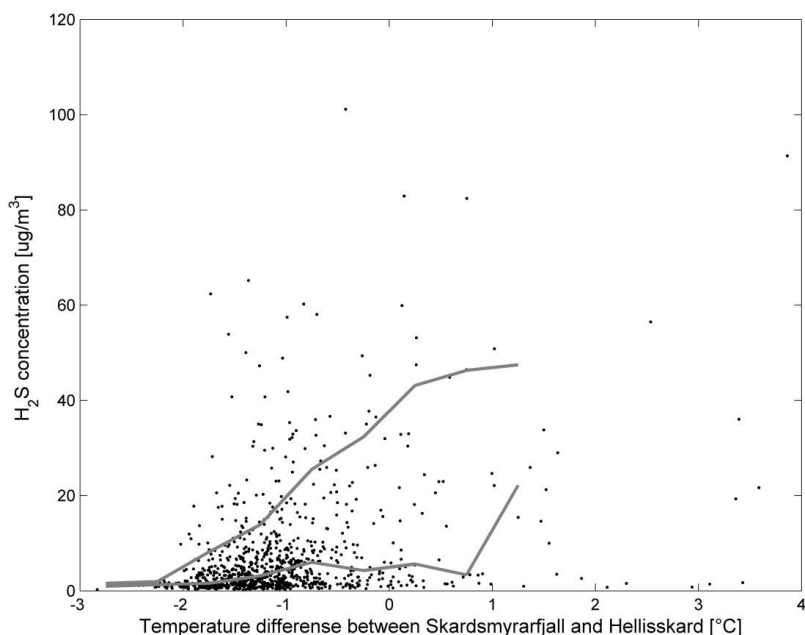
Figure 2–6. Mean concentration of hydrogen sulfide for events of consecutive easterly winds in Reykjavik plotted against the mean temperature difference between Skardsmyrarfjall Mountain and Hellisskard Pass in each event. The solid lines show 50 and 90 percentiles, calculated at 0.5 °C intervals.

2.3.7 Precipitation

In Figure 2–7 the mean concentration of hydrogen sulfide is plotted as a function of the mean precipitation for the same events of consecutive easterly winds as in Figure 2–3, Figure 2–4, Figure 2–5 and Figure 2–6. The lines show the 50 and 90 percentiles, calculated at 0.2 mm intervals. The figure shows that the highest concentrations are measured in events with little or no precipitation. The 90 percentile decreases as the precipitation increases to about 0.8 mm with a spike above 1 mm due to the few recorded events for that interval. The 50 percentile line is relatively stable and below 7 $\mu g/m^3$. However, the data set is somewhat misleading as precipitation is rare during easterly winds as 88% of the time with easterly winds there was no precipitation, and less than 1% of the time the precipitation was greater than 2 mm. Also, for long events there was usually only precipitation for a portion of the event. Hence, although the results seem to indicate some reduction of H_2S events from increased precipitation it is hard to draw a strong general conclusion from the data.
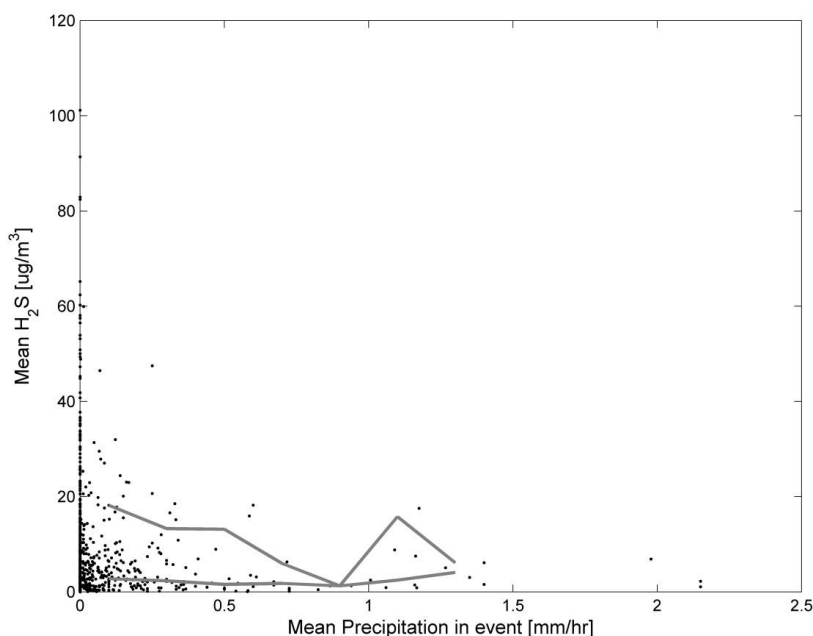
Figure 2–7. Mean concentration of hydrogen sulfide for events of consecutive easterly winds in Reykjavik plotted against the mean precipitation in Reykjavik in each event. The solid lines show 50 and 90 percentiles, calculated at 0.2 mm intervals.

2.3.8 Temperature vs. wind speed

Figure 2–8 shows temperature plotted as a function of wind speed when hydrogen sulfide is greater than 7 $\mu g/m^3$. The data points are grouped by color according to hydrogen sulfide concentration, a total of 7274 data points. The figure does not show any obvious correlation between temperature and wind except lower winds were more prevalent for lower temperatures. For the highest concentrations, 175-225 $\mu g/m^3$, the temperature was always

below zero with a wind speed between 2 and 4 m/s. For the concentration range 150-175 µg/m^3, the highest wind speed was 4.1 m/s, with only one measurement with a temperature greater than 0°C. For the concentration range 125-150 µg/m^3, the wind speed was lower than 4 m/s for 52 out of 54 measurements, but the temperature was more variable.   Similarly for the range 100-125 µg/m^3, 110 out of 114 events had a wind speed lower than 4 m/s (and all less than 5 m/s). Only the two lowest concentration categories, that is, 7-25 µg/m^3 and 25-50 µg/m^3, had measurements of wind speeds higher than 8 m/s and only the lowest one had a wind speed over 10 m/s. In Figure 2–8, the mean temperature and wind speed for each H$_2$S category is depicted as a star in the corresponding color. The stars show that, generally, increased H$_2$S concentration correlates with decreased temperature within a very narrow wind speed band, 2-3.5 m/s, with only the lowest concentration category exceeding 3 m/s. These results correspond with the results discussed in Sections 2.3.4 - 2.3.6.
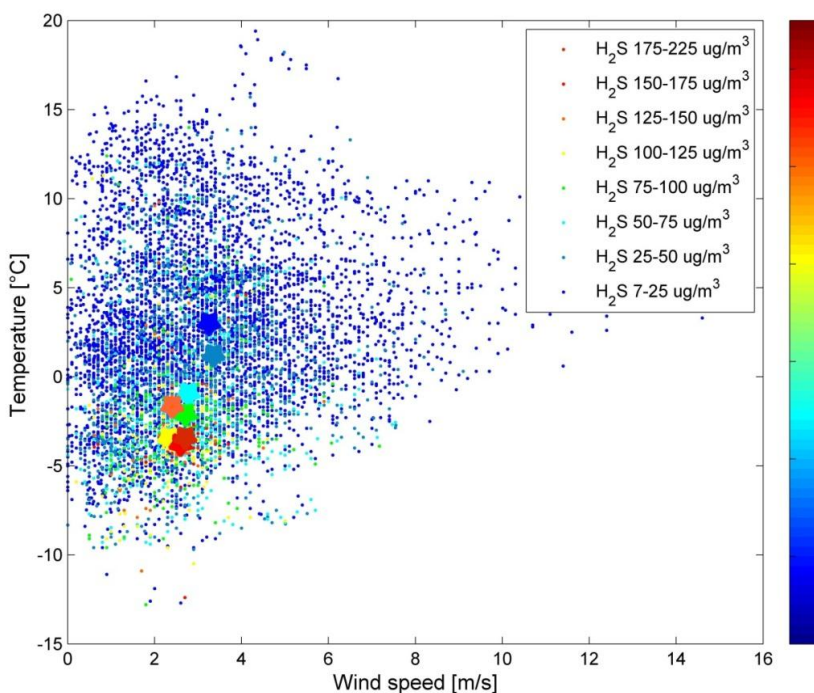
Figure 2–8. Temperature plotted as a function of wind speed with each measurement color-coded for hydrogen sulfide concentration. The stars show mean temperature plotted against mean wind speed for each H$_2$S concentration category.

2.3.9 Air stability vs. radiation

Figure 2–9 shows the sun radiation in Reykjavik plotted as a function of the temperature difference between Skardsmyrarfjall Mountain and Hellisskard Pass when H_2S concentration in Reykjavik was greater than 7 µg/m^3. The data points were grouped by color according to H_2S concentration, a total of 7204 data points. The difference in height between the two weather stations is 217 m and the temperature difference is used to indicate the air stability, as explained in Section 2.3.6. On a sunny summer day the radiation in Reykjavik is between 500 and 900 W/m^2. Radiation has an effect on air stability because as radiation heats the ground surface the air next to the ground heats up by conduction, convection and radiation. The air heats upwards from the hot ground, changing the vertical temperature profile and thereby impacting the air stability by contributing to the air becoming more unstable. The figure shows that when an inversion is present the radiation decreases dramatically, never reaching 400 W/m^2. All of the measurements with radiation above 500 µg/m^3 were in the lowest H_2S concentration category, that is, with a concentration from 7 to 25 µg/m^3. No measurements greater than 150 µg/m^3 had radiation above 40 W/m^2. The mean radiation and temperature difference for each category is depicted as a star in the corresponding color. All the categories had a low mean radiation; the category with the highest mean radiation was the one with the lowest H_2S concentration. The second lowest concentration category (25 and 50 µg/m^3) had similar air stability as the lowest concentration category but the radiation was somewhat lower. As the mean H_2S concentration rises the mean radiation generally decreases, and the highest concentration (175-225 µg/m^3) category has the lowest mean radiation. The mean H_2S concentration rises as the mean air stability becomes more stable up to 175 µg/m^3. The category with the highest concentration has a temperature difference close to zero, which is the fourth lowest temperature difference. This indicates that high peaks of H_2S are not common during strong inversion although Figure 2–6 indicates that mean concentration over a period of time is more likely to be high during inversion. It should, however, be noted that the highest concentration category had the fewest measurements or 8 measurements; these results are thus not conclusive. Figure 2–9 indicates that air stability and radiation have an effect on the H_2S concentration. However, this is not conclusive enough to claim that radiation has more effect on the H_2S concentration than it does by affecting the air stability. Whether the radiation has an effect by contributing to the oxidation of H_2S cannot be detected with this dataset.
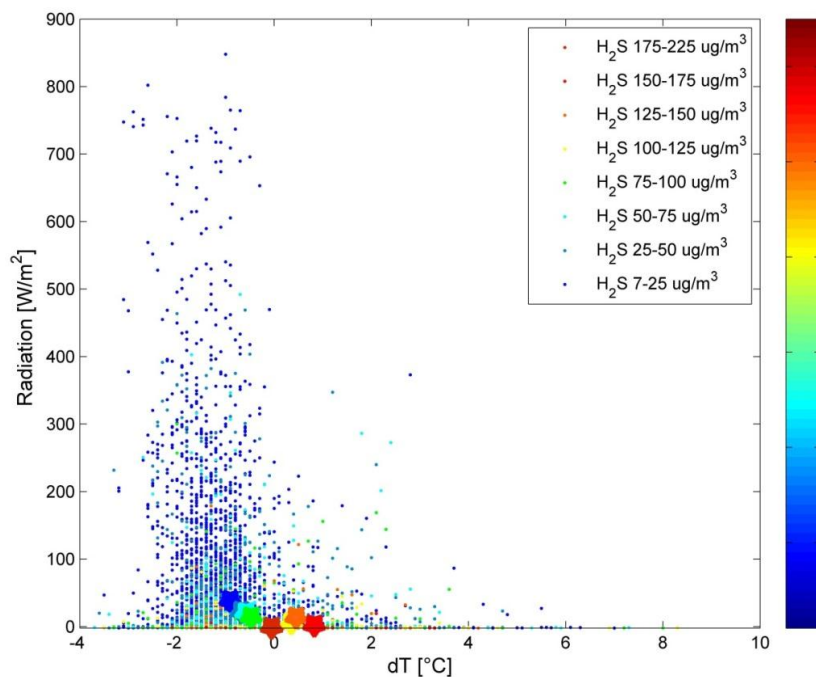
Figure 2–9. Radiation plotted as a function of temperature difference between Skardsmyrarfjall Mountain and Hellisskard Pass with each measurement color-coded for hydrogen sulfide concentration. The stars show mean radiation plotted against mean temperature difference for each H₂S concentration category.

2.3.10 Probability of an event with high H₂S concentration

The probability of weather conditions that can lead to a high H_2S concentration can be calculated when the weather parameters have been identified. Weather data from the Bustadarvegur Weather Station in Reykjavik from July 17th 1996 were obtained from the Icelandic Meteorological Office. The weather data were analyzed according to the previous analysis to estimate the frequency of favorable weather conditions for high H_2S concentrations.

Table 2–3 shows the results where the probability of an easterly wind is calculated, then within that time period the probability of wind speed being within a certain range, then temperature range was considered, then the air stability (data only available for 2006-2012), and finally the duration of the event. The range of the parameters is based on the analysis in previous sections. The table shows that favorable weather conditions are very dependent on air stability, as the percent of time is about 1/10 less when the air stability is used as a condition filter. The H_2S concentration in Reykjavik increased as the air became more stable. The table shows results for two air stability indicators (dT>=0°C (inversion) and dT>=-1°C (stable)), but in both cases the percent of time was less than 1%. Expanding the wind range to 0-4 m/s had more effect on the probability where the air temperature difference was from 0°C (Conditions 3.1) than changing the temperature from 0 to 3°C (Condition 2.1) but vice versa with the conditions where the temperature difference was greater than -1°C (Conditions 2.2 and 3.3). The results in Table 2–3 can be used to calculate the expected number of events per year, for example for Weather Condition 1.1, which narrows Condition 1, yielded a 0.18% chance of favorable weather conditions for 6 to 50 hours. This equals 0.66 days or about 16 hours. The median length of an event between 6 and 50 hours in the dataset from 2006 was 7.5 hours. Dividing the total number of hours in the events per year with the median gives about 2 events which are expected per year with Condition 1.1.

Table 2–4 shows the number of easterly events and the mean number of easterly events per year in 10 equal concentration increments from 0 to 100 µg/m³ of H_2S for the dataset from 2006 to 2010 (about 51 month as shown in Table 2–1). The table can be used to give an indication of H_2S concentration that can be expected when the weather conditions in Table 2–3 are present. For example, Conditions 1.1 in Table 2–3 are expected to yield the highest H_2S concentration and are expected to occur on average twice a year. According to Table 2–4, this corresponds to events that exceed 50 µg/m³. It is emphasized that this estimate is only indicative as the H_2S dataset is much shorter than the weather dataset and thus not as reliable. Nevertheless, the analysis presented here can be used to predict, with some certainty, when high H_2S concentration events might be expected by using a current weather forecast.

Table 2–3. Probability of an event of easterly winds, with wind speed and temperature favorable to high H_2S concentration. Data from 7.17.1996 to 1.9.2012 and from 6.21.2006 to 1.9.2012.

Conditions	Wind Direction (degrees)	Wind Speed (m/s)	Temperature (°C)	Air stability dT (°C)	Duration (hours)
Cond. 1 1996-2012	54°-125°	1.5-4	<=0°C	-	6-50
	32.4%	15%	4.3%	-	1.7%
Cond. 1.1 2006-2012	54°-125°	1.5-4	<=0°C	>=0	6-50
	33.1%	15.7%	4.5%	0.9%	0.18%
Cond. 1.2 2006-2012	54°-125°	1.5-4	<=0°C	>=-1	6-50
	33.1%	15.7%	4.5%	1.9%	0.52%
Cond. 2 1996-2012	54°-125°	1.5-4	<=3°C	-	6-50
	32.4%	15%	7.2%	-	2.7%
Cond. 2.1 2006-2012	54°-125°	1.5-4	<=3°C	>=0	6-50
	33.1%	15.7%	7.2%	1.1%	0.23%
Cond. 2.2 2006-2012	54°-125°	1.5-4	<=3°C	>=-1	6-50
	33.1%	15.7%	7.2%	3.1%	0.81%
Cond. 3 1996-2012	54°-125°	0-4	<=0°C	-	6-50
	32.4%	19.4%	5.8%	-	2.8%
Cond. 3.1 2006-2012	54°-125°	0-4	<=0°C	>=0	6-50
	33.1%	19.8%	5.8%	1.2%	0.38%
Cond. 3.2 2006-2012	54°-125°	0-4	<=0°C	>=-1	5-50
	33.1%	19.8%	5.8%	2.7%	0.97%

Table 2–4. Number of easterly events and the mean number of events per year in equal concentration increments for the H_2S dataset from 2006 to 2010.

Mean H_2S in event (µg/m³)	Number of events	Mean number of events per year
0-10	360	83.7
10-20	64	14.9
20-30	29	6.7
30-40	19	4.4
40-50	5	1.2
50-60	5	1.2
60-70	2	0.47
70-80	0	0
80-90	1	0.23
90-100	1	0.23

2.4 Conclusion

The dependency of hydrogen sulfide concentration on weather parameters, such as wind direction, wind speed, temperature and air stability was analyzed by using measurements of concentration in Reykjavik due to emission from geothermal power plants in the vicinity of the city. The results show that the H_2S concentration at the Grensasvegur Measuring Station in Reykjavik was elevated when the wind direction measured at the Bustadarvegur Weather station was between $54°$ to $125°$. This result was slightly off from the physical location of the power plants, likely due to topographical effects. The prevailing wind direction in Reykjavik is from the east as about 35% of all wind measurements fall within easterly winds, as defined in this research. The duration of easterly winds is also important as the concentration of H_2S increased with longer duration, up to about 20 hours, but when easterly winds had been prevailing for over 50 hours the mean H_2S concentration over the period decreased. The H_2S concentration in Reykjavik was highest when the wind speed in Reykjavik was between 1.5-4 m/s, but the concentration decreased rapidly with higher wind speeds as the air became more turbulent and the plume dispersed. For slower wind speeds the plume usually does not reach Reykjavik fast enough to make an impact unless there is a strong temperature inversion, in which case the cold air closest to the ground flows downhill to Reykjavik. H_2S concentration showed correlation with air temperature below $3°C$ in Reykjavik; as the concentration rose the temperature decreased. Air stability is an important factor in generating favorable circumstances for high H_2S concentration in Reykjavik. When there is a temperature inversion the air flow is laminar, leading to little dispersion and the mean concentration rises further. The quantitative effects of precipitation on H_2S concentration could not be determined in this study although the events with the highest H_2S concentration occurred when there was no precipitation. Radiation has an effect on air stability but whether it had other effects such as stimulating the oxidation of H_2S could not be determined. Probability calculations for weather conditions favorable to high H_2S concentrations within the timeframe of 6 to 50 hours showed that air stability is an important factor in H_2S concentration. The results showed that events of favorable conditions for high H_2S events can be expected in Reykjavik 2-6 times per year and events with H_2S concentration exceeding 50 $\mu g/m^3$ might be expected on average about 2 times per year. The results also indicate that events with high H_2S concentration can be predicted by using a current weather forecast.

3 Spatial distribution of Hydrogen Sulfide from two Geothermal Power Plants in Complex Terrain

Abstract

Concerns have arisen about the health impact and odor annoyance of hydrogen sulfide (H_2S) emissions associated with geothermal power production. Measurements have been made at stationary measuring stations in inhabited areas but little is known about the spatial behavior of the H_2S plumes. This study presents field measurements of the spatial distribution of the ground concentration of H_2S within a 30 km radius of two geothermal power plants during 20 distinct events spanning one year. The results showed that high H_2S concentration was correlated with high air stability, low wind speed and absence of precipitation. The odor threshold (11 µg/m^3) was exceeded in all events. The instantaneous measurements exceeded the 24-hour average national health limit (50 µg/m^3) up to 26 km from the power plants. The shape of the measured plumes at the same location was similar between events, indicating repeated patterns in plume distribution. Convergence of plumes was observed due to spatial variability in wind direction. Plumes were found to follow mountain passes and accumulate alongside a mountain range. AERMOD modeling demonstrated that narrower plumes with higher concentration can be expected for smoother terrain, such as lakes, consistent with measurements.

Keywords: Hydrogen sulfide; Air quality; Spatial distribution; Dispersion modeling; Geothermal emissions

3.1 Introduction

Development of geothermal energy as a clean and sustainable energy source is growing worldwide. Some concerns have been raised with regard to environmental and health impacts, such as hydrogen sulfide (H_2S) emissions to the atmosphere (Kristmannsdottir and Armannsson, 2003, Ermak et al., 1980).

For the past two decades geothermal utilization has been increasing in southwest Iceland in close proximity to the capital of Reykjavik, rural settlements and recreational areas. In 2010 local authorities established a health limit of 50 µg/m^3 for a 24-hour running average (Ministry for the Environment and Natural Resources, 2010) which represents over four times the mean odor threshold of 11 µg/m^3 (WHO, 2003). Prior research has established the connection between H_2S concentration in nearby towns and cities and weather conditions. Olafsdottir and Gardarsson (2013) reported a correlation between H_2S concentration and wind speed, air temperature and increasing air stability. Kristmannsdottir et al. (2000)

reported a negative correlation with precipitation. Thorsteinsson et al. (2013) found occurrence of high H_2S concentration with low atmospheric exchange and autochthonous weather. Field measurements of H_2S include stationary measuring stations (Kourtidis et al., 2008, Susaya, 2011a) and passive samplers (D'Alessandro, 2009, Horwell et al., 2005). Latos et al. (2011) used a hand held device for multiple measurements. To the authors' knowledge, large scale measurements of H_2S, up to 30 km distance from the source, have not been reported before.

Modeling air pollution is an important tool to devise strategies to manage pollution. AERMOD, the recommended model by the US EPA, has been used to model the distribution of various air pollutants including mercury (Heckel and LeMasters, 2011), SO_2, NO_x and PM_{10} (Zhang et al., 2008), and VOC's (Venkatram et al., 2009). The model has also been used to determine H_2S emission rates, based on measurements (O'Shaughnessy and Altmaier, 2011). AERMOD has been found to perform well for modeling buoyant tall stacks in moderate to complex terrain, where samplers were generally between 2 and 8 km from the source (Perry et al., 2005). Seangkiatiyuth et al. (2011) reported that the performance of the model for complex terrain and wind field was problematic for locations more than 5 km from the source. Peralta et al. (2013) found that AERMOD results compared well with measurements when wind direction and speed were stable.

This paper presents results from field measurements of near surface H_2S concentration levels within about 30 km distance of two geothermal power plants situated in a mountainous terrain. Spreading, directionality and strength of plumes were analyzed under different weather conditions and in relation to topological ground features. Selected characteristic events were modeled in AERMOD to identify the importance of meteorology and topography. The analysis provides an enhanced understanding of the behavior of H_2S plumes in complex terrain and therefore a base for predicting H_2S concentration.

3.2 Methods

3.2.1 Site Description

The study encompasses area up to 30 km from the two geothermal power plants in the Hengill volcanic system. The geothermal power plants Hellisheidi (HH, 260 m.a.s.l.) and Nesjavellir (NV, 180 m.a.s.l.) are 10 km apart, located on each side of Mt. Hengill (max 805 m.a.s.l., Figure 3−1). Northeast of the mountain is Iceland's largest natural lake, Lake Thingvallavatn (84 km[2]). The NV Power Plant is located near the lake shore in a small valley, with ridges rising 200 m to the west and 100 m to the east. The HH Power Plant is located at the southwest base of Mt. Hengill with Middalsheidi Heath to the west sloping towards the capital of Reykjavik. In the southern part of the area are volcanic fissures with crater rows (Gunnlaugsson et al., 2010). Four local towns are located in the area, in addition to the capital (dark shaded in Figure 3−1), as well as a few farms and summer houses. Most of the land is uninhabited, characterized by moss, grass and small shrubs. Further description of the power plants may be found in Olafsdottir and Gardarsson (2013).
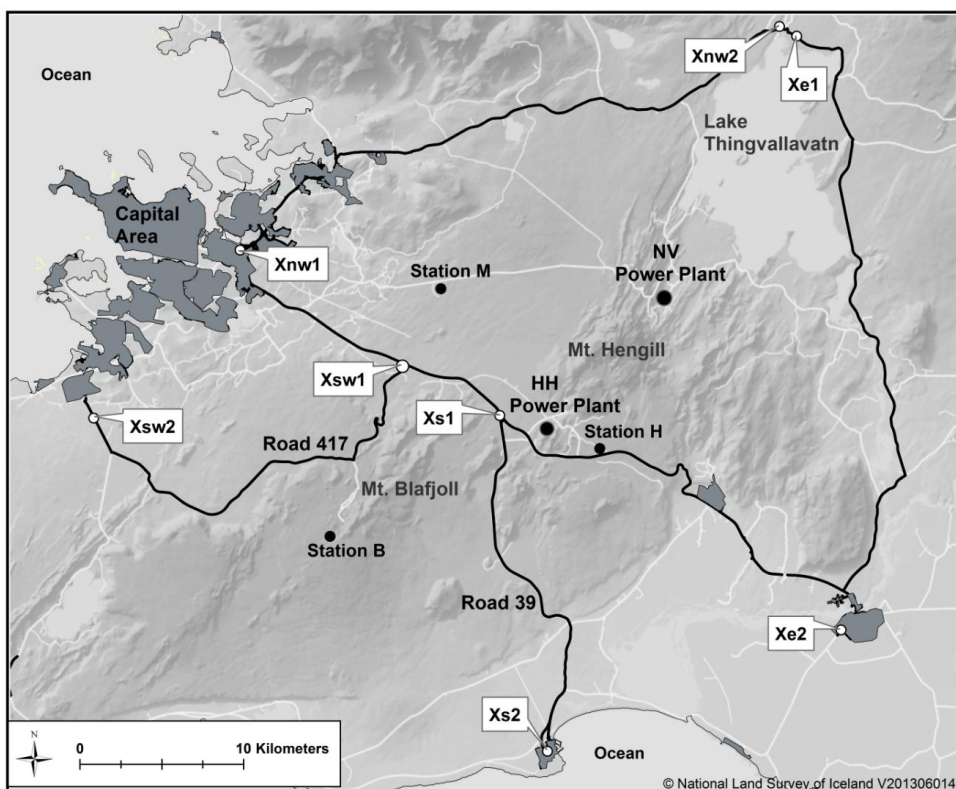
Figure 3–1. The study area. Black lines show the measurement roads. Dark shaded areas are the locations of local towns and/or inhabited areas.

3.2.2 H₂S Measurements and Analysis

A 12 month measurement program was carried out in 2009 in order to determine the areal extent and strength of geothermal plumes in different wind directions and weather conditions. H_2S measurements were performed along the major highways, at different spatial intervals between events, downstream of the plumes to the northwest, east, south and southwest (black roads in Figure 3–1). Measurements were made for 3-4 days in a row (randomly chosen) each month for 1-3 hours each day. In total, measurements were conducted on 44 days. A total of 20 events were chosen for further analysis based on the following weather conditions and data availability criteria: (1) steadiness of wind direction during the event; (2) range of air temperature, stability and wind conditions between events; and (3) spatial resolution of the H_2S measurements. Measurements were made with a handheld measuring instrument, Jerome 631-X (Arizona Instruments, USA), which has a 4-7100 µg/m^3 detection range and a ±4 µg/m^3 accuracy. Two nearly instantaneous (~20 sec) measurements were made at each location and the average concentration was converted using the conversion factor of 1 ppm = 1420 µg/m^3 H_2S (at 20° and 1 atm). The background value of H_2S is zero as the measurement roads are not on a geothermal field.

The calculation of the lateral spread of the plumes was partially limited by the spatial resolution of the measurements and the instruments lower detection limit and accuracy (4

$\mu g/m^3$). The spread was calculated as the distance where the measured profiles exceeded 2 $\mu g/m^3$ or half the accuracy of the measuring instrument. For further clarification of the plume spread in a northwest direction, a stationary H_2S measuring station, located in the capital area 4-5 km southwest of where the measurements started (Xnw1, Figure 3–1) was used.

3.2.3 Weather Data and Analysis

Wind and air temperature data from weather stations at Middalsheidi Heath (Station M), Hellisheidi Heath (Station H) and Mt. Blafjoll (Station B) (see Figure 3–1), measured at 10 minute intervals, were obtained. Accumulated hourly precipitation was obtained from the weather station at Hellisskard Pass, 2 km northwest of Station H. Ceiling height and cloud cover was measured every 3 hours in Reykjavik, about 30 km from the power plants. Bi-daily upper air data were measured at Keflavik airport, about 60 km southwest of the power plants. All weather data were provided by the Icelandic Meteorological Office except for data from Station H, owned by the Icelandic Road Administration.

Solar radiation is always moderate or slight at the northerly latitude of Iceland, such that very unstable air conditions rarely occur. In winter, the air can be stable during the day. The Pasquill air stability class during the selected events was estimated by calculating two local air temperature gradients, from ground to the 925 hPa height measured at Keflavik airport for both Station M and H, and categorizing them according to Woodward (1999). In addition, the upper air temperature profile at Keflavik airport at noon was plotted and compared to the adiabatic lapse rate. The three air stability estimates were generally consistent within one stability class.

3.2.4 Modeling with AERMOD

The American Meteorological Society-Environmental Protection Agency Regulatory Model (AERMOD) is a steady state Gaussian plume model aimed at short range (under 50 km) dispersion of airborne pollutants (US EPA, 2004a). The model, with the commercial interface AERMOD View, version 8.2 (Lakes Environmental Software, Canada), was run for selected events for comparison with measurements.

AERMOD has two pre-processors, AERMET and AERMAP. AERMET calculates boundary layer parameters (e.g. mixing height) based on hourly surface weather data, cloud cover, ceiling height, upper air data, surface albedo, surface roughness and the Bowen ratio. The smallest time resolution in AERMOD is 1 hour, which was used for comparison with the instantaneous measurements. The median wind direction, mean wind speed and mean temperature in each event, found from 10 min data, were set as the hourly surface weather data for the hour run by the model to best represent the weather conditions during each event. The plumes from NV and HH Power Plants were modeled with data from Station M and H, respectively. Variable surface roughness was used based on the topography downstream of each power plant. The Wieringa-Davenport roughness classification (Wieringa, 1992) was used for the modeling. Given the volcanic landscape the classifications used were "Roughly open" (z_0=0.1m) to the northwest and "Rough" (z_0=0.25m) to the east, except when the plume traveled partially over water, when "Sea" (z_0=0.0002 m) classification was used to calculate the total roughness. The Bowen ratio was set equal to 1 and the albedo to 0.2 based on measured summer values at Gunnarsholt (South Iceland) by Aradottir et al. (1997). The terrain data input was on a 25 m grid used by AERMAP to calculate the terrain height for each receptor location and the receptor grid had 0.5 km spacing in all modeled events.

The key H_2S source input data for AERMOD from the cooling towers at HH and NV Power plants are presented in Table 3–1. The H_2S gas is vigorously mixed with the steam in four closely spaced outlets, with fans to accelerate the emission and cool the water further. The outlets were modeled as one point source (for each power plant) with a combined area of all four outlets. The gas exit temperature used was the steam temperature and the velocity was calculated from the airflow through the fans on top of the cooling towers.

The reported annual H_2S emissions from each power plant (Arnalds and Sigurdardottir, 2011) were converted to monthly emissions proportionally to monthly reported power generation. The emissions at the NV Power Plant ranged from 311 to 405 g/s, with a median of 399 g/s, and at the HH Power Plant from 218 to 289 g/s with a median of 279 g/s.

The modeled pollutant type in AERMOD was set to "other" as no option was available for hydrogen sulfide. The model treats the gas as inert and does not account for oxidation, washout or density, although the density of H_2S is 18% higher than that of dry air.

Table 3–1. Source input data for AERMOD. Data from Reykjavik Energy.

Power Plant	Hellisheidi	Nesjavellir
Base elevation (m a.s.l.)	258	176
Release height (m above ground)	13.8	13
Stack inside diameter (m)	19.8	17.8
Gas exit velocity (m/s)	8.5	9.6
Gas exit temperature (°C)	30	40

3.3 Results and Discussion

3.3.1 Northwestward distribution

Steady H_2S plumes towards the northwest were measured during eight separate days, summarized in Table 3–2. The events were divided into categories based on location and profile shape. Figure 3–2 shows the detailed H_2S measurements conducted along the road from point Xnw1 (x=0) to Xnw2 (x=41) in Figure 3–1 for the events in Table 3–2.

First consider the three events in Category I measured on the far west side of the road during the darkest winter months. Event Ia occurred in the most easterly wind direction, with most divergence between wind directions in the two weather stations (25°) as well as most wind variability (20-35°, Table 3–2). H_2S concentrations (2-16 μg/m^3) were measured along the first 8 km of road, and a long tail of lower concentrations for another 9 km (Figure 3–2). A stationary/portable air quality station at x ≈ -4 km (not shown in Figure 3–2) reported a concentration up to 8 μg/m^3 during this 1 hour measurement period, indicating that the main plume, at a minimum, was 14 km wide. H_2S was measured with a steep rise and a minor shoulder along the measurement road in the other two events. The lateral extent of both plumes was around 10-12 km, but the maximum concentrations were double during Event Ic compared to Ib. Both events had almost identical wind directions and wind speeds at stations H and M. The vastly higher concentration in Event Ic than Ib may be contributed to the following factors: 1) less precipitation; 2) higher air stability; and 3) smaller range in wind direction. It is interesting to note that despite almost identical wind directions measured at both weather stations M and H, Event Ic peaked almost 10 km more to the east than Event Ib.

The three H_2S distributions in Category II, measured further east along the road, exhibited considerable self-similarity, with concentrations below 5 µg/m^3 for a few kilometers, followed by a steep rise to a maximum and then a slow decrease, either with a shoulder or a short second rise. Interestingly, the more westward location of the maximum concentration did not match the shorter distance to the measurement road or stronger emission from the NV Power Plant, compared to the HH Power plant. The converging winds at Stations M and H in Event IIb, may indicate that the location of the maximum value is where the plumes converge. Converging winds are a meteorological feature supported with spatial modeling of the wind field in this area (Belgingur - Institute for Meteorological Research, 2013). The similarity in the profiles indicates that the plumes converged in all events in Category II. The maximum concentration (41 µg/m^3) was measured in Event IIa during moderately unstable air conditions and a light varying breeze (1-3 m/s, 60-70° wind range). The maximum concentrations were similar in Events IIb-c, about 25 µg/m^3. As expected, the lateral spreading of the plumes during unstable conditions (33 km, IIa) was considerably wider than during neutral conditions (22 km, IIb and IIc).

The two Category III plumes, measured farther east, were distinguished by their narrow spread and decisive maxima. Both events occurred during similar weather conditions, except for precipitation. The maximum H_2S concentration measured in Event IIIa was 58 µg/m^3 during little precipitation, but only 16 µg/m^3 in Event IIIb during more precipitation in the hour before measurements started. This may indicate that the difference in maximum concentration between the events was due to washout.

To summarize, the eight northwest profiles in Figure 3–2 and Table 3–2 suggest a continuous H_2S plume of 10-33 km width on the road northwest of the two power plants, as opposed to two distinctive plumes. The H_2S distributions exhibited self-similarity along the same sections of the road, generally with a singular decisive maximum and a long shoulder (or minor secondary maximum) which is likely due to the convergence of the two plumes from the power plants. The odor threshold (11 µg/m^3) was exceeded in all events for up to 13 km on the road in Category II events and the maximum instantaneous concentrations exceeded the 24-hour average national health limit of 50 µg/m^3 up to 18 km away from the plants during two out of eight events. High H_2S concentrations were correlated with low wind speeds, high air stability and lack of precipitation both during and in the hour preceding the measurements. The maximum spread was measured during unstable conditions 16-18 km downstream of the plumes (IIa), consistent with the theory that lateral dispersion increases with distance from source and air instability

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Table 3–2. Climatic conditions and H₂S measurements northwest of NV and HH Power Plants, 2009. Values in parenthesis are based on limited data.

Category/ Event number	Date Time	Weather Station	Climatic Conditions						Measurements					
			Median wind direction (°)	Wind range (°)	Mean wind speed (m/s)	Mean temperature (°C)	Precip.[a] (mm)	Stability Class	Median H_2S ($\mu g/m^3$)	$N_{C>0}$ [b]	Maximum H_2S ($\mu g/m^3$)	Distance from NV[c] (km)	Distance from HH[c] (km)	Plume width (km)[d]
Ia	11-Nov 11:10-12:20	M	113	20	7	2		E	2	11	16	24	21	(10)
		H	88	35	3	2	0							
Ib	10-Dec 09:30-13:00	M	123	14	9	3		E	15	8	27	24	21	10
		H	109	19	6	2	0.7							
Ic	19-Jan 10:10-10:50	M	121	4	9	-2		F	(14)	5	57	18	19	12
		H	110	8	7	-2	0.1							
IIa	27-Apr 10:40-12:20	M	278	72	3	7		B	9	17	41	16	18	33
		H	184	59	1	6	0.3							
IIb	17-Jul 11:00-12:10	M	145	6	5	15		D	5	14	24	15	19	22
		H	162	17	3	12	0							
IIc	18-Sep 10:10-11:20	M	149	19	4	7		D	11	18	26	15	19	22
		H	150	6	4	6	0							
IIIa	16-Sep 11:00-11:50	M	164	11	10	9		D	9	9	58	12	21	11
		H	161	6	8	8	0.4							
IIIb	17-Sep 11:00-12:00	M	196	13	7	9		D	7	3	16	12	21	(3)
		H	175	9	10	8	1.3							

[a] Total precipitation at Hellisskard Weather Station an hour before measurements started and during the measurements
[b] Number of measurements exceeding zero
[c] Distance from the NV and HH Power Plants to the location where maximum H₂S was measured
[d] Distance where the profile exceeded 2 μg/m³. Estimated from Figure 3–2

Figure 3–2. Measured H₂S concentration along the road northwest of the power plants (x=0 and x=41 are marked as Xnw1 and Xnw2 in Figure 3–1, respectively).

3.3.2 Eastward distribution

H₂S plumes propagated east during four events. Table 3–3 summarizes the climatic conditions and H₂S measurement statistics and Figure 3–3 shows detailed H₂S measurements conducted on the road east of the power plants from the northerly point Xe1(x=0) to the southerly point Xe2 (x=41) in Figure 3–1.

The NV Power Plant plumes for the two Category IV events, measured to the north along the road, crossed Lake Thingvallavatn, while the HH plumes generally crossed an uneven mountainous terrain. Both events show sharp and distinct maxima associated with the emission from the NV Power Plant, which was located 10 km closer to this section of the road than the HH Power Plant. Plume IVa also demonstrates a secondary peak, corresponding to less than 1/3 of the first spike (34 μg/m³) with a total spread of about 13 km. Profile IVb, however, does not exhibit a distinct shoulder or secondary peak and has a considerably narrower lateral spread (7 km) and a higher maximum concentration 48 μg/m³. As discussed in Category I events, the higher measured maximum concentration in Event IVb than IVa was likely associated with less precipitation, lower wind speeds and higher air stability (Table 3–3). It is interesting to note, however, that the drop in maximum concentration as a result of precipitation was not as strong as in Category III, despite similar rainfall differences (0.9 mm). This could be because the most of the precipitation (0.9 mm) in Event IVa fell during the latter part of the measuring time (from 9 to 10 am), as opposed to falling in the hour preceding the event. The converging winds between Station H and Station M in Event IVa may explain the close proximity of the secondary peak associated with the HH Power Plant

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emissions. However, diverging winds, greater range in wind direction and less stable air may all have contributed to the fact that the HH plume was not detected in Event IVb.

The Category V events were measured farther south on the same road. Event Vb had a wide profile with H_2S concentrations between 10 and 16 µg/m^3, extending about 12 km, with no decisive maximum and a total spread of 21 km. Event Va has a somewhat narrower plume spread (12 km) and a more decisive maximum of 29 µg/m^3. The wind range was larger in Event Vb than Va, which may have contributed to more spreading and lower concentrations.

To summarize, the locations of eastward plumes were strongly determined by median wind direction. Category V plumes spread over a wider region with elevated concentrations but had lower maxima than Category IV, both may be attributed to less stable air. A secondary plume was observed in Event IVa, which can be explained by convergence of the winds instead of diverging as in Event IVb, where the plume from HH Power Plant was not detected.

Table 3–3. Climatic conditions and H₂S measurements east of NV and HH Power Plants, 2009.

Category/ Event number	Date Time	Weather Station	Climatic Conditions						Measurements					
			Median wind direction (°)	Wind range (°)	Mean wind speed (m/s)	Mean temperature (°C)	Precip.[a] (mm)	Stability Class	Median H_2S ($\mu g/m^3$)	$N_{C>0}$ [b]	Maximum H_2S ($\mu g/m^3$)	Distance from NV[c] (km)	Distance from HH[c] (km)	Plume width[d] (km)
IVa	19-Feb 09:30-10:50	M	241	10	7	-1		D/E	4	13	34	15	26	13
		H	219	18	10	0	1.1							
IVb	10-Nov 10:00-11:00	M	247	5	6	4		E	2	11	48	12	22	7
		H	260	7	7	4	0.2							
Va	12-Aug 13:50-14:30	M	281	15	6	11		C/D	11	10	29	15	21	12
		H	282	14	9	11	0.2							
Vb	13-Aug 14:40-16:00	M	287	24	5	13		C/D	11	16	16	17	22	21
		H	255	76	3	11	0							

[a] Total precipitation at Hellisskard Weather Station an hour before measurements started and during the measurements
[b] Number of measurements exceeding zero
[c] Distance from the NV and HH Power Plants to the location where maximum H₂S was measured
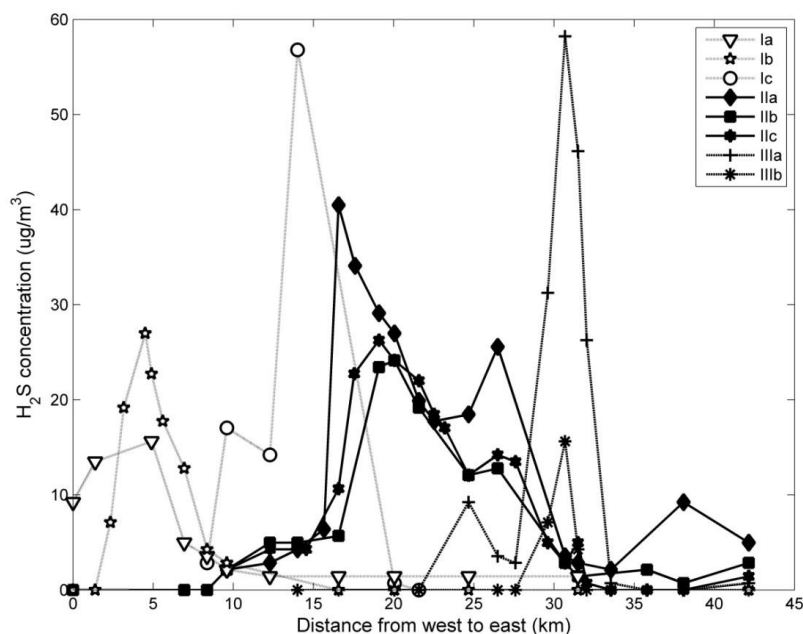[d] Distance where the profile exceeded 2 µg/m³. Estimated from Figure 3–3

Figure 3–3. Measured H₂S concentration along the road east of the power plants (x=0 and x=41 are marked as Xe1 and Xe2 in Figure 3–1, respectively).

3.3.3 Southerly- and Southwestward distribution

Six measured events with H_2S plumes directed towards the south and southwest are summarized in Table 3–4. The events were categorized based on whether a major part of the plume was measured along Road 39 south of the HH Power Plant (Category VI), along Road 417 southwest of HH Power Plant (VII), or along both roads (VIII) (see Figure 3–1 and Figure 3–4). The climatic conditions measured at three different weather stations are summarized in Table 3–4, including mountain Station B which is southwest of the HH Power Plant, at elevation 530 m a.s.l. The terrain to the south and southwest is more complex than for the other directions as mountain ranges lie alongside the plume direction with identifiable plume pathways. The difference in wind direction between Stations H and B ranged from 7° to 99°, demonstrating the spatial variability in the wind field south of the power plants.
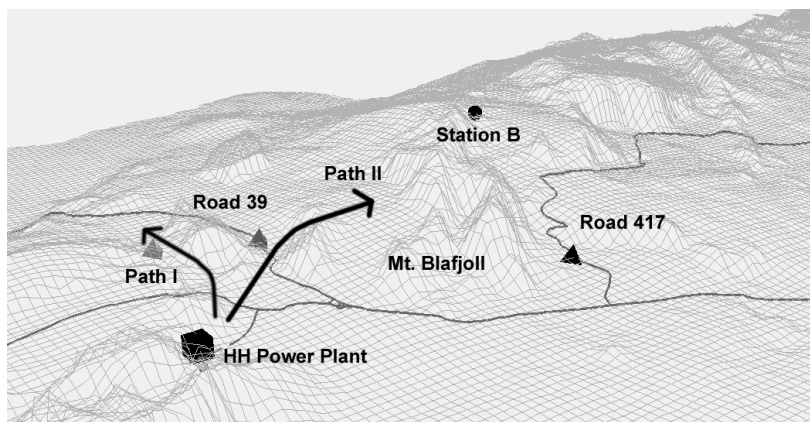
Figure 3–4. View from northeast to southwest towards the sea, looking south from HH Power Plant. Estimated plume paths are shown.

Figure 3–5 shows the detailed H_2S measurements conducted along Road 39 from point Xs1 (x=0) to Xs2 (x=23) in Figure 3–1 for events in Categories VI, VII and VIII. In Event VIa, H_2S was only detected along Road 39 after about 8 km, where the road starts to bend towards the east, indicating that the initial plume path was along Path I in Figure 3–4 The concentration decreased for about 2 km but then increased again to a maximum of 127 $\mu g/m^3$ at the bottom of a slope (Figure 3–5, lower panel). High concentrations (above 50 $\mu g/m^3$) were measured for about 6 km. The air stability was moderately stable with an inversion up to about 80 m.a.s.l. at Keflavik Airport. Wind speeds were low at all stations. These weather conditions restrict vertical movements such that the plume is guided by the terrain. The profiles for Events VIb and VIII along Road 39 rose slowly at first and then steeply at about 10 km to a maximum of 36 $\mu g/m^3$ and 31 $\mu g/m^3$, respectively, and then leveled off. The location of the H_2S concentration rise is consistent with Path I (Figure 3–4) being the initial plume path, as in Event VIa. The air was less stable in these two events and their concentration decreased further south on the road as opposed to increasing at the bottom of the slope as in Event VIa. All events in Category VII show decreasing concentrations within the first 5 km of Road 39 in Figure 3–5. All events recorded a more easterly wind at Station B than at Station H (Table 3–4), indicating that an initially southwest flowing plume could turn off towards the west, south of the HH Power Plant and thereafter be measured on Road 417. This possible plume path is depicted in Figure 3–4 (Path II).

Figure 3–6 shows the detailed H_2S measurements conducted along Road 417 from point Xsw1 (x=0) to Xsw2 (x=26) in Figure 3–1 for the events in Categories VII and VIII. In Event VIIa, overall continuously decreasing concentrations along Road 417 may indicate that the plume was aligned along the direction of the road consistent with standard plume theory. The measured fluctuation along the way may be explained by the road winding, resulting in measurements being conducted at different distances from the plume center. The concentrations were elevated (> 40 $\mu g/m^3$) in the first 15 km and reached 75 $\mu g/m^3$ at x=23 km (26 km from source). In Event VIIb the concentration had a steep rise to a maximum of 64 $\mu g/m^3$ with a total spread of roughly 7 km. This narrow spreading of the plume indicates that the plume path was more perpendicular to the road than along it as in Event VIIa. Profiles VIIc and VIII gradually rose to about 20 $\mu g/m^3$ at x ≈ 6 km and maintained this concentration for about 10-20 km, contradicting the theory that concentration decreases with distance from

source. This may suggest possible trapping of negatively buoyant H_2S alongside Mt. Blafjoll. Event VIII was the only event detected along both Roads 39 and 417. The wind direction at Station B was more from the north than in Category VII but the wind range at Station H was considerably larger (113°) indicating that the plume may have been split during the measurement time rather than changing direction on the way as discussed for the Category VII events.

To summarize, the plume was observed to be guided by the terrain through mountain passes and along ridges south of the power plants. An instantaneous maximum concentration of 127 $\mu g/m^3$ was measured during thermal inversion. This value was 2-3 times greater than the 24-hour average national health limit of 50 $\mu g/m^3$. However, these measurements are not a confirmation of the national health limit being exceeded as they were instantaneous measurements and not daily averages. In two events (VIIc and VIII) the concentration was steady and elevated (~20 $\mu g/m^3$) for 10-20 km which might indicate trapping of the plume alongside a mountain range. One event (VIII) indicated splitting of the plume on either side of Mt. Blafjoll. Plumes were shown to deviate from Road 39 to the west onto Road 417 when easterly winds were recorded on Mt. Blafjoll (Station B). Hence, these measurements highlight a complex spatial wind field in complex terrain, which may lead to the fate of H_2S being heavily dependent on the terrain, especially during slightly stable or moderately stable conditions when the vertical distribution of the plume is constrained.

Table 3–4. Climatic conditions and H_2S measurements south and southwest of NV and HH Power Plants, 2009.

Category/ Event number	Date Time	Weather Station	Median wind direction (°)	Wind range (°)	Mean wind speed (m/s)	Mean temperature (°C)	Precip.[a] (mm)	Stability Class
VIa	07-Dec 09:50-10:50	M	299	168	1	0		F
		H	308	47	4	1	0	
		B	47	28	3	-1		
VIb	18-Jun 12:30-13:30	M	357	9	8	10		D
		H	335	13	7	10	0	
		B	328	17	8	8		
VIIa	20-Oct 13:00-15:20	M	57	12	6	2		E
		H	31	23	5	2	0	
		B	81	27	6	2		
VIIb	08-Dec 11:20-12:40	M	76	10	12	2		E
		H	51	4	9	2	0	
		B	86	17	11	1		
VIIc	23-Oct 12:00-14:00	M	49	9	9	4		E
		H	24	10	8	3	0	
		B	89	5	8	4		
VIII	21-Oct 14:40-16:40	M	248	160	3	5		D
		H	18	113	5	4	0.2	
		B	34	38	4	3		

[a] Total precipitation at Hellisskard Weather Station an hour before measurements started and during the measurements

Figure 3–5. Upper panel: Measured H$_2$S concentration along Road 39 (x=0 and x=23 are marked as Xs1 and Xs2 in Figure 3–1, respectively). Lower panel: Elevation of Road 39 from Xs1 to Xs1 in Figure 3–1.
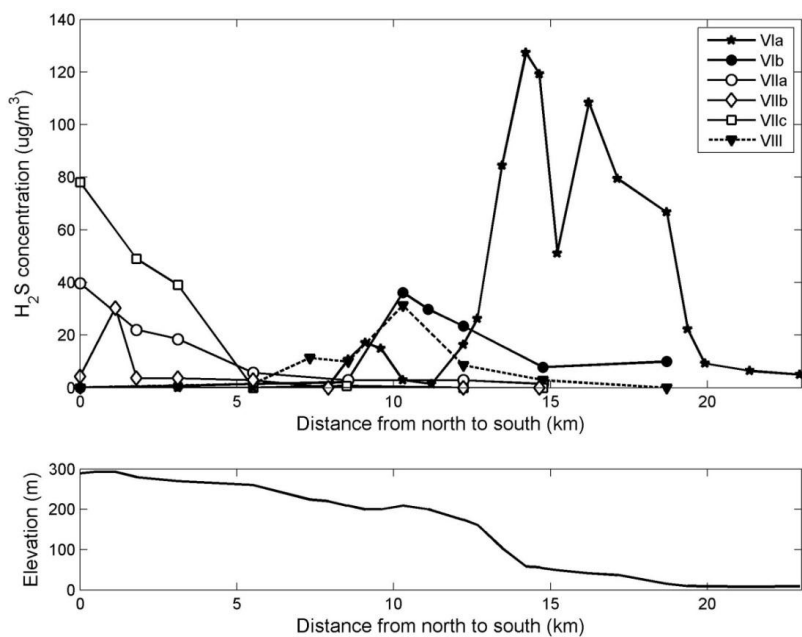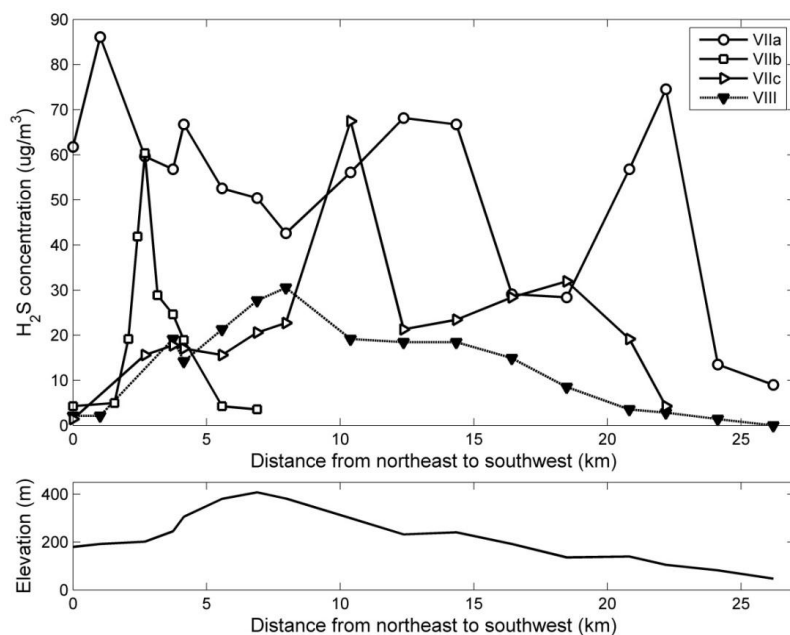
Figure 3–6. Upper panel: Measured H_2S concentration along Road 417 (x=0 and x=26 are marked as Xsw1 and Xsw2 in Figure 3–1, respectively). Lower panel: Elevation of Road 417 from Xsw1 to Xsw2 in Figure 3–1.

3.3.4 AERMOD Modeling

The plume measurements suggested that differential roughness (land vs. water), spatial variability in the wind, and terrain obstructions are factors that may affect H_2S concentrations in the vicinity of geothermal power plants. Three characteristic events were modeled using AERMOD with steady weather inputs (Table 3–2 and Table 3–3) to better understand the effects these factors have on the H_2S distribution. It should, however, be noted that AERMOD is neither able to capture spatial wind variability nor the interplay between the wind and the mountainous terrain so the results are more indicative rather than absolute.

Figure 3–7 shows the model calculations for Event IVb. The plumes traveled over different land surfaces as the plume from the NV Power Plant was partly over land and partly over water and was thus modeled as 40% "Sea" and 60% "Roughly open" (Wieringa, 1992) yielding z_0=0.06 m. The HH plume travelled over a rough area modeled as "Rough". This led to the plume from the NV Power Plant being narrower with a higher concentration in the middle ~10 km away from the source, whereas the plume from the HH Power Plant had the highest concentration near the source and diluted further away (Figure 3–7). This indicates that the narrow plumes with relatively high maximums measured in Category IV were the result of low roughness over Lake Thingvallavatn. The lateral spread of the measured plume (7 km for > 2 µg/m^3) was fairly well represented by the modeled plume (5 km) from the NV Power Plant however, the modeled maximum was considerably lower than the measured maximum (see Table 3–5). The weaker plume from the HH Power Plant was modeled to have a 4 µg/m^3 maximum concentration on the measurement road but the plume was not detected in the measurements as discussed in Section 3.3.2.

Figure 3–8 shows the model calculations for Event IIb. The wind measured at Stations M and H converged, resulting in one composite plume being modeled, demonstrating that the spatial variability in the wind field may play an important role in the H_2S plume distribution. The model simulations indicated that the measured west shoulder (x ≈ 10-15 km, Figure 3–2) corresponded to the HH plume, the maxima to overlapping of the two plumes, and the east shoulder to the NV plume. The maximum was less than one third of the measured maximum (see Table 3–5), which led to an underestimation of plume spreading, based on the distance where the concentration exceeded 2 µg/m^3. Lastly, AERMOD did not predict the actual location of the measured maximum, which supports that additional changes in local wind direction may occur between Stations M and H and the northwestward measurement road.

Figure 3–9 shows the model calculations for Event IIIa. Similar wind directions were measured at Stations M and H so two distinct plumes were modeled on the road, although the HH Power Plant plume was narrow and was likely missed on the road due to low spatial measurement resolution and perhaps low concentration. The modeled maximum H_2S value, associated with the NV Power Plant, was eight times lower than the measured value. Perhaps more interestingly, the location of the modeled maximum was 5 km west of the measured one (Table 3–5). This may indicate that the wind direction within the valley where the NV Power Plant is located followed the valley towards the lake and as the plume exited the valley it turned with the southeasterly winds towards the maximum location (see possible plume path in Figure 3–9).

AERMOD was unable to model the events south of the power plants (Categories VI-VIII, Figure 3–5 and Figure 3–6) as the model does not simulate spatial variability in wind

direction. The model was not able to capture the plumes being guided along valleys and passes during neutral and stable conditions in the mountainous terrain.

Sensitivity analysis was conducted on surface input parameters as well as emission amounts but none could explain the difference between modeled and measured maximum concentrations shown in Table 3–5. For example the emissions in Event IVb would need to be about 70% higher during the event than the monthly average used in the modeling, which is improbable given the relative steady operation of the power plants. This discrepancy is probably in large part due to the fact that the measurements are instantaneous and therefore the maxima should be higher than the one hour averages calculated by the model. Two additional modeling factors were identified that might have contributed to the model underestimation: 1) aerodynamic downwash, which may be formed as hills near outlets of emission can have a strong enough downward component to carry the plume downward, thus increasing ground level concentration. (De Nevers, 2000); 2) the density of H_2S is 18% higher than that of dry air, which may have contributed to a downward drift towards the surface. Other modeling factors that might, however, partially counteract the first two are: 3) initial plume rise, which may have been larger than the model predicted as it did not account for the condensation of the steam in the atmosphere (Wigley, 1976); 4) washout of H_2S which may have had an effect at the cooling tower release point where H_2S may have dissolved as steam condensates in the atmosphere. A fifth modeling inaccuracy was 5) data input uncertainties such as a lack of time resolution, especially concerning the H_2S emissions. These five factors need to be investigated further and taken into account in modeling H_2S emissions from the NV and HH Power Plants to provide more reliable data on, for example where the national health limit will be exceeded in the vicinity of the power plants.

Table 3–5. Measured and modeled H_2S concentration and distribution.

Event	Date	Maximum instantaneous measured H_2S ($\mu g/m^3$)	Maximum 1-hour modeled H_2S ($\mu g/m^3$)	Distance[a]
IVb	10-Nov	48	28	1.5 km
IIb	17-Jul	24	7	1 km
IIIa	16-Sep	58	7	5 km

[a] Distance between measured and modeled maximum H_2S concentration
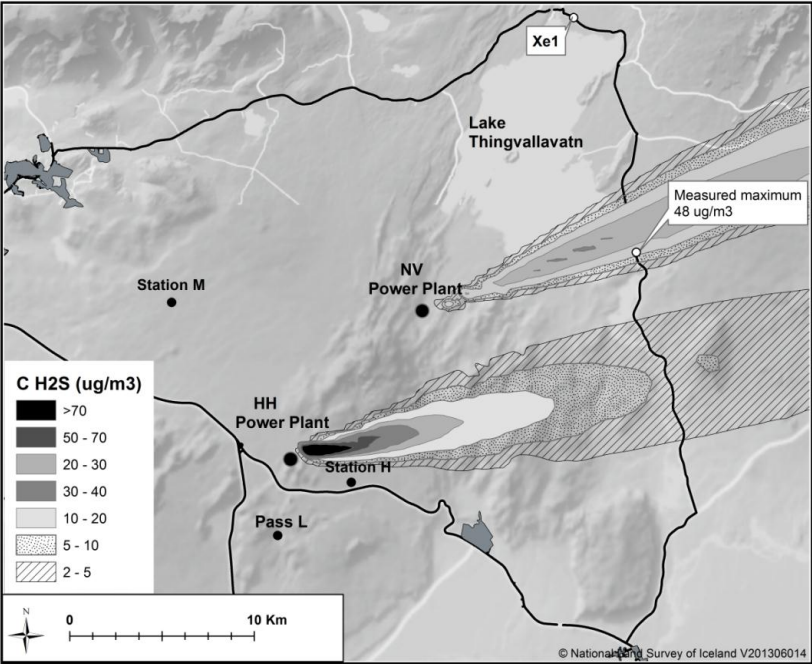
Figure 3–7. AERMOD modeling of Event IVb
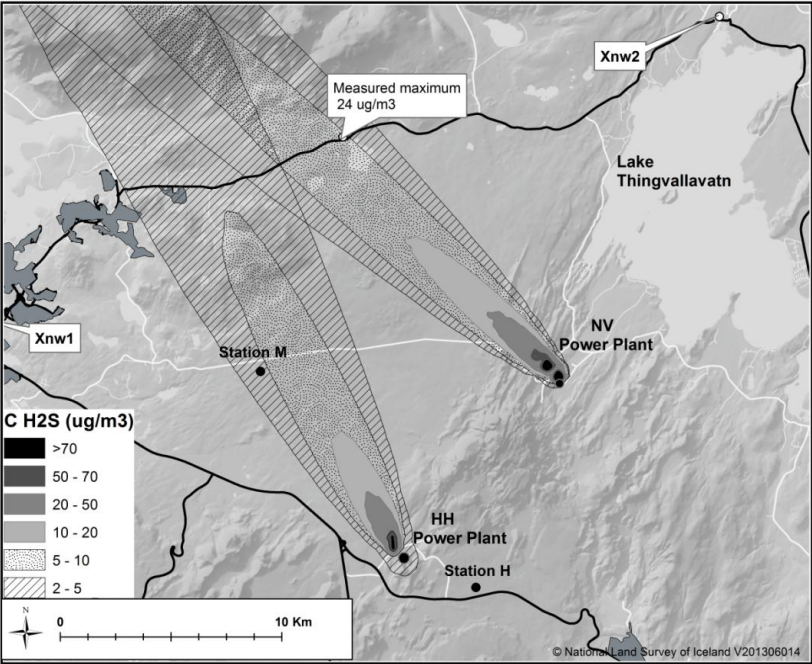
Figure 3–8. AERMOD modeling of Event IIb.
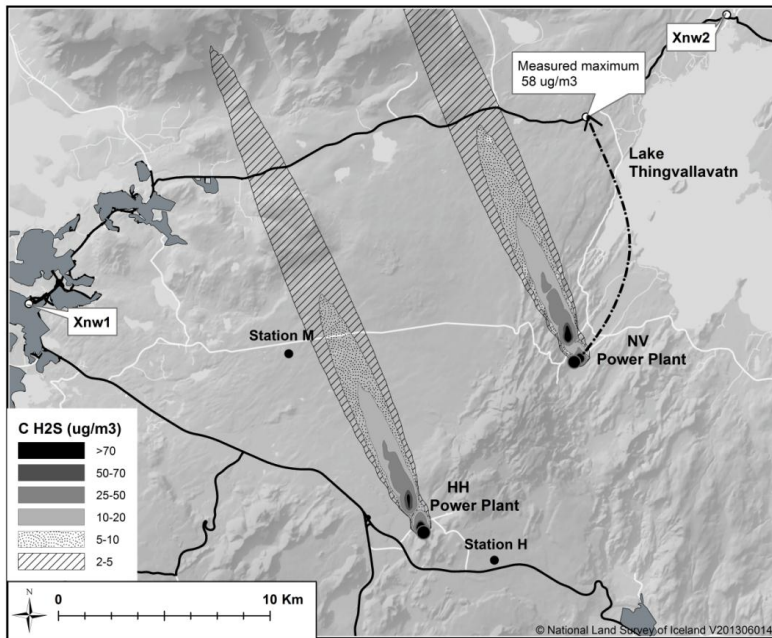
Figure 3–9. AERMOD modeling of Event IIIa. Dotted line shows possible plume path.

3.4 Conclusions

Measurements of H$_2$S plumes within a 10-30 km distance from power plants showed that low wind speeds, high air stability and absence of precipitation resulted in higher concentrations. Plumes with wider spread were observed to have lower maxima and were measured during unstable conditions, consistent with the theory that lateral dispersion increases with air instability. An instantaneous maximum concentration of 127 μg/m^3 was measured during a thermal inversion, which was 2-3 times greater than the 24-hour average national health limit of 50 μg/m^3. The health limit value was exceeded up to 26 km from the source. H$_2$S distributions exhibited self-similarity between events, indicating repeated plume patterns. Some convergence of the two plumes from the power plants was reflected due to spatial variability in wind direction yielding higher concentration. Plumes were observed to be guided in mountainous terrain by mountain ridges and passes. Wind direction was observed to shift considerably over mountain ridges changing the path of the plumes. In two events, during neutral and stable air, the concentration was steady and elevated (~20 μg/m^3) for 10-20 km alongside a mountain range which may indicate trapping of the plume. Measurements thus indicated that the fate of H$_2$S was heavily dependent on the terrain in mountainous areas, especially during stable conditions when the plume's vertical distribution was constrained.

AERMOD modeling demonstrated that narrower plumes with higher concentrations further from the source can be expected for smoother terrain, such as lakes, and that plumes may converge leading to higher concentration. The modeling showed the importance of capturing spatial variability in the wind field as well as local terrain.

Acknowledgments

4 Natural near Field Sinks of H_2S from two Geothermal Power Plants

Abstract

Hydrogen sulfide (H_2S) emissions have been growing with increasing utilization of geothermal resources. Atmospheric H_2S concentration has been measured and studied but less is known about the natural sinks of the chemical. This study investigates the atmospheric depletion of H_2S within a 35 km distance from two Icelandic power plants. The results showed that estimated atmospheric oxidation by the OH radical was the largest sink in the area. The second largest sink was H_2S uptake in surface water, in a neighboring lake, but it was, however, small compared to the reported difference of sulfur amount in the lake in- and outflow. Sulfur was measured to accumulate in moss close to the power plants at an estimated rate of about 1500 mg S/kg moss per year at maximum and decrease exponentially from the source, being negligible in a distance of few kilometers. Soil uptake was limited by diffusion of H_2S into the porous media and was thus much smaller than the estimated soil uptake potential. Washout with precipitation was estimated to be the smallest sink due to the low H_2S reactivity in the precipitation (pH = 5.6), compared to the surface water (pH = 8.5). Depletion of H_2S from the atmosphere in the study area was estimated to be about 1% of the 2012 power plants emissions of over 28,000 tons. Although the uncertainties in the depletion estimates were considerable vast majority of the H_2S emitted from the power plants was strongly indicated to be transported out of the study area as H_2S.

Keywords: Hydrogen sulfide; Air quality; Atmospheric sinks; Geothermal emission; Near field fate

4.1 Introduction

The sources of H_2S to the atmosphere are diverse. They are both natural, such as volcanic and geothermal areas (Chiodini et al., 2001), as well as anthropogenic, such as geothermal power plants (Kristmannsdottir and Armannsson, 2003), kraft pulp mills (Bordado and Gomes, 2003), coal gasification plants (Ko et al., 2006), landfill sites (Song et al., 2007, Shon et al., 2005), and wastewater treatment facilities (Latos et al. 2011). The sinks of H_2S are not as well known as the sources. Watts (2000), stated that there were few data and large uncertainties in the size of the global H_2S budget when estimating its size. Oxidation with OH radicals has been acknowledged as the dominant tropospheric removal process (Wallace and Hobbs, 2006). Watts (2000) assumed that the only sink of H_2S in the atmosphere was a reaction with OH radicals. In an unpolluted area OH radicals are formed primarily with a photolysis of ozone (O_3) to electronically excited $O(^1D)$ at wavelengths

below 320 nm, followed by a reaction to water vapor (Wallace and Hobbs, 2006). The rate of OH formation thus depends on the strength of incoming radiation and the humidity. Bottenheim and Strausz (1980) estimated the lifetime of H_2S, in a hypothetical clean air mixture at 55°N, to be 0.93 days during the summer and 41.9 days during the winter. The seasonal difference resulted from negligible gas-phase reactions during winter because of low radiation.

Other sinks have been indicated. A decrease in H_2S concentration has been reported during and following precipitation (Kristmannsdottir et al., 2000, Olafsdottir et al. 2014 and Thorsteinsson et al., 2013). However, Susaya et al. (2011) found that airborne H_2S showed positive correlations with relative humidity, dew point and rainfall. Washout calculations for H_2S have not been reported before to the authors' knowledge. Uptake by vegetation has been reported, e.g. in leaves (Bussotti et al., 1997). Studies have shown that the capacity of soils for sorption of H_2S can be substantial (Smith et al., 1972). Soil properties that influence the capacity of soils for sorption of H_2S include sand and clay content, DCB-soluble manganese and surface area (Cihacek and Bremner,1990). Watts (2000) assumed soil and vegetation to be sources of H_2S but not a sink.

H_2S emissions have been growing as geothermal utilization has been increasing worldwide as part of an effort to decrease reliance on carbon based energy in countries that have geothermal resources, including Iceland. Knowledge of H_2S interaction with the local environment is fundamental in assessing its environmental impact. This paper investigates the depletion processes of H_2S from the atmosphere within a 35 km radius from two geothermal power plants in southwest Iceland. The analysis provides an enhanced understanding of the natural depletion processes of H_2S from the atmosphere and its magnitude put into context with the geothermal emissions.

4.2 Background

4.2.1 Site description

The Hellisheidi (HH) and Nesjavellir (NV) Geothermal Power Plants are 10 km apart on each side of Mt. Hengill in the Hengill volcanic system in southwest Iceland (Figure 4–1). The capital area is situated by the coast in the westernmost part of the area, and there are four local towns in the southeast part. Northeast of the NV Power Plant is Lake Thingvallavatn, Iceland's largest natural lake (83 km^2). The southern part covers the coastal area and extends to the ocean. Most of the area is sparsely populated or uninhabited. Local vegetation is characterized by moss, grass and small shrubs. Most Icelandic soils are Andosols, making the largest area of such soils in Europe (Arnalds, 2004). Soils in the study area are mostly Brown and Gleyic Andosols and Leptosols (Arnalds, 2004). Electricity production started at NV Power Plant in 1998 at 60 MW with two subsequent enlargements to the current production of 120 MW. The HH Power Plant started production in 2006 at 90 MW with three enlargements to the present production of 303 MW. In 2012 the H_2S emissions were 28,230 tons from both power plants (Thorarinsdottir and Sigurdardottir, 2013). Further description of the study area can be found in Olafsdottir et al. (2014) and of the power plants in Olafsdottir and Gardarsson (2013).
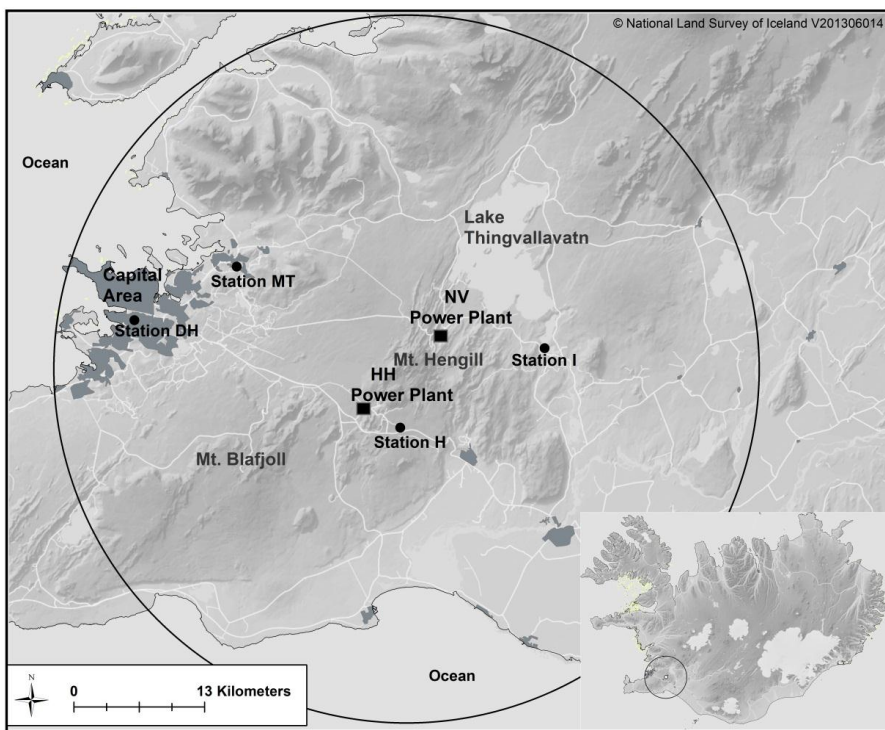
Figure 4–1. The study area in southwest Iceland.

4.2.2 Chemical features of H₂S

Hydrogen sulfide (H₂S, CAS No. 7783-06-4) is a colorless flammable gas with a characteristic odor (US EPA, 2003). It is heavier than air with a molecular mass of 34.08 g/mol, therefore it is about 18% heavier than air. H₂S is a weak diprotic acid and dissociates via reactions (4.1)-(4.3) (Arnorsson et al., 1982),
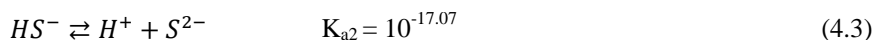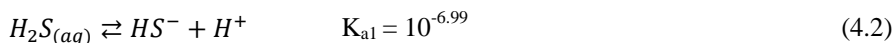
$$H_2S_{(g)} \rightleftharpoons H_2S_{(aq)} \tag{4.1}$$

$$H_2S_{(aq)} \rightleftharpoons HS^- + H^+ \qquad K_{a1} = 10^{-6.99} \tag{4.2}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad K_{a2} = 10^{-17.07} \tag{4.3}$$

where $H_2S_{(g)}$ and $H_2S_{(aq)}$ refer to H₂S in the gas and aqueous phase respectively, K_{a1} and K_{a2} are the first and second acid dissociation constants. The pH of the solution determines the predominant form of the species (O'Brien and Birkner, 1977). Dissolved H₂S can be oxidized in the presence of absorbed oxygen to form elemental sulfur, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} (Brown and Webster, 1994). The reactivity of aqueous H₂S is largely dependent on the pH of the solution. Balls and Liss (1983) reported that at pH 5 to 6 H₂S behaved like an unreactive gas of moderate solubility but as the water pH was raised increasing chemical enhancement was observed. Chen and Morris (1972) found the oxidation of sulfide by O₂ to be slow at pH<6 where H₂S was the predominating sulfide species. Brown and Webster

(1994) reported that negligible oxidation of H$_2$S was detected in acidic and neutral aerosol solutions when gaseous H$_2$S was pumped through aerosols.

In the atmosphere H$_2$S can be oxidized to SO$_2$ by the OH radical via reactions (4.4)-(4.8) (Wallace and Hobbs, 2006).

$$H_2S + OH \rightarrow HS + H_2O \qquad\qquad (4.4)$$

$$HS + O_3 \rightarrow HSO + O_2 \qquad\qquad (4.5)$$

$$HS + NO_2 \rightarrow HSO + NO \qquad\qquad (4.6)$$

$$HSO + O_3 \rightarrow HSO_2 + O_2 \qquad\qquad (4.7)$$

$$HSO_2 + O_2 \rightarrow HO_2 + SO_2 \qquad\qquad (4.8)$$

Spedding and Cope (1984) found that H$_2$S was oxidized to SO$_2$ in a series of experiments in a broad, ground-level plume from geothermal vents in New Zealand. The dominant oxidant was reported to be the OH radical but that additional unknown mechanisms were also a possibility.

4.2.3 Data

Atmospheric H$_2$S measurements

Long term measurements of H$_2$S have been made with both stationary and portable (stationary for a few weeks/months) stations in the Capital Area. Measurements at Mosfellsbaer Town (Station MT, Figure 4–1) northwest of the power plants from October 5, 2013 to May 14, 2013 were obtained from the Environmental Agency of Iceland. H$_2$S, SO$_2$ and NO$_x$ measurements from Digranesheidi Measuring Station (Station DH) from September 1st 2011 to September 19th 2012 were obtained from the Environmental and Health Protection Department of Hafnafjordur, Kopavogur and Gardabaer (Figure 4–1).

Sulfur in precipitation and particulate matter

Sulfur measurements have been made in 24-hr precipitation and particulate matter samples collected at Irafoss Hydropower Plant (Station I, Figure 4–1) since 1980. Sulfur with oceanic and rock origin was subtracted from the samples using chloride and other salt measurements and the known ratio in the ocean and Icelandic rocks. Measurements were obtained from the Icelandic Meteorological Office with corrections for oceanic and rock originated sulfur.

For the present study isotope measurements were made in 9 precipitation samples collected in a line extending about 16 km northwest from the HH Power Plant (gray circles in Figure 4–2). As the sulfur content of the precipitation was low and a certain minimum amount was needed for the analysis 1 gallon bottles were used for the collection. The bottles had to be out long enough for them to be filled up and ended up being collected from Nov. 2010 till Jan. 2011, with some of them freezing in the ground with the samples. This long collection time and having some of the precipitation falling as snow resulted in measurement uncertainty.

Sulfur in moss

In 2008 the sulfur content of Woolly Fringe-moss (Racomitrium lanuginosum) was measured in the vicinity of the HH and NV Power Plants by EFLA Consulting Engineers for Reykjavik Energy. Mosses are highly dependent on the atmosphere for nutrients as they have no root system and have therefore been widely used for biomonitoring of various pollutants (Foan et al., 2014, Berg et al., 1994). The measurements were divided into three categories at the HH and NV Power Plants based on their location at the site (white circles, Figure 4–2). The samples were within 2.5 km from the power plants and all were within a few hundred meters from either the power station or other smaller outlets of gas (such as boreholes). Comparison samples were taken at Mt. Blafjoll (Figure 4–1).
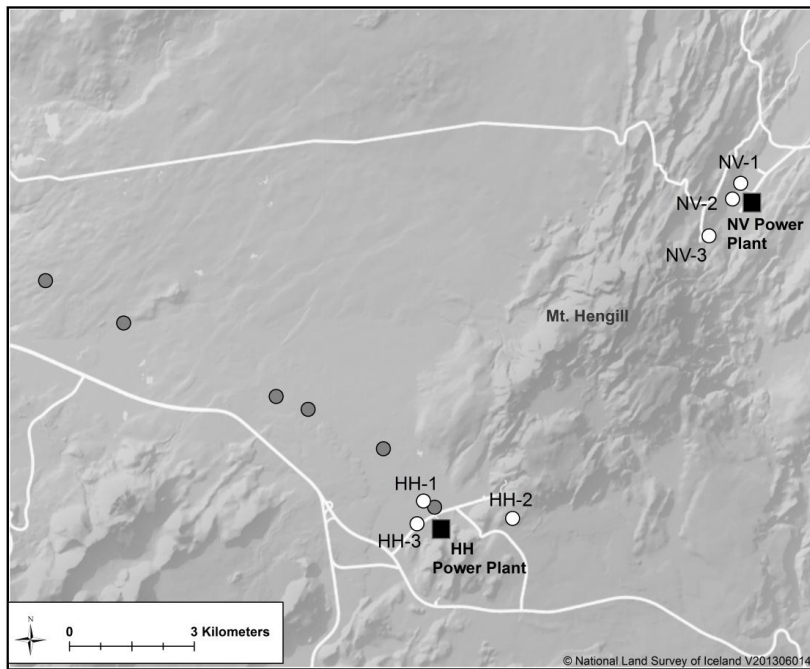
Figure 4–2. Measurement sites of moss samples (white circles) and precipitation samples (for isotope measurements, gray circles). Power Plants are depicted with black squares.

Sulfur in surface water

Measurements of pH, temperature and sulfur in Lake Thingvallavatn (Figure 4–1) 2007-2012 were obtained from the Natural Science Department of the University of Iceland (Eiriksdottir and Gislason, 2013). Measurements were made by two of the main groundwater inflows and the outflow. Other surface waters were not estimated and the ocean was excluded in this analysis.

Meteorological data

Wind and temperature data measured at 10 min intervals were obtained from the weather station at Hellisheidi Heath (Station H, Figure 4–1), provided by the Icelandic Road Administration and from Mosfellsbaer Town (Station MT), provided by the Environment

Agency of Iceland. Accumulated hourly precipitation from Hellisskard Pass, 2 km northwest of Station H, were provided by the Icelandic Meteorological Office.

4.3 Results and discussion

4.3.1 General assumptions

The estimation of the depletion of H_2S from the atmosphere was based on an idealized box model approach. Neglecting spatial variability and differences in surface types, the H_2S concentration was assumed to be homogeneous in a volume with the horizontal area of a standard Gaussian plume (Figure 4–3), where the source was assumed to be at the center of mass of the combined emissions. The plume's horizontal and vertical dimensions were found by applying a Gaussian plume model in neutral air, over a 35 km distance, with an average wind speed of 7 m/s (Station H). The plume was assumed to expand from the source to $4\sigma_y$, 6.57 km, while $2\sigma_z$ was used for the plume height, 544 m, with an areal extent of $1.1\cdot10^8$ m^2 and travelling time of 83 min (see Appendix). The H_2S concentration was determined by assuming the emissions during the travelling time (4.5 tons on average in 2012) created the homogeneous plume yielding H_2S concentration of 72 µg/m^3, here after noted as C_{air}.

The five sinks and associated models are: 1) oxidation, $\frac{dC_{air}}{dt} = -k_o C_{air}$; 2) washout, calculated with Henry's law $C_{precip} = HC_{air}$; 3) vegetation uptake, $\frac{m_{veget}}{t} = \int_0^\infty F \exp(-k_m r)\,\rho_{moss} h_{moss} \pi r dr$; 4) soil uptake (diffusive transfer to soil), $m_{soil} = -D_{air} A_{plume} \frac{dC}{dz} n$; 5) surface water uptake, $m_{water} = -k_w A_{water} dC$. The depletion of H_2S from the atmosphere for each sink within 35 km from the power plants was compared to the 2012 emissions to determine if the near field depletion was significant. Subsequent subsections discuss each of these sinks and estimate the H_2S depletion.
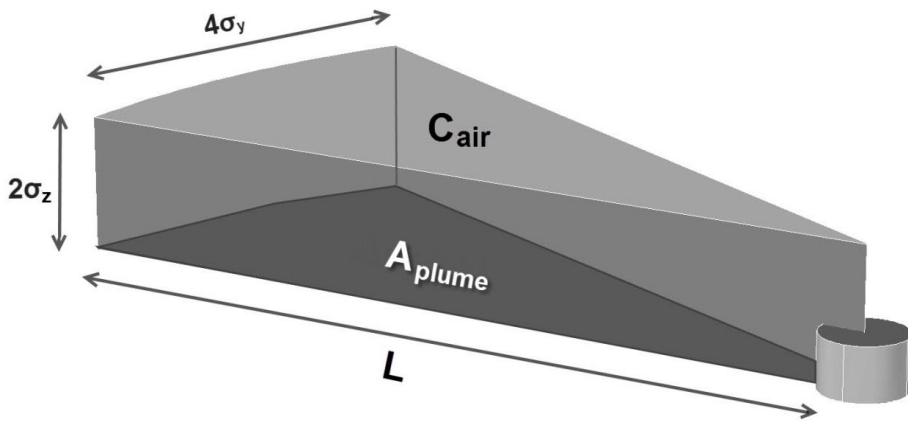
Figure 4–3. A schematic of the control box of the Gaussian plume.

4.3.2 Oxidation

In order to estimate the potential oxidation amount of H_2S within the study area the oxidation rate in reaction (4.4) was used as that is the reaction H_2S undergoes. The general equation for the reaction is

$$\frac{dC_{air}}{dt} = -k_o C_{air} \qquad (4.9)$$

where C_{air} is the H_2S concentration in the atmosphere, $k_o = k_{OH+H_2S} \cdot C_{OH}$, where k_{OH+H_2S} is the rate constant for reaction (4.4), $5 \cdot 10^{-12}$ $cm^3/molecule \cdot sec$ (Cox and Sheppard, 1980) and C_{OH} is the concentration of the OH radical. The rate of oxidation is thus dependent on the availability of the OH radical. The OH formation was assumed to be stable over the year and its concentration constant as the mean of OH concentration found by Spivakovsky et al. (2000) at 60°N latitude ($2.75 \cdot 10^5$ $molecule/cm^3$). The OH radicals were assumed to be available only for H_2S oxidation. Assuming the plume defined in Section 3.1, the oxidation mass rate is

$$\frac{dm_{air}}{dt} = k_{OH+H_2S} C_{OH} C_{air} V_{plume} \qquad (4.10)$$

where V_{plume} is the volume of the plume. These assumptions yield an oxidation of H_2S of 187 tons in one year or 0.66% of the 2012 emissions.

This is likely to be an overestimate as OH is very reactive and reacts with various other chemicals in the atmosphere and is therefore not necessarily available to react with H_2S. Also, the OH formation is likely to be slower than assumed, especially in the middle of the plume, where the geothermal gases are dense. The oxidation amount also varies seasonally as there is no OH formation during the darkest winter months.

Measurements support this low estimate. Figure 4–4 shows the concentration of H_2S plotted against SO_2 at Station DH (Figure 4–1), where gray circles present measurements for radiation below 400 W/m^2 and black stars when it exceeded 400 W/m^2. High SO_2 values due to exhaust were eliminated for better comparison of the sulfur compounds by using only measurements where a known traffic pollutant, nitrogen oxide (NO_x), had low concentration (< 15 $\mu g/m^3$). The data do not show any decisive correlation between the two chemicals, neither with high or low radiation, indicating that the H_2S was not fully oxidized to SO_2 within the study area. Station DH was about 30 km and 25 km from the NV and the HH Power Plants, respectively.

H_2S can be oxidized via the nitrate radical (NO_3) (Finlayson-Pitts and Pitts, 2000). This radical is formed with the reaction of nitrogen dioxide (NO_2) and ozone. The rate constant for its formation is relatively small ($3.2 \cdot 10^{-17}$ $cm^3/molecule \cdot sec$, Finlayson-Pitts and Pitts, 2000) and it photolysis takes place rapidly by day so that its other reactions are restricted to hours of darkness. As exhaust is the main source for NO_2 the radical formation in the study area would be almost limited to the capital area. It is concluded that this type of oxidation is insignificant as the source of NO_2 is limited and the rate constant is small.

The above calculations and analyses of data indicate that H_2S is not oxidized within the study area in significant amounts compared to the 2012 emissions.
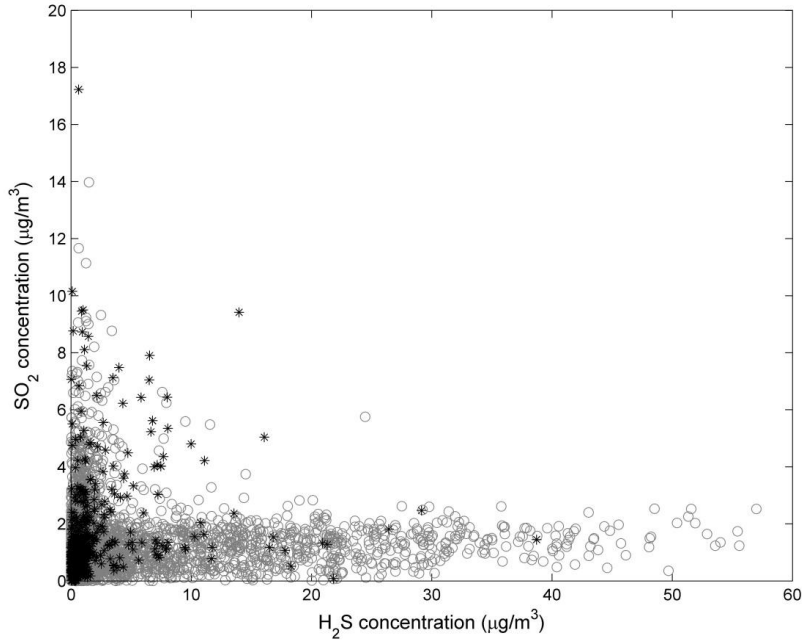
Figure 4–4. SO₂ concentration plotted against H₂S concentration at Station DH when NOₓ values were below 15 μg/m³. Gray circles: radiation below 400 W/m²; black stars: radiation exceeding 400 W/m².

4.3.3 Washout

Plume estimations

The potential washout is the amount of H_2S that can potentially dissolve in the amount of precipitation that falls through the plume. The gas and water phase of the H_2S were assumed to reach equilibrium during the time it takes the precipitation to reach the ground. According to Henry's law the H_2S concentration in the water precipitated, $C_{precip,}$ is

$$C_{precip} = HC_{air} \qquad (4.11)$$

where C_{air} is the H_2S concentration in air and H is the dimensionless Henry's constant. Fernandez-Prini et al. (2003) and Seinfeld and Pandis (2006) were used to find the effective Henry's constant at 10°C and pH 5.6 (see Appendix).

The total precipitation at Hellisskard Pass in 2012 was 2068 mm, yielding $2.27 \cdot 10^8$ m³ of water over the plume area for the plume defined in Section 3.1. Using the above assumptions, the equation gives about 60 kg of H_2S that can potentially be dissolved in the precipitation (see Appendix). This is only 0.0002% of the total amount of H_2S emitted in 2012, which was negligible. Varying the H_2S concentration and/or the precipitation amounts within a plausible range did not increase the possible washout by any significant amount.

Cooling tower estimations

The H$_2$S is emitted through the cooling tower of the power plants. At the HH Power Plant the gas is vigorously mixed with the steam in four closely spaced outlets (2-by-2), with fans to accelerate the emission. Steam, 57 kg/s, is emitted from the cooling towers, with the pH of the water at about 6.7 and temperature about 30°C. The magnitude of H$_2$S possible to dissolve in the steam was calculated using Henry's law as before and assuming the gas was evenly distributed through a cylinder with the diameter of two outlets (19.8 m) and the height of the plume rise. In 2012, 535 g/s were emitted on average at the HH Power Plant. Total H$_2$S absorbed by the steam amounted to 1300 kg/year, assuming the dissolved H$_2$S did not return to the gas phase if the steam evaporated. Assuming similar absorption in the steam at the NV Power Plant, the absorbed H$_2$S in the cooling tower steam equaled 0.009% of the total 2012 H$_2$S emissions, which was insignificant.

Supporting data

The above estimates are supported by various measurements where no distinct H$_2$S concentration decrease was found during precipitation: 1) In Figure 4–5(a) one hour measurements of H$_2$S at Station MT are plotted as a function of precipitation while the wind direction was towards the station and from the power plants. The 90 and 50% percentile lines show no correlation with precipitation amount; 2) Figure 4–5(b) shows the mean sulfur in precipitation samples at Station I where the sulfur that originated at sea has been subtracted. The mean sulfur was found in 24-hour collections of precipitation at Station I during which the prevailing wind direction was towards Station I from the power plants as measured at Station H. There was no apparent correlation between the changes in sulfur concentration in the precipitation and the H$_2$S emissions although the emissions increased with time as the power plants were built and expanded; 3) For the present study sulfur isotopes were measured in 9 precipitation samples collected in a line extending about 16 km northwest from the HH Power Plant. The range in δ^{34}S values was 12.5–17.8‰ (median 16.8‰). Figure 4–5(c) shows the δ^{34}S values with distance from the HH Power Plant. No correlation was observed; however the lowest δ^{34}S value was closest to a main road which might indicate influence from traffic. As mentioned in Section 2.3 there were some problems with the sampling resulting in possible uncertainties of the measurements; 4) Dissolved H$_2$S can be oxidized to elemental sulfur in the presence of absorbed oxygen. Figure 4–5(d) shows measurements of sulfur in particulate matter samples collected at Station I where the sulfur that originated at sea has been subtracted as well as soil sulfur. No increase was observed in the sulfur content with time though the power plants increased emissions.

These results may appear to contradict the findings of other studies (Kristmannsdottir et al., 2000, Thorsteinsson et al., 2013) where measurements of H$_2$S were reported to decrease during precipitation. However, the results do not exclude decrease during precipitation but indicate that it was not due to dissolution.

For comparison it is informative to consider sulfur dioxide (SO$_2$) which is a sulfur compound that is known to be easily washed out by precipitation. According to Seinfeld and Pandis (2006) the Henry's constant of SO$_2$ is 1.23 M/atm and for H$_2$S 0.1 M/atm at 298 K. This difference increases when the effective Henry's constant is calculated via Seinfeld and Pandis (2006). For pH 5.6 at 298K the effective Henry's constants becomes $H^*_{SO_2} = 6534\ ^M/_{atm}$ compared to $H^*_{H_2S} = 0.104\ ^M/_{atm}$, indicating a large difference in the potential washout of these two sulfur chemicals.

The above calculations and analyses of data indicate that H$_2$S was not washed out with precipitation or steam at the source in any significant amount compared to the 2012 emissions.
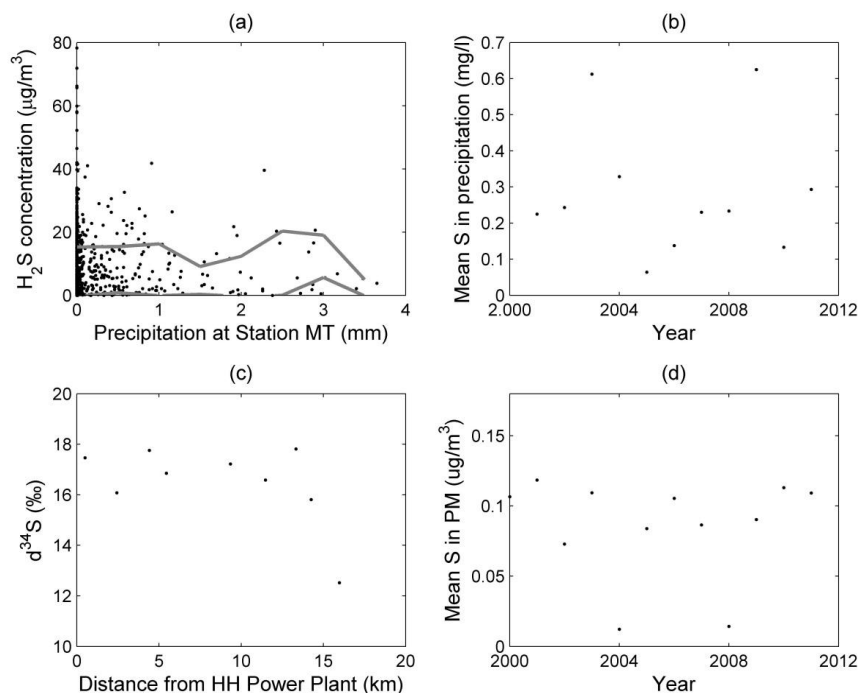
Figure 4–5. (a) H$_2$S plotted against precipitation at Station MT when winds were from the power plants towards the town (84°-159°). The solid lines show 50 and 90 percentiles, calculated at 0.5 mm intervals; (b) Mean sulfur content in precipitation measurements at Irafoss when the prevailing wind direction was from the power plants (corrected for oceanic sulfur); (c) δ^{34}S measurements in precipitation samples with distance from HH Power Plant; (d) Mean sulfur in particulate matter samples at Station I (corrected for oceanic and rock sulfur).

4.3.4 Vegetation uptake

Table 4–1 shows the mean sulfur concentration measured in the Woolly Fringe-moss at each sampling site at the NV and HH Power Plants (Figure 4–2), calculated as the per year accumulation since the start of power production. The amount is scaled with the time the wind directed the plume to the sites according to Station H, and the sulfur amount at Mt. Blafjoll was subtracted as the naturally occurring amount. The accumulated sulfur per year was plotted against the distance from source as shown in Figure 4–6, and an exponential fit was made through the dataset to best represent the accumulation. The amount of sulfur accumulated near field of each power plant per year can thus be represented by

$$\frac{m_{veget}}{t} = \int_0^\infty F \exp(-k_m r)\rho_{moss}h_{moss}\pi r\,dr,\qquad(4.12)$$

where m_{veget} is the amount of sulfur accumulated per kg of vegetation (moss), t is time (year), F is the accumulation at the source (1486.6 mg/kg/year, fit through dataset), k_m is the exponential decay constant (0.828 km^{-1}, fit through dataset), r is the distance from source, h_{veget} is the thickness of mature Woolly Fringe-moss (5 cm, Bjarnason, 1991) and ρ_{veget} is the density of Woolly Fringe-moss (44 kg/m^3 as measured in one sample). Assuming that there is continuous moss cover from the source, the equation yields 15 tons/year of sulfur or about 16 tons/year of H$_2$S accumulated at each power plant. Thus 32 tons of H$_2$S is accumulated at the power plants combined, which equals 0.11% of the 2012 emissions.
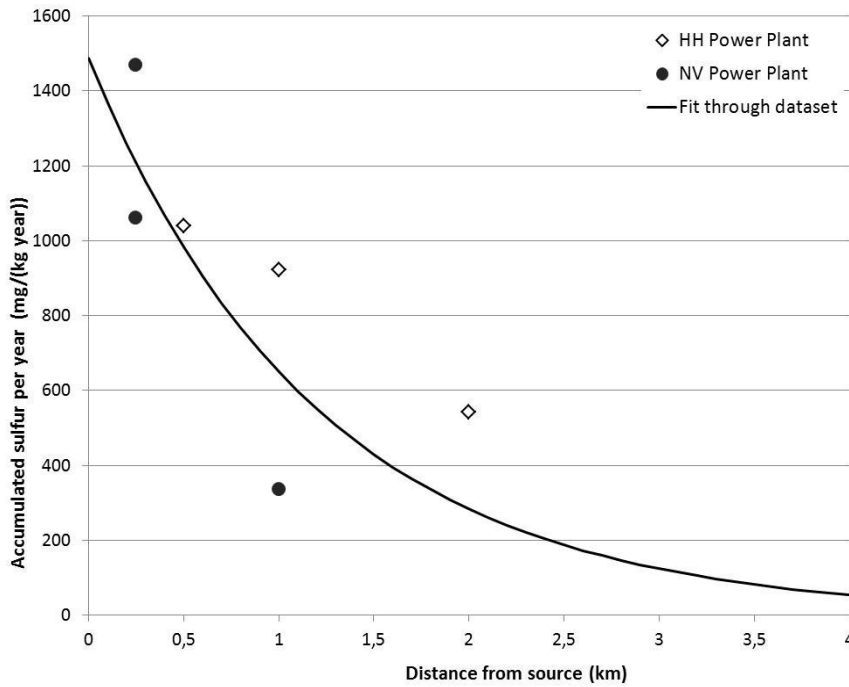
Figure 4–6. Sulfur accumulation plotted against distance from source. Points are measurements at NV and HH Power Plants, circles and diamonds, respectively. The line is a fitted exponential curve through the dataset.

It is emphasized that that this estimate is uncertain and it might be higher than the actual sulfur accumulation as continuous moss cover from the source was assumed. The sulfur content measurements at the HH Power Plant, both in the Woolly Fringe-moss and additional measurements in Glittering Wood-moss (made by the Icelandic Institute of National History, not shown), indicate that there might be more sulfur accumulation in the moss where hydrogen sulfide is more likely to accumulate, as in lowlands (Olafsdottir et al., 2014) and at the mountain sides close to the power plants where the plumes may contact the vegetation more easily than on the ground.

The above calculations and analyses of data indicate that uptake of H_2S by vegetation was insignificant compared to the 2012 emissions.

Table 4–1. Surface samples of Woolly Fringe-moss at HH and NV Power Plants.

	Location	Distance from cooling tower (km)	Mean sulfur content (mg/kg)	Time under stress from H_2S (%)	Accumulated sulfur per year (by EFLA) (mg/kg year)	# of measurements
HH Plant	HH-1 (emergency exit)	1	638	17	922	3
	HH-2 (HE-17)	0.5	562	12	1039	3
	HH-3 (power station)	2	515	18	542	6
NV plant	NV-1 (North)	0.25	3671	23	1469	6
	NV-2 (South)	0.25	1690	13	1061	4
	NV-3 (NE-19)	1	1010	21	336	1
Back-ground	Mt. Blafjoll	14	321			2

4.3.5 Soil uptake

The mass flux of H_2S into the soil, m_{soil}, is modeled by Fick's law,

$$m_{soil} = -D_{air} A_{plume} \frac{dC}{dz} n,$$ (4.13)

where D_{air} is the molecular diffusivity of H_2S in air, dC/dz is the concentration gradient in the soil and n is the assumed porosity of the soil (0.3). Judeikis and Wren (1977) found the deposition velocity of H_2S, V_g, from the diffusive flux in a laboratory experiment as follows:

$$-D_{air} \frac{dC}{dz} = V_g C_{air}$$ (4.14)

where C_{air} is the H_2S concentration at the boundary with the soil. The deposition velocity was found to be 0.015 cm/s for Adobe clay soil (±20%). By substituting the product of V_g and C_{air} in Fick's law and assuming the areal extent of the plume defined in Section 3.1 (with homogeneous surface), the gas transfer into the soil becomes 11 tons/year or 0.04% of the 2012 emissions.

It is emphasized that this is likely to be an overestimate as air does not diffuse freely into the soil neither during wintertime when earth is frozen, nor in the spring during the thawing period when the soil is saturated. This period is from November to March in Iceland, leaving about 7 months available for H_2S flux.

Once the H_2S has diffused into the soil, it can be absorbed onto the soil surfaces. Cihacek's and Bremner's (1990) laboratory experiments to assess the H_2S sorption capacities of soils suggest that Astoria silt loam can absorb 11.7 g of sulfur per kg of soil

when dry but 7.44 g/kg when moist. The result for moist Astoria silt loam was used for the Brown Andosol (BA), as the organic carbon content and clay content were the most similar of the soil samples tested. The soil area was assumed to be the total area of the study area excluding the area of Lake Thingvallavatn. Hence, depending on the soil density (BA, Arnalds, 2004), the top 10 cm of soil can absorb $1.4 \cdot 10^6$ tons of sulfur at a minimum, or $1.5 \cdot 10^6$ tons of H_2S. This is more than 50 times the amount emitted from the power plants in one year (2012); thus the sorption capacity of the soil is not a restriction on the soil uptake of the H_2S, but rather the diffusive transport of air into the soil.

The above calculations and analyses of data indicate that uptake of H_2S by soil was insignificant compared to the 2012 emissions.

4.3.6 Surface water uptake

Atmospheric H_2S can be dissolved in Lake Thingvallavatn when the wind direction is towards the lake, which is 10% of the time (on the basis of measurements at Station H). The flux of H_2S through the surface of the lake is modeled with

$$m_{water} = -k_w A_{water} dC, \qquad (4.15)$$

where m_{water} is the mass of H_2S dissolved in the water, k_w is the gas transfer velocity, A_{water} is the areal extent of water the gas covers and dC is (C_{sat} - C_0) where C_{sat} is the saturation concentration in the lake and C_0 is the H_2S concentration in the lake. Gaussian plume theory predicts that the average plume width over Lake Thingvallavatn during neutral air conditions is about 3 km. The length of the lake in the direction of the plume is about 10 km; thus about 30 km^2 of the lake are covered by the plume. Temperature and pH measurements made in the lakes in- and outflow were used for calculating the effective Henry's constant and C_{sat}. The C_0 in the lake was assumed to be zero as H_2S is quickly depleted from the water. Table 4–2 shows the parameters used and calculated. Using the overall transfer velocity reported for pH = 8 by Balls and Liss (1983) for a laboratory experiment, 36.9 cm/h (± 5%) for the equation above and parameters in Table 4–2 yields an uptake of 94 tons/per year or 0.33% of the H_2S emissions.

The uncertainty in the calculation is mainly dependent on the uncertainty in the transfer velocity estimate. The mass of H_2S dissolved in the lake is linearly dependent on the transfer velocity and saturation concentration which both increase with increasing pH. Balls and Liss (1983) give the transfer velocity at pH = 8 which was the highest pH measured in the outflow (Eiriksdottir and Gislason, 2013), hence yielding a conservatively high uptake. C_{sat} was calculated to give an even more conservative value by using the mean pH measured in the in- and outflow, but the inflow measurements were made straight from the spring entrance entering the lake. Hence, it is reasonable to expect that the uncertainty is within 100%.

The above calculations and analyses of the data indicate that insignificant amounts of H_2S were dissolved in Lake Thingvallavatn compared to the 2012 emissions.

Table 4–2. Parameters for Lake Thingvallavatn.

Parameter	Value	Reference
Mean pH in in- and outflow[*]	8.5	Eiriksdottir and Gislason (2013)
Mean lake temperature[*]	5 °C	Eiriksdottir and Gislason (2013)
k_w	36.9 cm/h	Balls and Liss (1983)
C_{sat}	0.0097 g/m^3	Fernandez-Prini et al. (2003)/ Seinfeld and Pandis (2006)
C_0	0	
A_{water}	30 km^2	

*Mean values found from measured inflow and outflow

4.4 Summary and conclusions

Table 4–3 shows a summary of the sinks and associated estimates of H_2S depletion set forth in the previous section. The table shows that the total of H_2S sinks identified in the study account for about 1% of the total H_2S emissions in 2012.

Table 4–3. Summary of H_2S depletion from the atmosphere by identified sinks.

	Atmospheric H$_2$S depletion	
	(tons/year)	% of 2012 emission
Oxidation	187	0.66
Washout	0.06	< 0.001
Dissolved in steam	2.6	0.009
Vegetation	32	0.11
Soil	11	0.04
Lake Thingvallavatn	94	0.33
Total	327	1.15%

Oxidation is the largest sink estimated, depleting 187 tons/year, on the basis of the 2012 emissions, but leaving the sulfur still in the gas-phase which is likely to be transported rapidly out of the area. The H_2S depleted by other sinks, about 140 tons, are retained in the area, mostly in the surface water of Lake Thingvallavatn or 94 tons/year. Eiriksdottir and Gislason (2013) report an increase of over 1000 tons/year of sulfur in the lake outflow compared to the inflow (when measured mean sulfur amount in the inflow is extrapolated to the whole inflow), or about 1100 tons/year of H_2S if this difference was because of uptake in the lake. This is more than ten times the estimated uptake in the Lake Thingvallavatn; thus atmospheric uptake does not solely seem to explain the difference between the in- and outflow. About 32 tons/year of H_2S are estimated to accumulate in moss within a few kilometers of the power plants as the accumulation rate decreased exponentially from the source. Moss damage has been confirmed to a greater extent at the NV Power Plant, which has been in operation longer than the HH Power Plant. Whether the damage is because of sulfur accumulation or other processes has not been established. Atmospheric transfer to soils was estimated with Fick's law to be about 11 tons/year which are likely to leach out of the soil (Smith et al., 1972). The estimated uptake is much less than the estimated uptake potential of the soils. Washout with precipitation (pH = 5.6) and steam at the source (pH = 6.7) were estimated to be about 60 kg/year and 2.6 tons/year, respectively. The H_2S is unreactive at low pH as in the precipitation making it the smallest estimated sink.

There were considerable uncertainties in the depletion estimations, both in models used and parameters measured. However, for oxidation, H_2S dissolved in steam, uptake by vegetation, soil and surface water the estimation calculations were conservative, that is, yielding an approximated upper bound estimate of the depletion. The oxidation assumed that the OH radical was solely reacting with H_2S. The steam from the cooling towers was assumed not to evaporate. The uptake by both vegetation and soil assumed homogeneous surface in the study area, over the whole year and the uptake by Lake Thingvallavatn was modeled using the upper limit of pH measurements as higher pH yield more H_2S being dissolved. For the washout, the uncertainty is mainly associated with the precipitation amount and the time it takes the H_2S dissolving in the water to reach equilibrium but the amount is so small that even uncertainty of two orders of magnitude will not affect the total depletion in any significant way. Hence, the results strongly indicate that the depletion of H_2S from the atmosphere in the study area was insignificant compared to the emissions. Therefore the greater part of the emission from the power plants, of over 28,000 tons, in 2012, was transported out of the area.

Appendix

Table A4-1. Definitions:

Symbol	Definition	Value	Reference
σ_y	Horizontal dispersion parameter (m)	1642 m	Turner, 1994
σ_z	Vertical dispersion parameter (m)	272 m	Turner, 1994
$k_{H,H2S}$	Henry's constant (Pa)		Fernandez-Prini et al., 2003
p_{vap}	Vapor pressure (Pa)		Wagner and Pruss, 1993
T_C	Critical temperature (K)		
T	Temperature of solvent (K)	283 K	
T_R	T/T_C		
τ	$1-T_R$		
$k^*_{H,H2S}$	Effective Henry's constant (Pa)		Fernandez-Prini et al., 2003, Seinfeld and Pandis, 2006
$[H^+]$	10^{-pH}		
K_{a1}	First dissociation constant	$10^{-6.99}$	Arnorsson et al, 1982
K_{a2}	Second dissociation constant	$10^{-17.07}$	Arnorsson et al, 1982
p_{H2S}	Partial pressure of H_2S in air		
M_{H2S}	Molar mass of H_2S	34 g/mol	
R	Gas constant	0.08206 L·atm/K·mol	
x_{H2S}	Mole fraction of H_2S in water		

Simple Gaussian plume

In neutral air σ_y is 1642 m at distance of 35 km; 95% of the mass in the plume is within $4\sigma_y$ so the plume is assumed to be 6568 m wide at the edge of the study area. This gives a plume area of $1.1 \cdot 10^8\, m^2$. In neutral air σ_z is 272 m in distance of 35 km. The plume height was assumed to be represented by $2\sigma_z$ (as it is limited by the ground) at 35 km or 544 m over the whole area. The mean wind speed at Station H was 7 m/s, yielding 83 minutes of traveling time out of the area. In 83 min, 4.5 tons of H_2S were discharged into the atmosphere on average in 2012. Assuming homogeneous distribution within the plume volume, this yielded a concentration of C_{air}=72 µg/m^3.

Washout calculations

Henry's constant was found using (Fernandez-Prini et al., 2003),

$$\ln\left(\frac{k_{H,H_2S}}{p_{vap}}\right) = \frac{-4.51499}{T_R} + \frac{5.23538\tau^{0.355}}{T_R} + 4.42126T_R^{-0.41}\exp(\tau) \tag{A4.1}$$

Taking into account the ionization of H₂S in water at the pH of unpolluted precipitation in Iceland (pH 5.6) the effective Henry's law coefficient becomes (Seinfeld and Pandis, 2006)

$$k_{H,H_2S}^* = \frac{k_{H,H_2S}}{\left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1} * K_{a2}}{[H^+]^2}\right)} = \frac{k_{H,H_2S}}{1.04} \tag{A4.2}$$

The Henry's constant found for 10°C is $k_{H,H_2S} = 37.26\ MPa \Rightarrow k_{H,H_2S}^* = 35.80\ MPa$. The partial pressure of H₂S is found assuming the gas behaves ideally

$$p_{H_2S} = \frac{R \cdot T \cdot C_{air}}{M_{H_2S}} \tag{A4.3}$$

The molar fraction of dissolved H₂S in the water becomes

$$x_{H_2S} = \frac{p_{H_2S}}{k_{H,H_2S}^*} = 1.4 \cdot 10^{-10} \tag{A4.4}$$

Hence, in $2.27 \cdot 10^8$ m³ or $1.26 \cdot 10^8$ moles of water 1765.6 moles of H₂S are dissolved or 60 kg.

Acknowledgments

5 Summary of the Near Field Fate of Hydrogen Sulfide

The fate of a chemical from the time that it is emitted to the time it is depleted from the atmosphere depends on the chemical characteristics and the environmental conditions. The fate of hydrogen sulfide emitted from the geothermal power plants at Nesjavellir and Hellisheidi, in southwest Iceland, is largely controlled by the weather conditions and the surroundings of the power plants. In this research the focus has been on identifying factors that influence ambient air concentration of H_2S other than emission. The H_2S distribution in the atmosphere and how it is depleted from the atmosphere determines its fate and whether or not it has harmful effects on the environment.

In Chapter 2 (Journal paper 1) the impacts of meteorological factors on ambient air concentration are analyzed showing that wind features and air stability greatly affect the concentration. The paper in particular analyzed the conditions in Reykjavik City and the main conclusions were that H_2S concentration was elevated when the wind direction was 54°-125°, wind speed was between 1.5 and 4 m/s and the air was stable. An attempt was made to further analyze the H_2S concentration with respect to air stability by plotting the concentration as a function of the Richardson number. The results are shown in Appendix C and seem to further demonstrate the strong role the air stability plays in determining the H_2S concentration. However, as discussed in the appendix, the meteorology data used to calculate the Richardson number might not be conclusive.

In Chapter 3 (Journal paper 2) extensive measurements of H_2S plumes within a 10-30 km distance from the power plants were presented, analyzed and modeled. The results showed that terrain features and surface roughness as well as meteorological factors affect the H_2S distribution. The main conclusions were that plumes showed self-similarity, were guided in mountainous terrain and changed paths due to spatial variability in the wind field. Spatial distribution of H_2S is thus largely dependent on meteorological factors and terrain features. AERMOD modeling demonstrated some key features in the plume distribution such as narrower plumes with higher maxima further from the source when passing over smoother terrain such as lakes. However, the model was not able to capture the distribution in complex terrain showing the importance of incorporating spatial variability in the wind field in the model. The AERMOD model is a steady state model using an advection-diffusion model may give better results in complex terrain (as in Costa et al., 2005) and coupling it with a mass-consistent diagnostic wind model such as DWM (US EPA, 1990) as Granieri et al. (2013) did for the urban area of Naples.

The results reported in Chapter 4 (Journal paper 3) showed that the depletion of the chemical from the atmosphere within the study area was insignificant with about 99% of the 2012 emissions transported out of the area. The H_2S from the two power plants was thus indicated to be transported over long distances from its source. However, although great majority of the H_2S was transported out of the area large amounts are retained within the study area. In Figure 5–1 the estimated sinks in Table 4–3 are depicted, showing that the largest sinks of the chemical were oxidation with the OH radical, and uptake by surface water. Oxidation is indicated to be a slow process and slower during winter when there is

little radiation. After oxidation the sulfur is still in the gas-phase which is likely to be transported rapidly out of the study area. The H_2S, depleted by other sinks, is retained in the area, mostly in the surface water of Lake Thingvallavatn. About 90% of the water in the lake comes from large underground springs that travel a long way, resulting in more dissolved chemicals in the water. Eiriksdottir and Gislason (2013) reported an increase of over 1000 tons/year of sulfur in the lake outflow compared to the measured inflow (when expanding the measured sulfur in the inflow to the total inflow). If this difference resulted from H_2S uptake from the atmosphere it would equal about 1100 tons/year of H_2S being dissolved in the lake. This is more than ten times the estimated uptake in the Lake Thingvallavatn, indicating that atmospheric H_2S is not the sole reason for the difference between the in- and outflow. About 32 tons/year of H_2S were estimated to have accumulated in moss within a few kilometers of the power plans. Moss damage has been confirmed at both Nesjavellir and Hellisheidi Power Plants but to a greater extent at the Nesjavellir Power Plant, which has been in operation longer. Whether the damage is because of sulfur accumulation or other processes has not been established though other factors have been suggested e.g. hot water or steam. Atmospheric transfer to soils was estimated to be much smaller than the estimated potential uptake as diffusion of H_2S was a limiting factor. The H_2S taken up by soil is likely to leach out of the soil (Smith et al., 1972). Washout was estimated to be the smallest sink as H_2S had low partial pressure in the atmosphere and was unreactive at low pH as in the precipitation. The uncertainties in the estimations are large as most sinks were estimated with theory. But as discussed in Chapter 4 the estimated sink magnitudes are conservative, that is, yielding an approximated upper bound of the depletion.

Figure 5–2 shows the study area divided in two main segments, towards the land and towards the ocean. Table 5–1 shows the yearly amount of H_2S distributed towards each segment based on the 2012 emission data and the percentage of wind measured at Station H (data from 2001-2012, see Appendix B) towards each segment. About 40% of the gas emission was expected to go further inland and 60% towards the ocean. Some of the H_2S transported over the ocean is likely to be dissolved in the ocean. Majority of the H_2S is likely to be oxidized in the atmosphere over time to SO_2 as indicated by the estimated sinks in Chapter 4.

The two smaller segments in Figure 5–2 include the capital area and Lake Thingvallavatn. Based on wind data from Station H, wind direction was towards the capital area 15% of the time, indicating that about 4200 tons of H_2S were transported over the capital area in 2012. Chapter 2 showed that wind direction in which H_2S concentration at Grensasvegur Measuring Station increased was about 35% of the time. This difference indicates effects of terrain and shows in part the difference in estimating one main source instead of two. Furthermore, Olafsdottir et al. (2008) predicted that H_2S plumes did not distribute evenly over the city. This indicates that the amount of H_2S towards the capital area might be somewhat underestimated.

The estimation of H_2S sinks showed that the uptake in Lake Thingvallavatn was the second largest sink. The lake is the largest natural lake in Iceland (83 km^2). In spite of it being rather deep, cold and surrounded with lava with little vegetation, there is a diverse ecosystem in the lake (Jonasson and Hersteinsson, 2002). The lake and its river basin are considered one of Iceland's natural treasures. Table 5–1 shows that the wind blew towards the lake 10% of the time, yielding about 2800 tons of H_2S crossing over the lake and its surroundings per year, based on the 2012 emissions. Estimated uptake is 94 tons/year or about 3.3% of the atmospheric H_2S estimated to be transported over the lake. As formerly

mentioned, there seem to be larger sources of sulfur to the lake other than uptake of atmospheric H_2S.

The results of the research show that the H_2S from the Nesjavellir and Hellisheidi Power Plants is distributed with wind and terrain, often in narrow plumes, and that it may accumulate along mountain ranges or in lows in the landscape but in the end the most of it is transported out of the area as H_2S. The sinks estimated indicate that the H_2S is oxidized to SO_2 with time in the atmosphere or dissolved in the ocean. Other sinks are expected to be insignificant.
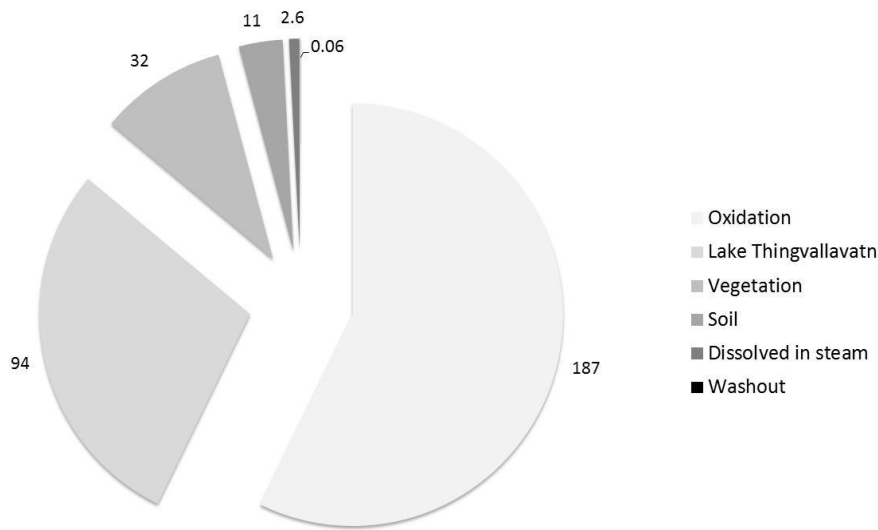
Figure 5–1. Depletion by each identified sink in tons/year.

Table 5–1. Segment division of the study area.

Segment	Angle size degree	Size (km²)	Wind direction towards segment (°)	Wind towards segment (%)	H_2S (1,000 tons/year)*
Lake Thingvallavatn	50	535	200-250	10	2,823
Capital area	50	535	80-130	15	4,235
Land	180	1924	130-310	41	11,574
Ocean	180	1924	310-130	59	16,656

*Based on 2012 emission data
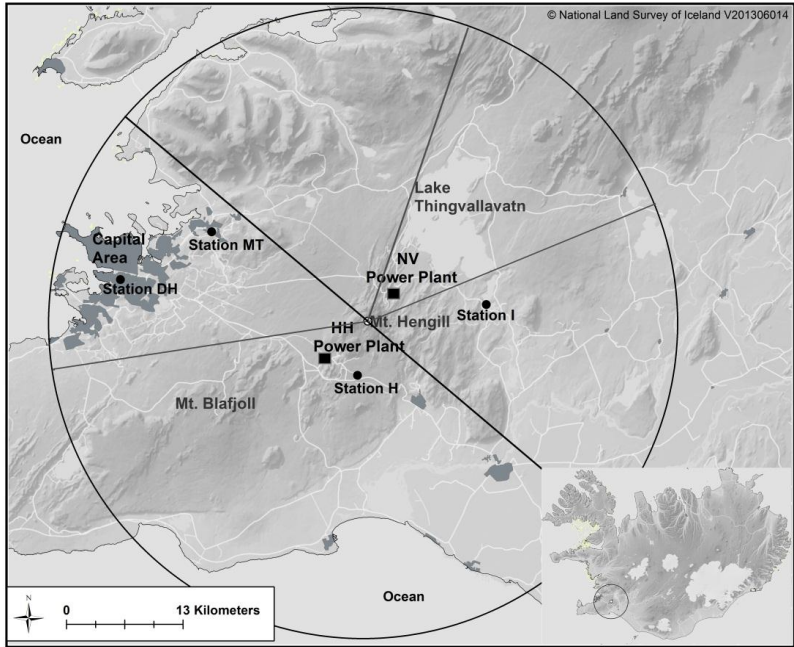
Figure 5–2. Segment division of the study area.

6 Conclusions and Future Directions

Emissions of hydrogen sulfide have been increasing worldwide as it is associated with various industries such as coal gasification plants, oil refineries, landfill sites and wastewater treatment plants as well as geothermal energy production. Geothermal energy production has been expanding in Iceland for the past few decades. Currently, there are six geothermal power plants in Iceland with total H_2S emission of about 36,400 tons per year. In 2012 over 28,000 tons of H_2S were emitted from the Nesjavellir and Hellisheidi Power Plants in southwest Iceland. Within a 35 km distance from the power plants is the capital area and a number of smaller towns and farms with over 200,000 inhabitants. The Icelandic Ministry for the Environment has set a health limit of 50 µg/m^3 for a 24-hr average but the odor can become a nuisance at a concentration as low as 7 µg/m^3 for half-hour values (WHO, 2000). This research investigated the distribution of H_2S from the Nesjavellir and Hellisheidi Power Plants, identified and analyzed factors impacting the atmospheric concentration, atmospheric spreading and depletion of the chemical from the atmosphere. The results will benefit those who are concerned about the atmospheric concentration of the chemical regardless of its source and those who may be implementing mitigation measures.

The research on H_2S concentration in Reykjavik City during events of easterly winds addressed the effects meteorological factors had on the atmospheric H_2S concentration while the analysis of measured plumes surrounding the power plants addressed the effects meteorological factors had on plume distribution. Furthermore, H_2S sinks of meteorological origin were identified with other sinks. The results showed that wind direction is one of the prevailing factors controlling atmospheric concentration and distribution. The concentration in Reykjavik City increased when the wind direction was in the range of 54°-125° as measured at the Bustadarvegur Measuring Station in Reykjavik. Some convergence of the two plumes from the power plants was shown and plumes were observed to shift from the original path, due to spatial variability in the wind field. Wind speed was found to be negatively correlated to H_2S concentration as plumes had higher maxima in lower wind speeds. H_2S concentration in Reykjavik City was highest when the wind speed was between 1.5 and 4 m/s and decreased rapidly with higher wind speeds. For slower wind speeds the plume did not reach Reykjavik fast enough to make an impact unless there was a strong temperature inversion, during which there is limited vertical movement and the cold air closest to the ground flows downhill from Hellisheidi Power Plant to Reykjavik. The highest concentrations observed both in Reykjavik City and in the plumes measured were during such an inversion. In more unstable air, plumes had more spread and lower concentrations. No correlation between H_2S concentration and radiation was found, other than radiation being correlated with air stability. Temperatures below 3°C were correlated with the H_2S concentration in Reykjavik City with concentration rising with decreasing temperatures. Washout of H_2S with precipitation in the area was estimated to be insignificant, although plume measurements showed lower H_2S concentration following precipitation. No correlation was observed between precipitation and H_2S concentration in Reykjavik City and the town of Mosfellsbaer. However, comparison of measured plumes in similar weather conditions showed that the concentration was lower following precipitation. These results may appear to contradict each other but the result

does not exclude a decrease during precipitation but rather indicated that it is not due to dissolution. The results showed which weather factors result in higher H_2S concentration and that events of high H_2S concentration in Reykjavik can be predicted by using a current weather forecast. Solely using the analysis from Reykjavik and weather forecast should give a good prediction for events of high H_2S concentration but the prediction may be enhanced further by using a diagnostic wind model coupled with a distribution model. Forecasts are made on a 3 km grid up to 48 hours in advance for the area which could be implemented in the model. This could potentially be utilized in mitigating the ambient air concentration.

The research on plume distribution addressed the effect that terrain and surface roughness had on the H_2S distribution. The results showed that the distribution of H_2S plumes was heavily dependent on terrain in mountainous areas, especially during neutral and stable air conditions. Plumes were found to be guided by the terrain through mountain passes and along ridges. In some events concentration was increased and steady along a mountain ridge, indicating trapping of the plume. Wind direction in Reykjavik City with elevated H_2S concentration was slightly shifted from the physical locations of the power plants and plume patterns were observed to be repeated between seasons, both indicating effects of terrain on the distribution. AERMOD modeling of the plumes showed that over smoother terrain such as lakes, plumes are narrower with higher concentration further from the source, consistent with measurements of narrow plumes on the other side of Lake Thingvallavatn.

The research on natural near field sinks of H_2S from the atmosphere addressed the depletion of H_2S emitted from the Nesjavellir and Hellisheidi Power Plants due to various environmental transport processes. The results indicated that the largest sink within a 35 km distance from the power plants was oxidation, depleting about 187 tons/year or 0.66% of the 2012 emissions. The oxidized H_2S is expected to be transported out of the area in the gas phase, but H_2S depleted by other sinks is retained in the area for some time. The second largest sink was estimated to be uptake in Lake Thingvallavatn with 94 tons/year of H_2S dissolved in the lake, or 0.33% of the 2012 emissions. This amount is small compared to the measured sulfur difference in the lakes in- and outflow. Soil has good potential for taking up H_2S but H_2S flux through soil is a limiting factor. Uptake by soil was estimated to be much less than the potential soil uptake, or 11 tons/year which is 0.04% of the 2012 emissions. Mosses surrounding the power plants accumulate sulfur from the atmosphere but the accumulation rate was found to decrease exponentially with distance from the source. The sulfur accumulated in moss was estimated to be 32 tons/year or 0.11% compared to the H_2S emissions. Washout with precipitation (pH = 5.6) and steam (pH = 6.7) at the source were estimated to be the smallest sinks of about 60 kg/year and 2.6 tons/year, respectively. This was due to H_2S having low partial pressure in the atmosphere and being unreactive in the low pH. The uncertainties in the depletion estimations were large, both in models used and parameters measured. However, the estimated sink magnitudes were conservative, that is, yielded an approximated upper bound of the depletion. Depletion of H_2S from the atmosphere in the study area was estimated to be 327 tons/year which was about 1% of the 2012 H_2S emissions, an insignificant amount compared to the total. About 60% of the H_2S was transported towards the sea while about 40% moved further inland as estimated with weather data from Station H. The sinks estimated indicate that the H_2S is oxidized to SO_2 with time in the atmosphere or is dissolved in the ocean and that other sinks are insignificant.

One of the main challenges of the research was found to be associated with terrain features and their impact on the plume behavior. The Nesjavellir Power Plant is situated in a valley open only towards the northeast and the Hellisheidi Power Plant is located at a mountain site. Weather at both of these locations can be governed by the local effects from the mountains. Having good meteorological stations at the sites would be useful when researching the plume distribution. Mapping the terrain features and further researching their effect on plume distribution, e.g. towards Reykjavik City, would enhance the understanding of the H_2S concentration distribution.

Other challenges of the research were associated with sampling of precipitation and their sulfur measurements. Wind direction in the area changes frequently, making it hard to take precipitation samples downwind from the power plants. The sulfur in the atmosphere has various sources such as the ocean and fossil fuels. Weather forecasting and mapping of meteorological events before sampling, short sampling time, as well as choosing sampling sites away from traffic, would give better results. Laboratory testing of washout in drops would also further increase the understanding of the nature of the washout.

Several limitations were found that point to directions for further study.

Limitations regarding the measurements of the plume distribution were found in using only one measurement device and thus measuring one sample at a time. Further mapping of H_2S plumes with more than one measurement device would give the distribution with greater accuracy. Measuring the plume in the vertical and horizontal with a measurement airplane would show the distribution even better, making it possible to compare the vertical distribution to known models.

There were limitations with the AERMOD modeling regarding spatial variability in the wind field and the local terrain. Better representing these features in the model would give better simulations of the plumes. The modeling showed that surface roughness is of great importance in estimating the distribution of the plumes and finding the location of the maximum concentration within the plume, demonstrating the significance of making a local assessment of the roughness for the modeling. Furthermore, factors such as albedo and the Bowen Ratio used in the AERMOD modeling have not been measured in the study area.

The results indicated that H_2S concentration can be predicted by using a current weather forecast. A future research could be to incorporate weather forecasts to a diagnostic wind model coupled with a distribution model to predict H_2S concentration in the ambient air.

Further analysis of the H_2S concentration in Reykjavik might include more extensive analysis of the H_2S concentration in relation to parameters that combine more than one meteorological factor, such as the Richardson number or the Monin-Obukhov length.

Limitations were found to be associated with background values and chemical reactions in Icelandic circumstances. No measurements or local modeling were found on OH formation, though the radical is one of the most important chemical species in the atmosphere with high reactivity with both inorganic and organic compounds. Establishing the formation rate and the concentration of the radical in Iceland would benefit chemical modeling of the atmosphere.

Basic modeling of H_2S uptake in Lake Thingvallavatn showed that this is one of the largest sinks of H_2S in the area. Better modeling of the flux of H_2S is needed for more accurate determination of the depletion rate, as well as taking into account other surface waters and rivers in the area. The rate of uptake in the ocean would also be an interesting research project as about 60% of the emissions were estimated to have been transported towards the sea.

Limitations regarding uptake of H_2S in vegetation were found regarding the sampling sites of the moss. Further sampling of the moss, with sites chosen with regard to atmospheric distribution, thus taking into account sites where trapping of H_2S in lows can be expected, would give better overall estimates of the uptake.

Soil uptake of H_2S was made with Fick's law. Further estimations should be made with sulfur measurements of the soil and estimations of the soil porosity.

In summary it is concluded that the distribution and the ambient air concentration of H_2S is dependent on meteorological factors, terrain features and other environmental factors in the surroundings of the source. Meteorological factors such as wind speed and temperature were negatively correlated to atmospheric H_2S concentration. Higher air stability yielded higher concentration. Plumes of H_2S were guided by terrain and their distribution affected by surface roughness. Modeled plumes gave important information on plume behavior but factors such as spatial variability in the wind field need to be incorporated in to the model for improved modeling. The depletion of H_2S from the atmosphere was estimated to be a slow process, H_2S can thus be transported over long distances. Oxidation was estimated to be the largest sink in the area and uptake in Lake Thingvallavatn the second largest. Smaller sinks were uptake by vegetation and soil, and washout in steam from the source, but the smallest sink was estimated to be washout with precipitation. Further mapping of plume distribution and terrain is needed for better understanding of the near field plume behavior. Estimation of various parameters needed for depletion assessment and further analyses of sinks should be carried out for more accurate depletion estimation.

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Appendix A

Appendix A describes the extent of measurements of atmospheric H_2S and precipitation samples taken for sulfur measurements. The H_2S measurements were made on roads surrounding the power plants while bottles for precipitation samples where put out to collect precipitation for 24-hours.

Figure A-1 shows locations of measurement points where atmospheric H_2S measurements were taken (black dots) and locations for precipitation sampling (pink diamonds) relevant to the Nesjavellir and Hellisheidi Power Plants (green and read squares, respectively). Furthermore, the figure shows the coastline (black line) and the location of Reykjavik City (blue star).

Table A-1 shows dates of measurements for both atmospheric H_2S and of precipitation sampling, also the start and end location of the measurements in each event.
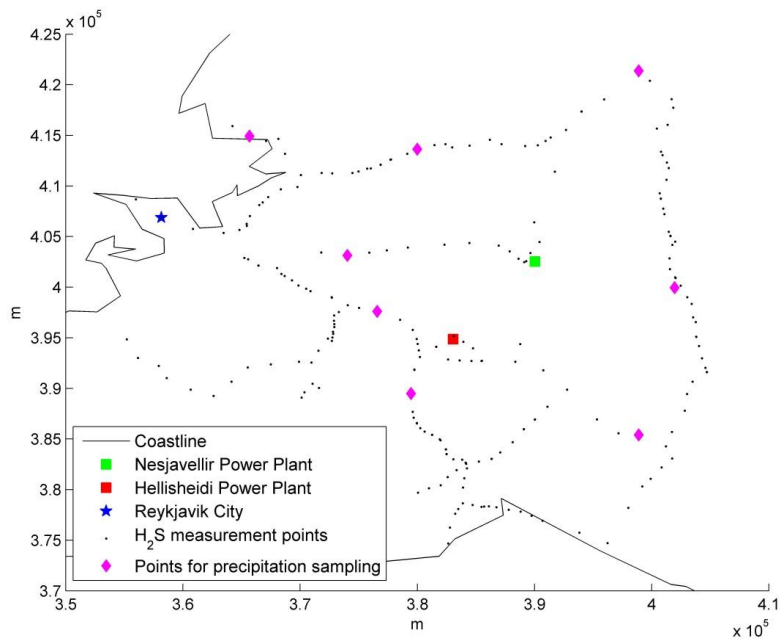
Figure A–1. Locations of atmospheric H₂S measurements (black dots) and precipitation sampling (pink diamonds). Nesjavellir and Hellisheidi Power Plants are depicted as green and red squares, respectively. Axes have ISN93 coordinates.

Table A–1. Date of atmospheric H$_2$S measurements and of precipitation sampling. Start and end locations of atmospheric measurements are also shown.

Date.	Measured H$_2$S	Measured precipitation	Measured from	Measured to
2009				
9-Jan		x		
10-Jan		x		
19-Jan	x		Kjalarnes	Miðdalsheiði
20-Jan	x		Mosfellssveit	Hellisheiði
21-Jan	x		Mosfellssveit	Miðdalsheiði
22-Jan	x		Reykjavík	Hveragerði
16-Feb	x	x	Mosfellssveit	Hellisheiði
17-Feb	x	x	Mosfellssveit	Þingvellir
18-Feb	x		Mosfellssveit	Þrastarlundur
19-Feb	x		Gljúfrasteini	Írafoss
24-Mar	x		Reykjavík	Selfoss
25-Mar	x		Reykjavík	Selfoss
26-Mar	x		Reykjavík	Selfoss
27-Mar	x		Reykjavík	Selfoss
27-Apr	x		Mosfellssveit	Þrastarlundur
28-Apr	x	x	Kjalarnes	Þingvellir
29-Apr	x	x	Kjalarnes	Þingvellir
30-Apr	x		Bláfjöll	Selfoss
15-Jun	x		Gljúfrasteinn	Reykjavík
16-Jun	x	x	Gljúfrasteinn	Bláfjöll
17-Jun	x	x	Kjalarnes	Selfoss
18-Jun	x		Bláfjöll	Selfoss
15-Jul	x		Kjalarnes	Miðdalsheiði
16-Jul	x		Reykjavík	Selfoss
17-Jul	x		Kjalarnes	Þingvellir
11-Aug	x		Reykjavík	Hveragerði
12-Aug	x		Reykjavík	Írafoss
13-Aug	x		Þingvellir	Hellisheiði
14-Aug	x		Reykjavík	Selfoss
24-Aug	x	x	Þingvellir	Hellisheiði
25-Aug	x	x	Mosfellssveit	Hellisheiði
15-Sep	x		Þingvellir	Selfoss
16-Sep	x	x	Gljúfrasteinn	Selfoss
17-Sep	x	x	Gljúfrasteinn	Selfoss
18-Sep	x		Mosfellssveit	Þrastarlundur
20-Oct	x		Reykjavík	Selfoss
21-Oct	x		Reykjavík	Selfoss
22-Oct	x	x	Reykjavík	Selfoss
23-Oct	x	x	Reykjavík	Selfoss
10-Nov	x		Þingvellir	Selfoss
11-Nov	x		Reykjavík	Írafoss
12-Nov	x		Reykjavík	Selfoss
7-Dec	x		Reykjavík	Þorlákshöfn
8-Dec	x		Reykjavík	Hveragerði
9-Dec	x	x	Reykjavík	Hellisheiði
10-Dec	x	x	Reykjavík	Þingvellir

Appendix B

Appendix B shows a wind rose of wind data measured at Hellisheidi Weather Station 2001-2012, data was obtained from the Icelandic Road Administration. The wind rose was used to estimate H_2S distribution, within the study area, and to estimate the proportion of H_2S transported further inland and towards the ocean.
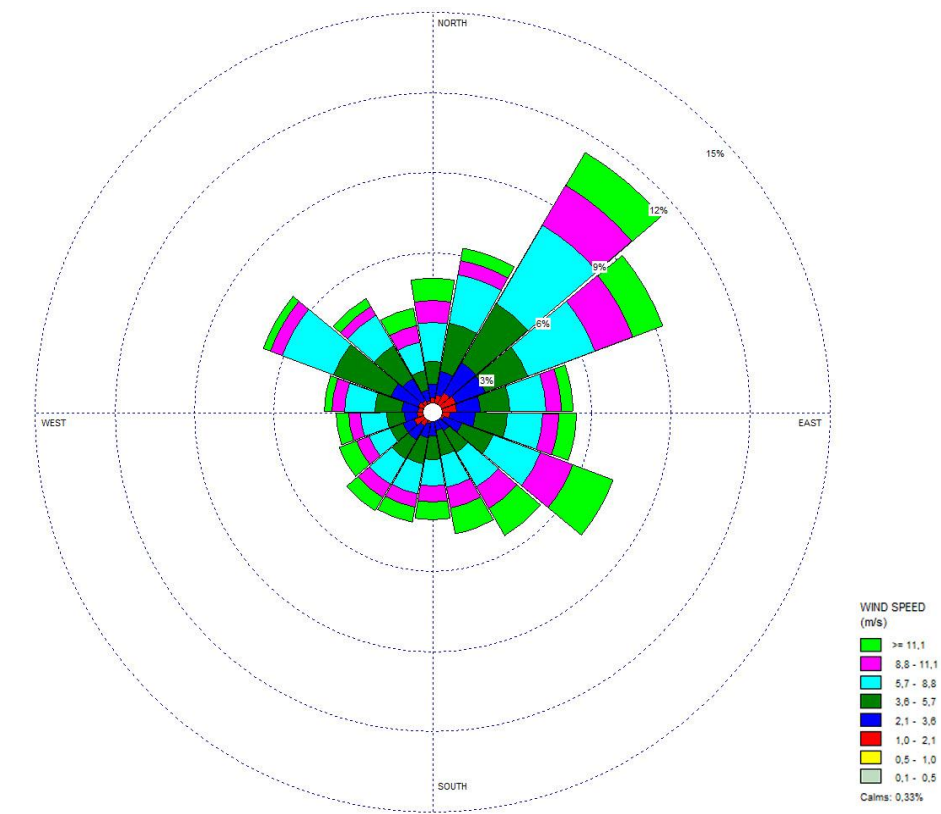
Figure B–1. Wind rose of wind data from Station H, 2001-2012.

Appendix C

Appendix C discusses an attempt in analyzing the H_2S concentration as a function of the Richardson number for selected events from Chapter 2.

In Chapter 2 the H$_2$S concentration was analyzed with respect to various weather variables. An attempt was made to further analyze the data by using the Gradient Richardson number (*Ri*) Method which is used in micrometeorology to determine air stability (Mohan and Siddiqui, 1998). The Richardson number is calculated by using the wind speed and temperature measurements at two heights to calculate the gradient Richardson number from the following equation:

$$Ri = \frac{g(\Delta\theta/\Delta Z)}{T(\Delta u/\Delta Z)^2}$$

(C.1)

where θ is the potential temperature, Z is the measurement height, u is the wind speed, T is the screen temperature, and g is the acceleration due to gravity. The method was applied to a sample of events of easterly winds in Reykjavik City from Chapter 2 by using upper air data from Keflavik airport (at noon and midnight), during the events or as close to the event time as possible. The Keflavik airport is about 60 km from the study area and the resolution of the data close to the ground is not optimal for such calculation. Furthermore, the different characteristics of the area might also introduce uncertainty. However, an attempt was made to calculate the *Ri* number for the above events. The result is shown in Figure C-1 where the mean H$_2$S in each event is plotted as function of the Richardson number. It is noted that five of the events are not shown as the *Ri* number calculated was deemed unreliably due to low resolution in the data collected. The figure seems to indicate that the H$_2$S concentration increases as the Richardson number increases which is consistent with results from Chapter 2 as higher *Ri* means increasing air stability. However, when the calculated *Ri* number was compared to the range given by Mohan and Siddiqui (1998), estimated for a site with roughness length 0.1 m, the *Ri* values are rather large. This may be due to low resolution of the upper air data or differences in site characteristics. Hence, the figure is shown here as further indication of the strong role air stability plays in determining the H$_2$S concentration but it is emphasized that the results shown in the figure based on the collected data might not be conclusive.
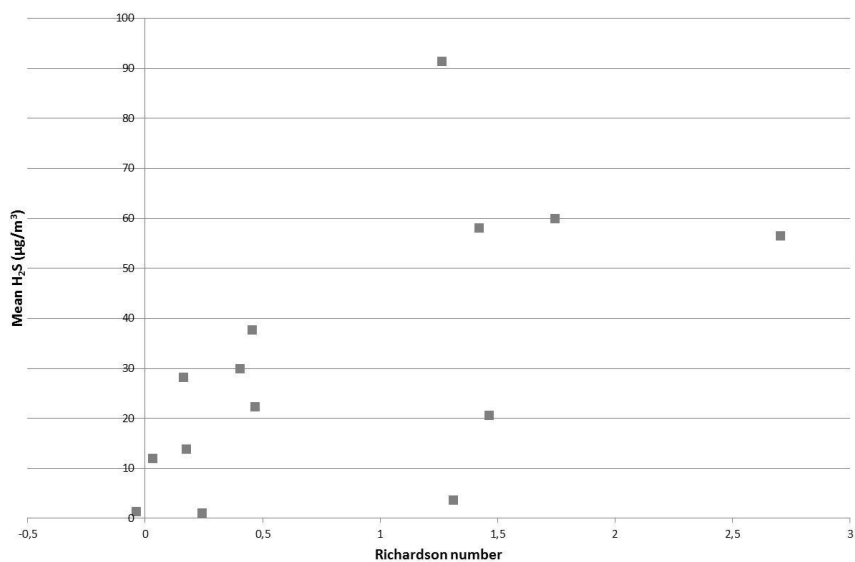
Figure C–1. H₂S concentration for selected events of easterly winds as a function of Ri number based on available meteorology data at Keflavik airport. The data quality is discussed in the text.

Appendix D

Appendix D contains a conference paper presented at the World Geothermal Congress 2010 in Bali. In the paper the H_2S concentration in Reykjavik was analyzed by comparing weather parameters measured in Reykjavik (Station BV) and at Middalsheidi Heath (Station M), during events of different H_2S concentration in the city. Events of H_2S measurements around the power plants were compared.

Olafsdottir, S., Gardarsson, S.M., Armansson, H. 2010. Concentration of hydrogen sulfide from geothermal power plants in the vicinity of Reykjavik City, Iceland 2007-2009. Proceedings World Geothermal Congress 2010, Bali, Indonesia, 25–29 April (2010).

Concentration of Hydrogen Sulfide from Geothermal Power Plants in the vicinity of Reykjavik City, Iceland, 2007-2009

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Keywords: Hydrogen Sulfide, Geothermal Power Plants, air pollution, weather factors

ABSTRACT

Gases emitted from geothermal power plants are among the key environmental factors of concern for the development of geothermal power plants. Sulfur gases are of most concern but also trace gas and carbon dioxide (CO_2) emissions. Sulfur is emitted from geothermal areas as hydrogen sulfide (H_2S), and when the areas are developed the emission is increased. H_2S is a volatile compound that may be oxidized in the atmosphere. Several environmental factors influence the H_2S oxidation rate, such as radiation, precipitation, temperature and concentration of other chemicals. Geothermal power production in the vicinity of Reykjavik City has increased considerably during the last few years. Electricity production at Nesjavellir Geothermal Power Plant started in 1998 and in October 2006 the Hellisheidi Geothermal Power Plant started operation and was enlarged in the fall of 2008. The Department of Environment of Reykjavik City started measuring hydrogen sulfide (H_2S) concentration at Grensasvegur Street in February 2006. In August 2007 H_2S measurements started in Hvaleyrarholt, Hafnarfjördur, and in June 2008 in Kopavogur town. The main objective of this paper is to shed light on which parameters influence the concentration of hydrogen sulfide in Reykjavik City and its surroundings.

1. INTRODUCTION

Gaseous sulfuric compounds in geothermal areas exist in the form of hydrogen sulfide (H_2S). When the geothermal areas are developed the hydrogen sulfide is, usually, emitted at a higher rate to the environment than before development (Armannsson, 2002). The hydrogen sulfide has a characteristic smell that can be detected at low concentrations. At about 300.000 µg/m^3 the sense of smell is lost, at 450.000 – 750.000 µg/m^3 pulmonary oedema can form with the risk of death (WHO, 2000). No health limit value is set for the concentration of hydrogen sulfide in air in Iceland. The World Health Organization (WHO) has given a guideline value of 150 µg/m^3 as an average value for 24 hours. WHO also gives a value for the smell to become a nuisance, at 7 µg/m^3 over a 30 minute average. The hydrogen sulfide is unstable in air compared to sulfur dioxide (SO_2) and if conditions are favorable oxidation may take place (Armannsson, 2002; Kristmannsdottir et al., 2000). The Nesjavellir power plant which is about 20 km east of Reykjavik started hot water production in 1990 and electricity production in 1998. Currently the hot water production is 300 MW and the electricity production 120 MW. The Hellisheidi power plant which is about 15 km southeast of Reykjavik was commissioned in October 2006. Currently the electricity production is 213 MW and hot water production is planned to start in 2010. The power plants and the weather stations used in the study are shown in Figure 1.

In 1993 short term measurements were made of hydrogen sulfide and sulfur dioxide concentrations (Kristmannsdottir et al., 2000) in 10 high-temperature geothermal fields in Iceland, both energy producing and non-producing fields. As a continuation of those measurements, long term measurements (4-6 months) were made in the producing fields of Svartsengi, Nesjavellir, Krafla and Namafjall in 1994-1996. The results show that the hydrogen sulfide concentration depends on both precipitation and wind conditions. Modeling using the data suggested that only a small fraction of the hydrogen sulfide is converted to sulfur dioxide within a 15-25 km radius. However due to uncertainties, for example insufficient number of measurements, the modeling did not give conclusive results.

D'Alessandro et al. (2008) report a rapid decrease of concentration values away from the emission points when analyzing the air concentrations and dispersion pattern of naturally emitted H_2S in the geothermal area of Sousaki (Corinthia, Greece). The decrease was more pronounced in summer than in winter which indicates that it is not only due to a dilution effect, but also to redox reactions favoured by higher temperatures and intense sunlight typical of the summer period.
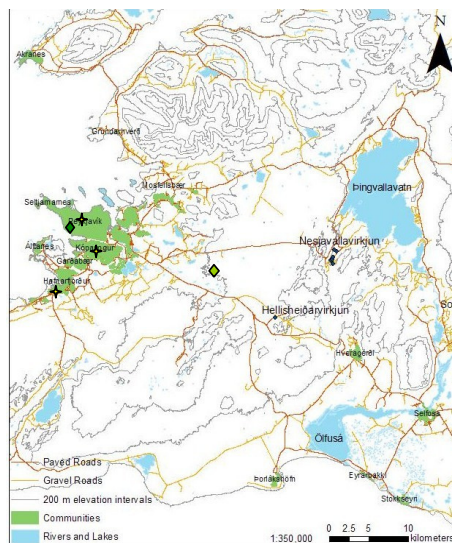

Figure 1. Map of the area showing Grensasvegur measuring station (✦), Kopavogur measuring station (✦), Hvaleyrarholt measuring station (✦) Reykjavik weather station (◆), Middalsheidi weather station (◆), Hellisheidi Power Plant (■) and Nesjavellir Power Plant (■■).

1

Olafsdottir, Gardarsson and Armannsson

When mapping the distribution of hydrogen sulfide across the City of Rotorua in New Zealand a passive sampler was developed (Horwell et al., 2005). Two of these were located in each square of a grid map of the city. The hydrogen sulfide concentrations could thus be measured simultaneously at approximately 70 locations. The results showed that City of Rotorua can be divided into three zones: A low concentration area in the west, a medium concentration area in the east and a high concentration zone in the centre.

In the 1-million-population city of Thessaloniki, Greece, the H_2S concentrations were measured in the center of the city at a crossing of two major roads (Kourtidis et al.). The highest concentrations of H_2S were observed in winter, while the highest hourly concentrations where observed during the 7:00–9:00 rush hour. Daily mean concentrations in winter were up to 30 µg/m³, while hourly concentrations were up to 54 µg/m³.

2. ANALYSIS OF H₂S IN REYKJAVIK CITY

Hydrogen sulfide has been measured in Reykjavik City since February 2006 at the Grensasvegur measuring station; in Kopavogur Town since August 2008; and in Hvaleyrarholt, Hafnarfjördur, since August 2007 (see Figure 1). Electricity production at Nesjavellir Geothermal Power Plant started in 1998. In October 2006 the Hellisheidi Geothermal Power Plant started operation. At first there was a 90 MW electricity production, in 2007 a 30 MW low-pressure turbine was brought into use. In fall 2008 the electricity production was increased with two 40-45 MW turbine units. Hot water production is planned to start in 2010.

In Figure 2 the concentration of hydrogen sulfide measured at Grensasvegur measuring station in Reykjavik from January 1st to May 1st in 2007, 2008 and 2009 is plotted. These are 30 min averages. This time period is chosen because a high concentration is more common in the winter time than in summer and because the measurement device at Grensasvegur measuring station was out of order from May to August 2008. The figure shows that except for one major event in early February the peaks in the concentration seem to be lower in 2009 than in 2008 and 2007. Further comparison can be seen in Figure 3 where the data is plotted as a histogram of the hydrogen sulfide concentration in Reykjavik for the same periods. In Figure 4 incidences with concentrations higher than 100 µg/m³ are shown larger. The highest concentration in the period in 2007 is about 190 µg/m³ and 30 measurements yield more than 100 µg/m³. The highest concentration measured in the period in 2008 is 186 µg/m³ and 26 measurements show more than 100 µg/m³. For the period in 2009 the highest concentration is 217 µg/m³ and 41 measurements give more than 100 µg/m³ (see Table 1).
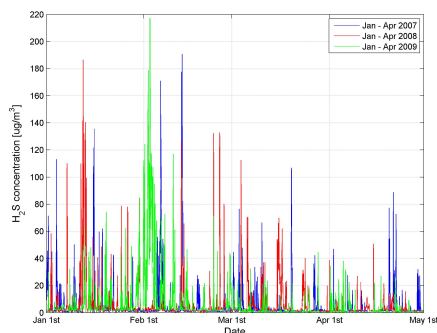

Figure 2. Measured hydrogen sulfide concentration at Grensasvegur measuring station in Reykjavik City from January 1st till May 1st 2007 (blue), 2008 (red) and 2009 (green).
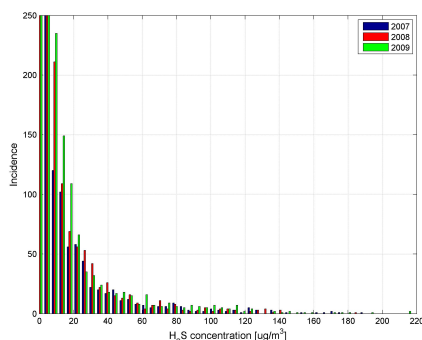

Figure 3. Histogram of measured 30 min hydrogen sulfide concentrations at Grensasvegur measuring station in Reykjavik City from January 1st to May 1st 2007 (blue), 2008 (red) and 2009 (green). Note that the plot is truncated at 250 incidents.
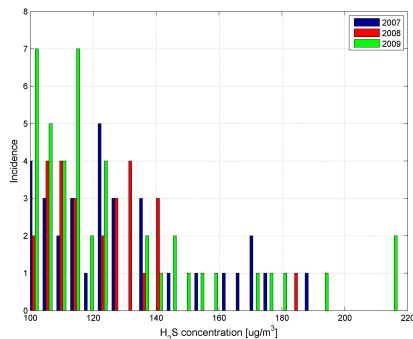

Figure 4. Histogram of measured 30 min hydrogen sulfide concentrations above 100 µg/m³. Measurements from Grensasvegur measuring station in Reykjavik City from January 1st to May 1st 2007 (blue), 2008 (red) and 2009 (green). Note that the plot is scaled from 0 to 8 incidences.

Table 1. Number of 30 min averages of measured H$_2$S that are higher than 100 and 150 µg/m^3 and the highest value for each year 2007, 2008 and 2009, January 1st to May 1st.

Year	Number of 30 min H$_2$S measurements giving more than 100 (150) µg/m^3	Highest 30 min value of H$_2$S [µg/m^3]
2007	30 (7)	190
2008	26 (1)	186
2009	41 (8)	217

When Hellisheidi Power Plant was enlarged in the fall of 2008 the number of turbines was doubled and so the gas emissions were also roughly doubled. This could affect the hydrogen sulfide concentration in Reykjavik. Weather conditions can have a large influence on hydrogen sulfide concentrations. Therefore it is necessary to analyze the weather parameters such as wind direction, wind speed, precipitation and temperature to estimate the effects of weather on the hydrogen sulfide concentration.

When winds are from the east the concentration is more likely to rise in Reykjavik than if the wind is coming from other directions since the Nesjavellir and Hellisheidi Power Plants are located east of Reykjavik. In Figure 5 the incidence of easterly winds in Reykjavik is plotted for January 1st till May 1st 2007, 2008 and 2009. The data used here are 10 minute values of wind and the data is plotted in intervals of 5 degrees from 75° to 125°. Winds directly from the east are measured as 90° and the Nesjavellir Power Plant is located at 97 degrees with respect to the Grensasvegur measuring station and Hellisheidi Power Plant 116 degrees. Figure 5 shows that winds from 100° to 125° were more common in the observation period in 2009 than in 2007 and 2008. This means that winds from the direction of Hellisheidi were more common in the 2009 period. Also since the Hellisheidi Power Plant enlargement is detected in the 2009 period one might not be surprised that the highest concentration in this comparison is in 2009. Most 30 min values over 100 µg/m^3 are also in 2009.
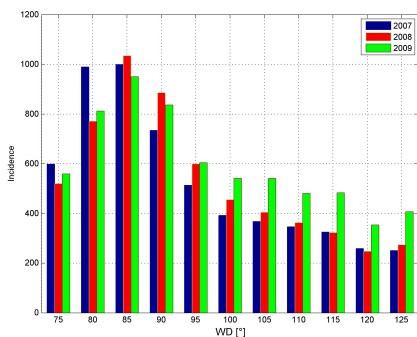
3. COMPARISON OF EVENTS

The analysis of the measured data in the previous section shows that high hydrogen sulfide concentration is event driven, that is, most of the time the concentration is low or zero but during certain weather condition the concentration rises. To analyze which weather conditions are favorable for high concentrations a search was performed in calm winds from the east, the direction of the power plants. Three events were identified and analyzed. Weather measurements from Reykjavik are carried out at the Icelandic Meteorological Office at Bustadarvegur in Reykjavik and the weather station in Middalsheidi highlands which is located between the power plants and Reykjavik. The locations of the weather stations are shown in Figure 1.

In the next three subsections the events are discussed and then a comparison is made.

3.1 February 1st – 4th 2009 (Feb. '09 event)

During the first four days of February 2009 high hydrogen sulfide concentrations were observed at the Grensasvegur measuring station in Reykjavik and the concentration on February 2nd was one of the highest on record as is shown in Figure 6. At a measuring station located in Kopavogur town (see Figure 1) even higher concentration were observed than at Grensasvegur as is shown in Figure 7. The highest recorded peak was over 350 µg/m^3 and the highest 24-hr. mean concentration at the Kopavogur station was 150 µg/m^3 which is equal to the health limit given by WHO. In Figure 8 the wind direction during this period is shown, both in Reykjavik and Middalsheidi highlands which is located east of Reykjavik, between the city and the power plants. The wind direction during this period was very stable, around 100° in Reykjavik and around 70° at Middalsheidi. Figure 9 shows the wind speed at Reykavik and Middalsheidi. The wind speed in Reykjavik is low and steady, always below 4 m/s. At Middalsheidi the wind speed is higher, mostly in the range 4-8 m/s. In Figure 10 the temperatures in Reykjavik and Middalsheidi highlands are compared. Temperatures were in the range 0 to -5°C for the whole period in Reykjavik, and slightly lower at Middalsheidi but highly correlated to those in Reykjavik. No significant precipitation was measured.
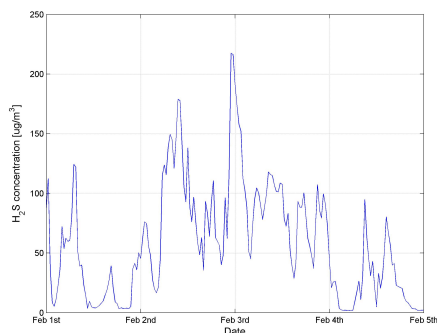

Figure 5. Histogram of easterly wind direction observed in Reykjavik City from January 1st to April 1st 2007 (blue), 2008 (red) and 2009 (green).

Figure 6. Measured hydrogen sulfide concentrations at Grensasvegur measuring station during the Feb. '09 event.
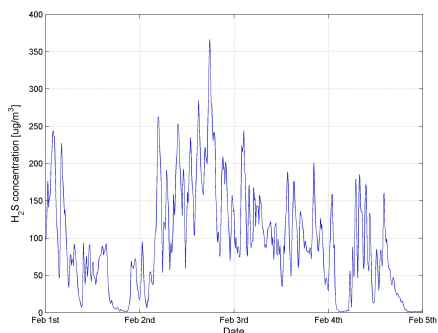
Figure 7. Measured hydrogen sulfide concentrations at Kopavogur measuring station during the Feb. '09 event. Notice that the scale is different from Figure 6.
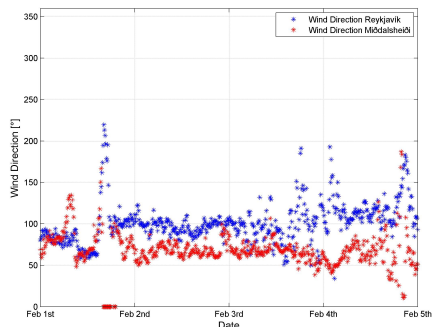

Figure 8. Wind direction in Reykjavik (blue) and at Middalsheidi highlands (red) during the Feb. '09 event.
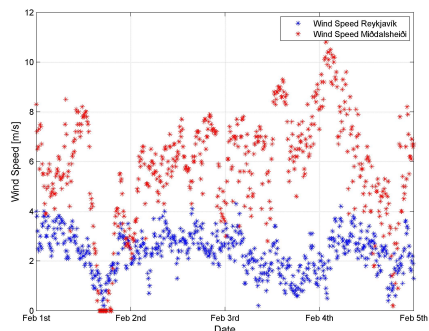

Figure 9. Wind speed in Reykjavik (blue) and at Middalsheidi highlands (red) during the Feb. '09 event.
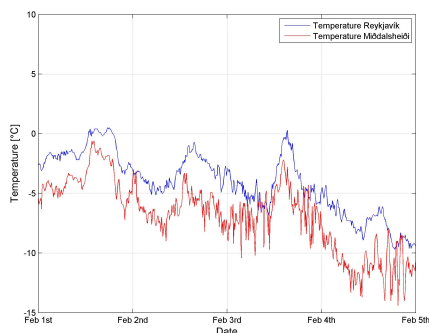

Figure 10. Temperature in Reykjavik (blue) and at Middalsheidi highlands (red) during the Feb. '09 event.

3.2 January 11th – 13th 2008 (Jan. '08)

From January 11th to January 13th 2008 the hydrogen sulfide concentration at Grensasvegur measuring station rose to rather high concentrations. The concentration signal is rather peaky, with three distinctive peaks the longest one on January 12th (see Figure 11). Figure 12 shows the wind direction during the event and it is remarkably similar to that of the Feb. '09 event, steady through the period, although it may be argued that the wind direction is slightly more unstable in Reykjavik during this event than during the Feb. '09 event. Figure 13 shows the wind speed and it is also comparable to that of the Feb. '09 event. The temperature is slightly higher in the Jan. '08 (see Figure 14) event than in the Feb. '09 event. No precipitation was detected during this period.
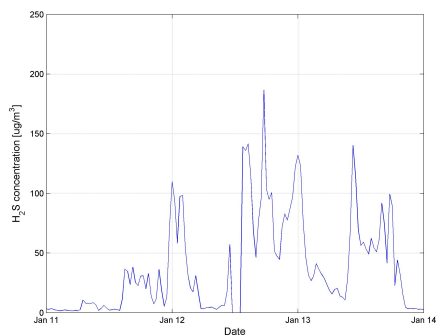

Figure 11. Measured hydrogen sulfide concentration at Grensasvegur measuring station during the Jan. '08 event.
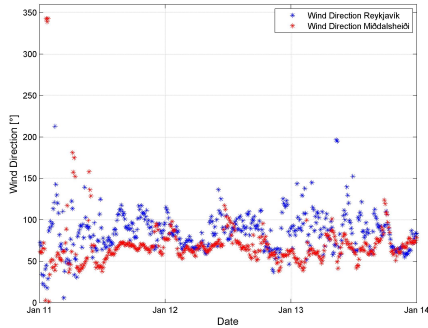
Figure 12. Wind direction in Reykjavik (blue) and at Middalsheidi highlands (red) during the Jan. '08 event.
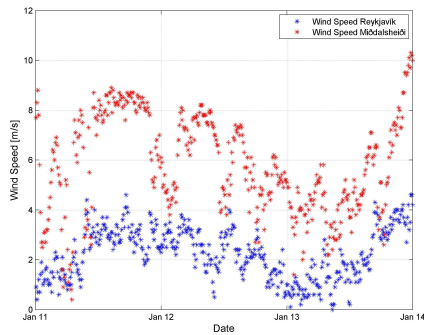

Figure 13. Wind speed in Reykjavik (blue) and at Middalsheidi highlands (red) during the Jan. '08 event.
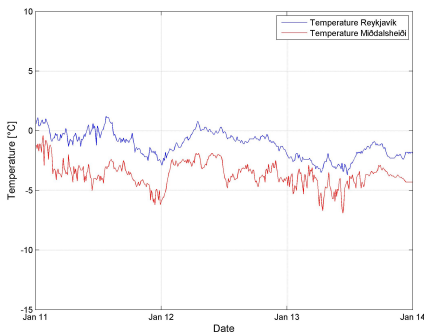

Figure 14. Temperature in Reykjavik (blue) and at Middalsheidi highlands (red) during the Jan. '08 event.

3.3 October 9th – 11th 2007 (Oct. '07)

The third event analyzed took place during October 9th - 11th, 2007. The concentration measured at the

Grensasvegur measuring station is very different from the other periods as shown in Figure 15. The concentration is consistently low and never exceeds 15 µg/m^3. Figure 15 shows the wind direction at the weather stations. The wind is from the east both in Reykjavik and on Middalsheidi highlands during Oct. 9th and 10th, similar to the other two events. On the 11th the wind turned to the north in the early morning but back to the east around noon. Figure 17 shows that on October 9th the wind speed was low but increased on the 10th and reached 10 m/s in Reykjavik and about 18 m/s in the Middalsheidi highlands. Late at night on the 10th and in the early morning on the 11th the wind speed had decreased but increased again during October 11th. It is clear that the wind conditions were similar on the 9th and partly on the 10th as during the previous two events but then the wind speed increased significantly although the wind direction remained unchanged. Figure 18 shows the temperature in Reykjavik during this period. It ranged from 5 to about 12 °C but the temperature on Middalsheidi highlands was about 3 °C lower. During this event there was some precipitation which is shown in Figure 19. There was some precipitation in the morning on the 9th and in the early morning on the 10th and then in the evening on the 11th.
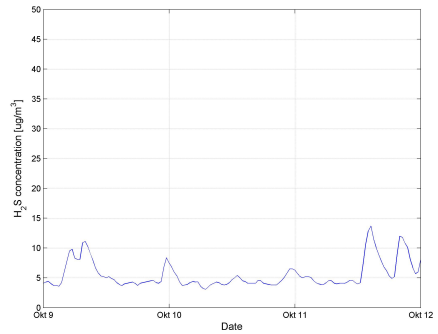

Figure 15. Measured hydrogen sulfide concentration at Grensasvegur measuring station during the Oct. '07 event.
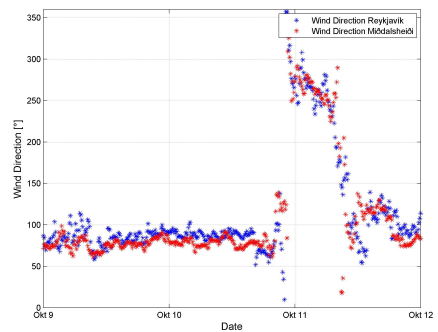

Figure 16. Wind direction in Reykjavik (blue) and at Middalsheidi highlands (red) during the Oct. '07 event.
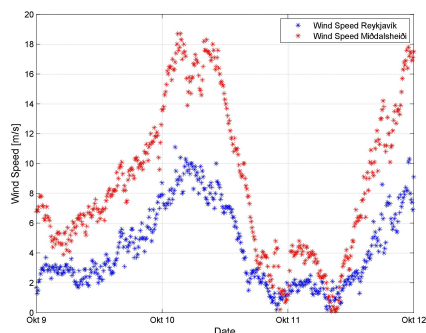
Figure 17. Wind speed in Reykjavik (blue) and Middalsheidi highlands (red) during the Oct. '07 event.
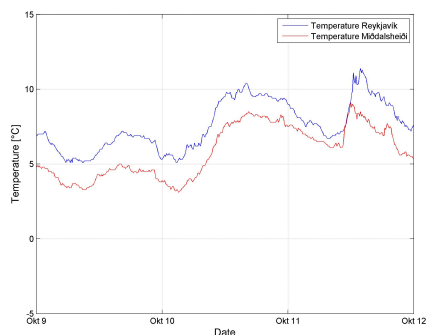

Figure 18. Temperature in Reykjavik (blue) and Middalsheidi highlands (red) during the Oct. '07 event.
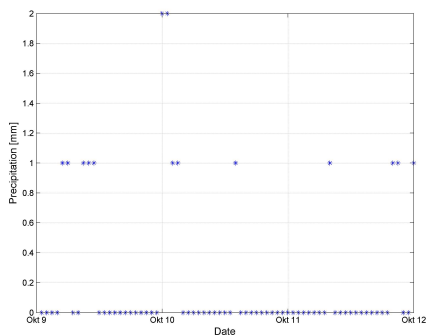

Figure 19. Precipitation in Reykjavik during the Oct. '07 event.

3.4 Comparison

The three events, discussed in previous sections, that were found for the measuring period 2007-2009 with steady wind from east, indicate the importance of the weather condition on hydrogen sulfide concentration.

During all events the wind direction was similar, that is, from the east although during the Oct. '07 event the wind direction changed to a different direction for a few hours. During the Feb. '09 and Jan. '08 events the wind speeds were low in Reykjavik and up to 10 m/s in Middalsheidi highlands. During the Oct. '07 event the wind speed was low early on Oct. 9th and Oct. 11th but higher on Oct. 10th and late Oct. 11th. Temperatures varied between the events. During the Jan. '08 and Oct. '07 events the temperatures were stable around 0°C and around 8 °C in Reykjavik, respectively. During the Feb. '09 event the temperature decreased from about -2 °C to -10 °C in Reykjavik. There was no precipitation during the Feb. '09 and Jan. '08 events but some during the Oct. '07 event.

The concentrations during the Feb. '09 and Jan. '08 events were much higher than during the Oct. '07 event, when the concentration was mostly around 5 µg/m^3. The difference between the Feb. '09 and Jan. '08 concentrations is mainly that in Feb. '09 the concentration stayed high for a longer period while the Jan. '08 concentration was peakier.

The Feb. '09 and Jan. '08 events are very similar both in weather and concentrations. The Feb. '09 event was the highest measured event on record. The WHO health limit was reached in Kopavogur and Nordlingaholt which is a district on the far-East side of the Reykjavik district (where test measurements were made at the time). The weather factors that are ideal for high concentrations in the Reykjavik area are winds from the East, cold weather, low wind speed and no precipitation. These were the weather conditions during the Feb. '09 and Jan. '08 events. The weather conditions in Oct. '07 were quite different, with higher temperature, varying wind speed and precipitation. The frequency of the ideal weather conditions for high H$_2$S concentration in Reykjavik could give an indication of how often high concentration should be expected in Reykjavik and how often they might have gone undetected. More data analyses are underway to detect which weather factor influences the concentration the most.

4. DISTRIBUTION OUTSIDE REYKJAVIK AREA

A measurement program is being executed to measure hydrogen sulfide concentration at point locations around Nesjavellir and Hellisheidi Power Plants. These measurements are performed with a hand held measuring device (Jerome 631-X). The measurements are taken during a trip lasting few hours, depending on weather conditions, repeated for four days in a row. On the morning of a measuring day the wind direction is observed and that determines where the measurements are performed. The measurements are performed in a segment some distance from the power plants at the locations where hydrogen sulfide can first be detected until the concentration has dropped to zero again. The area used for the measurements (see Figure 1) is a circle drawn from Reykjavik through Mosfellsbær to Þingvallavatn, around Lake Þingvallavatn and to the south on the east side of the lake to the Town of Selfoss, then down to Eyrarbakki and that way up to Hellisheidi power plant and to Reykjavik. Depending on the distance travelled (which depends on the distribution of hydrogen sulfide) the measurements take about 3 to 5 hours. These measurements will be taken during the course of one year and by doing so the summer and winter values can be compared. Also since the measurements are performed for a few days in a row a comparison can be made between days with similar but not identical weather.

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This program is underway and the results are still being analyzed. In the following section, an example of measurements from two days in March 2009 is discussed.

4.1 Comparison between two measuring days

On March 24th and 25th, 2009, the winds were from the north and northeast so that hydrogen sulfide measurements were made from Reykjavik City to the Town of Selfoss (see Figure 1). The measuring sites are shown in

Figure 20 and 21 with pink circles. On the 24th the highest concentration was about 140 µg/m³ close to Hellisheidi Power Plant. Farther south from the plant the highest concentration was about 51 µg/m³ (about 12 km from the plant). The second highest concentration farther from the power plant was about 16 km southwest from Hellisheidi Power Plant. A little west of the second highest concentration measurement a lower concentration was observed although this location was in a straight line from the power plant and the highest concentration.. This indicates fluctuations in the plume (see

Figure 20). During the measuring time the winds were from the north and north-northeast (about 0° - 30°). Wind speeds range from 7 to 10 m/s in the highlands.

On March 25th, the highest concentration measured is at Hellisheidi Highlands, 91 µg/m³ (see Figure 21). The hydrogen sulfide concentration was more diffuse than the day before. Two different highs in the concentration are seen in Figure 21, one at Hellisheidi Highlands and one closer to Reykjavik City. Since the winds were almost stable from the northeast, during the measuring time, this indicates two different sources.

There are slight weather differences between the two days. The wind direction had changed only slightly but the wind speed was much lower the second day and temperatures are also lower. The difference in hydrogen sulfide concentration is that on March 25th hydrogen sulfide was more widely distributed. This is possibly due to lower wind speeds that allowed the hydrogen sulfide to spread more widely in the crosswind direction.
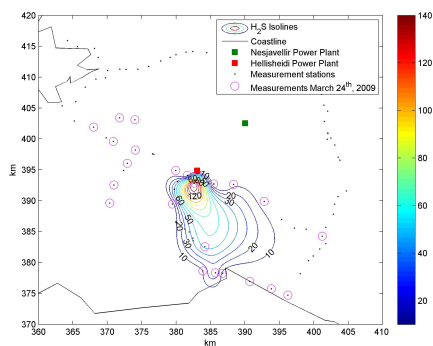

Figure 20. Contour plot of hydrogen sulfide concentration on March 24th 2009. Black dots are measurement spots used, the pink circled ones are the ones measured this particular measuring day. Green and red squares represent Nesjavellir and Hellisheidi Power Plant respectively. The axes have the ISN93 coordinates in km.
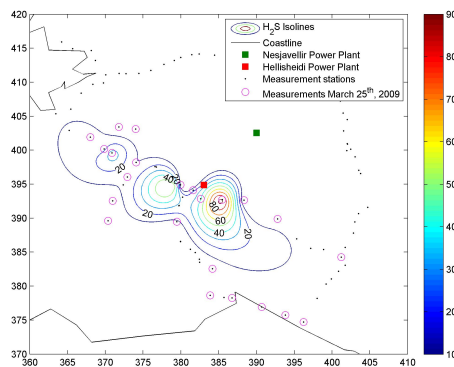

Figure 21. Contour plot of hydrogen sulfide concentration on March 25th 2009. Black dots are measurement locations used; the pink circled ones were used this particular measuring day. Green and red squares represent Nesjavellir and Hellisheidi Power Plant respectively. The axes have the ISN93 coordinates in km.

5. CONCLUSIONS

Hydrogen sulfide emission close to Reykjavik City has increased the least few years with growing geothermal power production. Preliminary analysis of measurements, both at fixed locations as well as at variable point locations, indicates strong influence of weather conditions on magnitude and frequency of raised hydrogen sulfide concentrations. Comparing events it seems that low wind speed, with cold air and little or no precipitation are conducive to high hydrogen sulfide concentrations in Reykjavik. Further analysis and measurements are underway to investigate which parameters exert most influence on the concentration. Preliminary results from measurements outside the capital area indicate that the hydrogen sulfide is more widely distributed at lower wind speeds.

ACKNOWLEDGEMENTS

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Appendix E

Appendix E contains a conference paper presented at the 19th International Symposium on Transport Phenomena, 2008 in Reykjavik. In the paper a Gaussian plume model with particle tracking was used for simulating H_2S concentration in Reykjavik City and compared to measurements. The model was also used to model the H_2S concentration at different sites in Reykjavik where measurements had not been made.

Olafsdottir, S., Gardarsson, S.M., Gustafsson, L., 2008. Measurements and modeling of hydrogen sulfide in Reykjavik City 2006 and 2007. Proceedings 19th International Symposium on Transport Phenomena 2008, Reykjavik, Iceland, 17-20 August.

MEASUREMENTS AND MODELING OF HYDROGEN SULFIDE
IN REYKJAVIK CITY 2006 AND 2007

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ABSTRACT

In view of the increasing geothermal power production near Reykjavik City, the Department of Environment of Reykjavik City started measuring hydrogen sulfide (H_2S) concentration at Grensasvegur Street in February 2006. These measurements yield 30 minute averages and the concentration is measured in $\mu g/m^3$. The main objective of this study is to use a Gaussian plume model with particle tracking for simulating hydrogen sulfide concentration in Reykjavik and compare to the measurements. The model is then used to calculate concentration at different sites in the Reykjavik area. Nine events were chosen for the study when high hydrogen sulfide concentration was measured in Reykjavik. Five of these occurred before the Hellisheidi power plant started production and four after. For three events analyzed, the modeled concentration was larger than the measured concentration. For another three events the modeled concentration was smaller (one was close to zero) and for another three events it was similar. Most events had some time lag in the concentration calculations compared to measurements. Nevertheless, the model results indicate that this method can be used, although some modifications are recommended.

INTRODUCTION

Gaseous sulfuric compounds from geothermal areas exist in the form of hydrogen sulfide (H_2S). When the geothermal areas are developed the hydrogen sulfide is, usually, emitted at a higher rate to the environment than before development (Armannsson, 2002). The hydrogen sulfide has a characteristic smell that can be detected at low concentrations. At about 300.000 $\mu g/m^3$ the sense of smell is lost, at 450.000 – 750.000 $\mu g/m^3$ pulmonary oedema can form with the risk of death. No health limit value is set for the concentration of hydrogen sulfide in air in Iceland. The World Health Organization (WHO) has given a guideline value of 150 $\mu g/m^3$ as an average value of 24 hours. WHO also gives a value for when the smell to become a nuisance, at 7 $\mu g/m^3$ for a 30 minute average. The hydrogen sulfide is unstable in air compared to sulfur dioxide (SO_2) and if conditions are favorable oxidation may take place (Armannsson, 2002; Kristmannsdottir et al., 2000).

The Nesjavellir power plant which is about 20 km east of Reykjavik started hot water production in 1990 and electricity production in 1998. Currently the hot water production is 300 MW and the electricity production 120 MW. The Hellisheidi power plant which is about 15 km southeast of Reykjavik was opened in October 2006. Currently the electricity production is 120 MW. Enlargement of the Hellisheidi power plant is underway and hot water production will start in 2009. The power

plants, the measuring station and the weather stations used in the study are shown in Figure 1.

A model was made for tracking the hydrogen sulfide from Nesjavellir and Hellisheidi Power Plants and to calculate the concentration in Reykjavik. The Gaussian plume model was used for concentration calculations. The model made was used to analyze nine events during 2006 where the hydrogen sulfide concentration in Reykjavik was raised. Five events where chosen before the Hellisheidi Power Plant started production and four after. Further information about the study can be found in Olafsdottir (2007). Here the model and the results will be described and a comparison of the concentration of hydrogen sulfide in Reykjavik before and after the start of production at Hellisheidi Power Plant is provided.
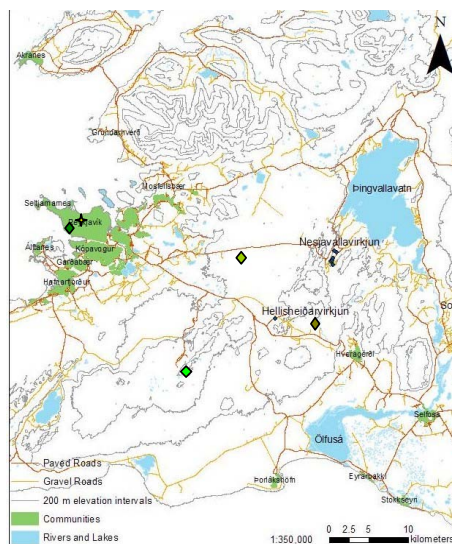

Figure 1.   Map of the area showing Grensasvegur measuring station (✦), Nesjavellir power plant (■■) , Hellisheidi power plant (■) , Reykjavik weather station (◆), Middalsheidi weather station (◆), Hellisheidi weather station (◆) and Blafjöll weather station (◆).

ANALYSIS OF H_2S IN REYKJAVIK CITY

Hydrogen sulfide has been measured in Reykjavik City since February 2006 at Grensasvegur measuring station (see Figure 1). At that time the electricity production at Nesjavellir Geothermal Power Plant had been in operation for about 8 years. Hence, the measuring station at Grensasvegur detected the hydrogen sulfide from Nesjavellir for the first few months of operation.

However, in October 2006 the Hellisheidi Geothermal Power Plant started operation. Hence, it is possible to analyze the effect of Nesjavellir Power Plant alone during 2006 and then the combined effect of both power plants for the year 2007.

In Figure 2 the concentration of hydrogen sulfide in Reykjavik from March 1st to September 1st in 2006 and 2007 is plotted. The figure shows that there are more measured peaks in 2007 and are of higher magnitude. Further comparison can be seen in Figure 3 where the data is plotted as a histogram of the hydrogen sulfide concentration in Reykjavik for the same periods. The highest concentration in the period in 2006 is about 60 µg/m^3 and only six measurements are higher than 50 µg/m^3. The highest concentration measured in the period 2007 is about 140 µg/m^3 and 41 measurements are over 50 µg/m^3.
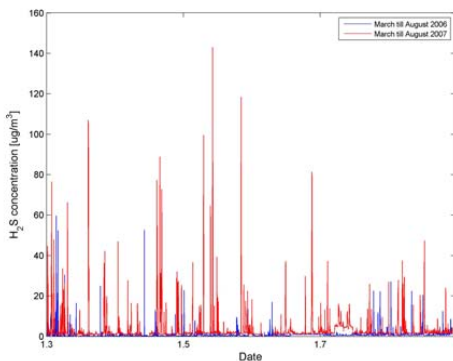

Figure 2. Measured hydrogen sulfide concentration at Grensasvegur measuring station in Reykjavik City from March 1st till September 1st 2006 (blue) and 2007 (red).
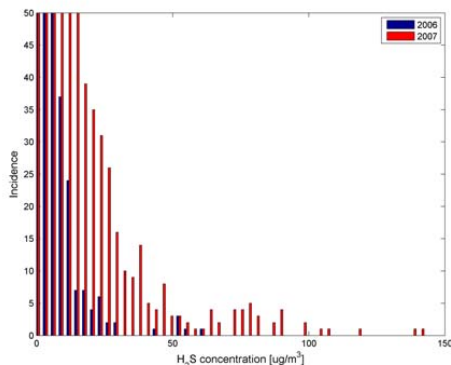

Figure 3. Histogram of measured hydrogen sulfide concentration at Grensasvegur measuring station in Reykjavik City from March 1st to September 1st 2006 (blue) and 2007 (red). Note that the plot is truncated at 50 incidents.

The reason for at least part of this increase in hydrogen sulfide concentration is likely due to the increase in hydrogen sulfide emissions when the Hellisheidi Power Plant began electricity production in October 2006. Also although Hellisheidi Power Plant emits less hydrogen sulfide than Nesjavellir the plume is emitted at lower level since there was no cooling tower till September 2007 at Hellisheidi Power Plant. This can increase the concentration at ground level. However, weather conditions can have a large influence on hydrogen sulfide concentration and therefore it is necessary to analyze the weather parameters such as wind direction, wind speed, rain and temperature.

When winds are from the east the concentration is more likely to rise in Reykjavik than if the wind is coming from other directions since the Nesjavellir and Hellisheidi Power Plants are located east of Reykjavik. In Figure 4 the incidence of easterly winds in Reykjavik are plotted for March 1st till September 1st 2006 and 2007. The data used here are hourly values of wind and the data is plotted in intervals of 5 degrees 80 to 125°. Winds directly from the east are measured as 90° and the Nesjavellir Power Plant is located at 97 degrees compared to Grensasvegur measuring station and Hellisheidi Power Plant is at 116 degrees. Figure 4 shows that easterly winds were more common in the time period in 2007 than 2006 especially under 100°. The total difference (from 80 to 125°) is though only about 8% which is not likely to be the reason the total increase.

Researches have shown that hydrogen sulfide is effectively washed out by rain (Kristmannsdottir et al.). In Figure 5 the precipitation from March 1st till September 1st 2006 (blue) and 2007 (red) is shown. It seems the rain is similar although there are more light showers in 2007 but less rain over the summertime. Further analysis is needed to establish the effect of rain and other weather conditions on hydrogen sulfide concentration. Further analysis is underway.
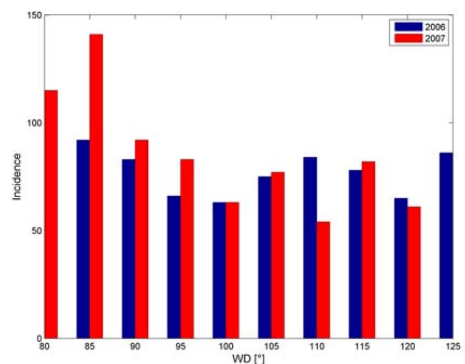

Figure 4. Histogram of measured easterly wind direction Reykjavik City from March 1st to September 1st 2006 (blue) and 2007 (red).
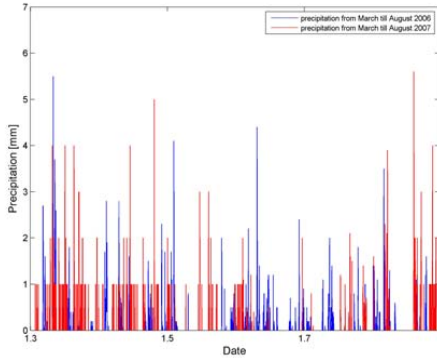
Figure 5. Measured precipitation in Reykjavik City from March 1st till September 1st 2006 (blue) and 2007 (red).

Model

Gaussian plume model with particle tracking is used to calculate the concentration of hydrogen sulfide in Reykjavik City. Wind direction and wind speed from weather stations at Middalsheidi highlands, Blafjoll mountain, Hellisheidi highlands and Reykjavik are used to track the path the hydrogen sulfide goes from the power plants to Reykjavik. The weather stations can be seen in Figure 1 with the Grensasvegur measuring station and the power plants.

If the hydrogen sulfide travels to Reykjavik the Gaussian plume model is used to calculate the concentration at the Grensasvegur measuring station. The calculations can then be compared to measurements.

As a plume travels and spreads it reaches the surface of the ground and is reflected. Above the mixing layer there can be a stratified inversion layer where the plume is assumed to be reflected as well as at the ground when the air stability is neutral or unsteady. A mirror-image plumes are inserted into the Gaussian equation to account for the reflections. The Gaussian equation for a ground-level receptor, with multiple reflections is (Schulman & Scire, 1980):

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{y^2}{2\sigma_y^2}\right] \left\{ \sum_{n=-\infty}^{\infty} \exp\left[-\frac{1}{2}\left(\frac{H+2nD}{\sigma_z}\right)^2\right] \right\} \qquad (1)$$

When the air stability is steady or the mixing layer is higher than 5 km the only reflection is form the ground:

$$\chi = \frac{Q}{\pi \sigma_y \sigma_z u} \exp\left[-\frac{y^2}{2\sigma_y^2}\right] \exp\left[-\frac{H^2}{2\sigma_z^2}\right] \qquad (2)$$

where

χ   Air pollutant concentration in mass per volume [g/m^3]
Q   Pollutant emission rate in mass per time unit [g/s]
u   Wind speed at stack height [m/s]
σ_y Horizontal dispersion parameter [m]
σ_z Vertical dispersion parameter [m]
y   The horizontal distance from the receptor to the plume center [m]

z   The vertical distance from the receptor to the plume center [m]
H   The effective height of the centerline of the pollutant plume [m]

The horizontal and vertical dispersion parameters are dependent on the air stability and the distance from the source. When the dispersion coefficients increase the centerline concentration decreases and the plume can be detected farther away from the plume center (Nevers, 2000; Turner, 1994). For further information on the Gaussian plume method, consult Nevers (2000) and Turner (1994).

The air stability is calculated by Turners method (WebMet, 2006) where the stability is dependent on sun radiation and wind speed. The Holzworth method is used to find the mixing height (WebMet, 2007) with temperature measurements from Middalsheidi highlands and upper air temperature data from Keflavik airport.

When the total concentration is found from both power plants the hydrogen sulfide concentration from each, at every time step is found and then added.

RESULTS

The results are first presented as comparison between the nine events and then one event is discussed in detail. For further discussion of all nine events see Olafsdottir (2007).

Comparison of events

In this project nine different events during 2006 were analyzed: February 27 and 28, March 4 and 5, April 19, July 30, September 4, October 17 and 18, October 28 and 29, November 7 and 8 and December 16 and 17. Five of the events are before the Hellisheidi Power Plant started production and four following the start of production. The nine events analyzed vary in size and duration. The maximum measured concentrations of the events range from 13 to 154 µg/m^3. Durations of the events range from four hours up to nineteen and a half hours. The character of the rise in the concentrations also vary between the events, some of the events have a gradual rise in the concentration for some time while in others the concentration spikes. The events are chosen from different times of the year although only one is during the summer.

Table 1 shows the maximum measured and modeled concentration and the corresponding ratio for each event as well as the length of the event. The length of each event is measured from the first occurrence that exceeds 5 µg/m^3 until the concentration drops below 5 µg/m^3 without rising again.

In Figure 6 the ratio of the 30 minute maximum modeled concentration and the maximum measured concentration form Table 1 is plotted against different parameters. The July event has been removed from the plots as the ratio for that event, 2248 %, is much larger than for the other events. The October event has also been removed because the modeled concentration for that event was close to zero implying that the model was unable to simulate that event.

In Figure 6(a) the ratio of the 30 minute maximum modeled concentration and the maximum measured

concentration is plotted against the length of the event. Little correlation is detected as can be seen in the figure. The period is fairly long for all events, the shortest four hours (April 18 and 19) and the longest nineteen and a half hour (February 27 and 28) although the concentration is not always high during the entire period. In some events, for example on February 27 and 28, the concentration spikes for a short period but rises again later.

In Figure 6(b) the ratio of the 30 minute maximum modeled concentration and the maximum measured concentration is plotted against the mean temperature on Middalsheidi highlands from 2 hours before the rise in the concentration starts till 2 hours before it decreases again. No certain correlation is observed. The mean temperatures for these events are in the range from -7 to 11°C.

In Figure 6(c) the ratio of the 30 minute maximum modeled concentration and the maximum measured concentration is plotted against the minimum mixing height during the event. When the mixing height is low there is less dilution of the hydrogen sulfide that is if the air is unstable or neutral, so if the mixing height is low there could be a tendency for the concentration to be higher. There does not seem to be any strong correlation in Figure 6(c), although most of the events have rather low minimum mixing heights and the two concentrations that have the highest minimum mixing height are the ones that have the lowest ratio. The fact that the minimum mixing height is in general this low is likely due to the fact that most of the events are in the winter time when low temperatures are more common. When comparing (b) and (c) it is observed that the highest and the lowest temperatures have similar minimum mixing heights. The minimum mixing height in the July event is 1979 m.

In Figure 6(d) the ratio of the 30 minute maximum modeled concentration and the maximum measured concentration is plotted against the mean effective stack height at Nesjavellir power plant. Because of the differences in emissions between the Nesjavellir and Hellisheidi power plants the effective stack height at Nesjavellir varies more between events. In Figure 6(d) it is observed that most of the maximum effective stack heights are of similar size or about 250 m. No strong correlation is observed but any correlation is hard to obtain with so few events. The mean effective stack height for the July 30 event is 190 m.

In Figure 7 the wind direction and mean wind speed at Middalsheidi highlands and in Reykjavik for the nine events are plotted. The prevailing wind direction in each event is found and the event given one wind direction accordingly. It is observed from Figure 7 that in all the events the wind direction is from the east and that the wind speeds are relatively low.

From these different plots it can be observed that the reason for different ratios of the modeled and measured hydrogen sulfide concentration between the events is not easily determined. All the events take place in easterly wind directions, which was expected since the power plants are situated east of Reykjavik. Also all the events take place when wind speeds are relatively low.

In eight of nine events the model shows a rise in the hydrogen sulfide concentration. The difference in the magnitude of the modeled concentrations and the measured concentrations vary between the events. Three events have the modeled concentration larger than the measured concentration. On February 27 and 28 there is a spike calculated over a period of one hour that is over six times the size of the maximum measured concentration. This is mainly due to a time lag that makes the calculated plumes all arrive in Reykjavik at the same time.

For April 19 the modeled values are also higher than the measured concentrations, about three times as high. Three spikes are modeled after one longer rise in the measured concentration. This is likely due to wind changes while the plumes are in the Reykjavik area, making the plumes form a cluster which moves back and forth. Small differences in wind speed and/or direction can lead to wrong location and/or magnitude of the plume concentration.

The largest modeled event is on July 30. The modeled concentration is over 20 times larger than the measured concentration but the modeled time for this event fits best with the measurements of all nine events. The difference in the concentrations is partly because the plumes travel a great distance before arriving in Reykjavik which magnifies the uncertainties in the dispersion parameters calculations.

Three events have modeled concentrations smaller than the measured concentrations. On March 4 and 5 the maximum modeled concentration is about half of the maximum measured concentration. This is likely due to long time intervals between the emissions of the modeled plumes.

On September 4 the maximum modeled concentration is about one third of the maximum measured concentration and the shapes of the curves are very different. This could be due to Esja Mountain northeast of Reykjavik. The model assumes that the plumes go straight over Esja Mountain but it is likely that some of them move in a more westerly direction alongside the mountain. Thus more of the transported hydrogen sulfide reaches Reykjavik.

On October 17 and 18 the modeled concentration is almost zero because the plumes modeled for this time period travel southwest without coming close to the Grensasvegur measuring station. This is probably due to insufficient weather measurements and because topography is not taken well enough into account in the model.

Three events have maximum concentrations similar to their maximum measured concentrations. In two of these events the timing of the maximum modeled concentration arrives several hours before the measured maximum concentration. On October 28 and 29 the modeled concentration has a maximum similar to that of the measured concentration although it is twelve hours earlier. This is most likely due to insufficient weather measurements and because topography is not taken well enough into account in the model.

On November 7 and 8 the modeled concentration has three peaks like the measured concentration at similar times and similar in size, although the first modeled increase is higher than the measured one.

On December 16 and 17 the modeled concentration has a maximum value similar to the measured

concentration although it is seven and a half hours earlier. This could be due to the fact that many of the plumes that arrive in Reykjavik start by traveling west from the power plants, thus increasing the uncertainties of having only a few weather measurements symbolizing the whole area.

Even though the differences in sizes and shapes of the modeled concentrations compared to the measured concentrations vary between the events and most of the events, with the exception of the July and November events, have modeled timing of the peaks slightly different from the measured one, the overall outcome of the modeling indicates that this kind of a model can be used for estimating the hydrogen sulfide concentration in Reykjavik.

Table 1. Measured and modeled maximum concentrations for each event and the length of each event.

Date of event	MM[1] [µg/m³] (1)	MC[2] [µg/m³] (2)	Ratio[3] [%] (3)	Period [hours] (4)
February 27 - 28	61	392	644	19.5
Mars 5	60	32	53	11.5
April 19	13	40	304	4
July 30	22	499	2248	7
September 4	132	45	34	7.5
October 17 - 18	106	0.12	0.11	14
October 29	139	185	133	14.5
November 8	45	78	172	15
Decemb. 16 - 17	154	146	95	10

(1) MM: Maximum measured concentration
(2) MC: Maximum modeled concentration
(3) Ratio: The ratio between the maximum modeled concentration and the measured concentration
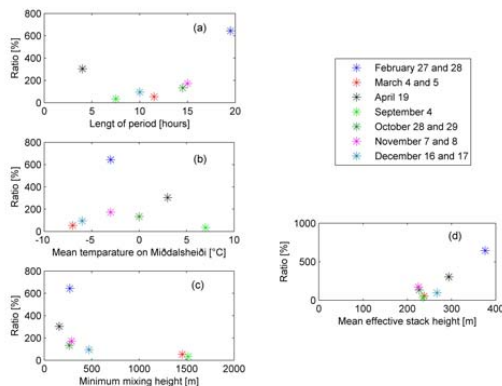

Figure 6. The ratio of the maximum modeled and measured hydrogen sulfide concentration plotted against a) length of period of increased concentration b) mean temperature on Middalsheidi highlands 2 hours before the rise in the concentration starts till 2 hours before it decreases again c) minimum mixing height and d) mean effective stack height.
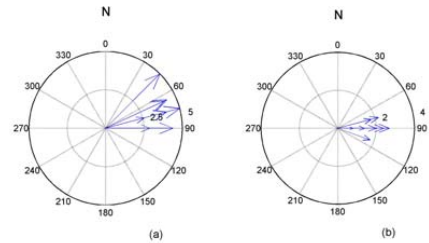

Figure 7. Wind grafs describing the wind conditions at (a) Middalsheidi highlands where the wind conditions plotted are from 2 hours before the rise in the concentration starts till 2 hours before it decreases again and (b) Reykjavik where the wind conditions during the rise in the measured concentration is plotted.

Analyzes of the November 7th and 8th event, 2006
On November 7 on Middalsheidi highlands winds from the south prevail, shifting gradually from southwest to southeast and east in the late evening. Wind speeds range from 4 to 6 m/s but in the evening it decreases to about 2-3 m/s. Temperatures range from -5 to +2°C, coldest in the late evening. In Reykjavik similar fluctuations are observed in the wind, shifting from southwest to the southeast and east in late evening. Wind speeds are gradually decreasing from 8 to 2 m/s during the day. The temperature ranges from 2 to 4°C but drops below 1°C in late evening. The sky was partly cloudy and wet ground in the early morning but no precipitation at Nesjavellir.

On November 8 on Middalsheidi highlands winds from the east prevail from midnight till noon but shift to the northwest in the early afternoon and back to the east about an hour before midnight. Wind speed mostly range from 2 to 4 m/s although in the afternoon the wind velocity reaches about 14 m/s for an hour or so and ranges from 8 to 10 m/s till the evening. Temperatures range from -9 to -1°C, coldest in the late evening. In Reykjavik east and southeast winds prevail till early afternoon when it shifts to the northwest. In the late evening it shifts back to the east. Wind speeds are generally in the range from 2-3 m/s but in the afternoon the wind speed rises and is in the range from 6 to 9 m/s till late evening. Temperatures range from -2 to +2°C, coldest in the late evening. Mostly cloudy with a few snow showers in the morning and afternoon. No precipitation in Nesjavellir.

On November 8 the concentration starts to rise at midnight and in the afternoon three peaks have come and gone, the largest one 45 µg/m³. The modeled 30 minute average concentration starts to rise shortly before midnight on November 7 and rises to 77.8 µg/m³ at midnight. It drops down again but rises twice more in the time period. All three rises are at similar time scales as the measured concentrations as can be seen in Figure 8 where the measured and modeled 30 minute average are plotted. In Figure 9 and Figure 10 maximum

concentration from calculated plumes from Nesjavellir and Hellisheidi power plants are plotted respectively. The concentration from Hellisheidi Power Plant is much higher than from the Nesjavellir Power Plant. One reason for this is the method of emission, the Nejsavellir Power Plant has a cooling tower that raises the plume higher than at Hellisheidi Power Plant. A cooling tower was to be installed in September 2008.
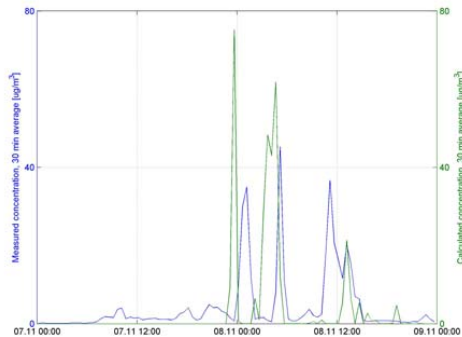

Figure 8. Measured (blue line, left axis) and modeled (green line, right axis) 30 minute average hydrogen sulfide concentration for November 7 and 8, 2006.
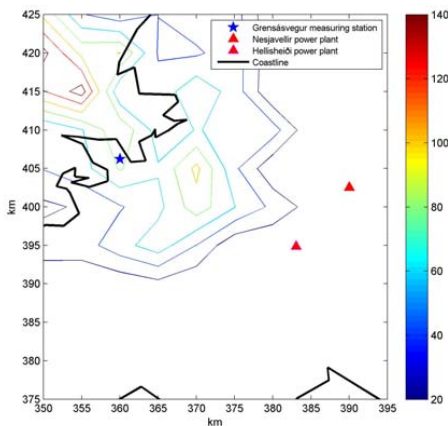

Figure 9. Maximum concentration due to emissions from Nesjavellir Power Plant for the November 7th and 8th 2006 event.
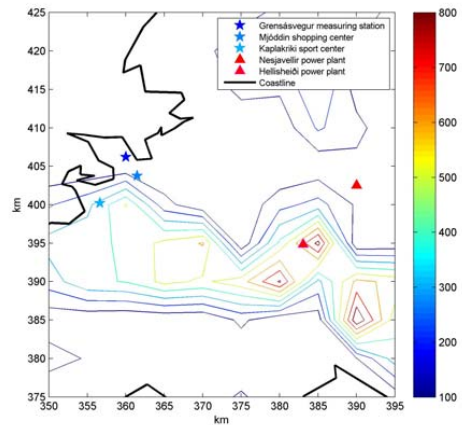

Figure 10. Maximum concentration due to emissions from Hellisheidi Power Plant for the November 7th and 8th 2006 event.

Concentration at different Sites in Reykjavik City
The maximum concentration can be very variable in space as has been shown in Figure 10. The concentration is also very variable in time, meaning that the concentration at each time step is not homogeneous in space.

The distance from the receptor to the plume center is an important factor in determining the hydrogen sulfide concentration. This means that different locations in the capital area will have different concentrations depending on the exact plume location. Two sites inside the capital area were chosen for comparison with the concentration modeled for Grensasvegur measuring station. These sites are Mjoddin shopping center in the Breidholt district in Reykjavik, about 3 km from the Grensasvegur measuring station and Kaplakriki sport center in the town of Hafnarfjördur about 7 km from the Grensasvegur measuring station. These sites are plotted in Figure 10 with other sites that have already been identified.

Concentrations were modeled for these two sites. The 30 minute average maximum concentrations are listed in Table 2 along with the maximum modeled concentration for the Grensasvegur measuring station. In Figure 11 the ratio between the maximum 30 minute average concentration modeled for these two sites and the maximum 30 minute average concentration modeled for the Grensasvegur measuring station are plotted for each event. Because the concentration at Grensasvegur measuring station on October 17 is almost zero that event is omitted in Figure 11. The modeled concentration at Kaplakriki sport center on October 17 is much higher than at Grensasvegur measuring station because Kaplakriki is northeast of Nesjavellir and much closer to the calculated plumes on that day.

Table 2. Calculated maximum 30 minute average concentration for Grensasvegur measuring station, Mjoddin shopping center and Kaplakriki sport center.

Date of event	Label	Grensasv. [μg/m³]	Mjoddin [μg/m³]	Kaplakriki [μg/m³]
Feb. 28 and 28	(28.02)	392	658	400
March 4 and 5	(05.03)	32	84	23
April 18 and 19	(19.04)	40	62	260
July 29 and 30	(30.07)	499	1110	176
Sept. 3 and 4	(04.09)	45	96	65
Oct. 17 and 18		0.12	4	31
Oct. 28 and 29	(28.10)	141	154	79
Nov. 7 and 8	(07.11)	75	84	189
Dec. 16 and 17	(17.12)	146	52	329

Figure 11 shows that the maximum concentration in Mjoddin shopping center is about the same magnitude or greater than at the Grensasvegur measuring station for every event but one. This was expected since Mjoddin shopping center is a little closer to the power plants than the Grensasvegur measuring station (see Figure 10). Kaplakriki sport center is a little farther away from the power plants than the Grensasvegur measuring station so its maximum concentration was expected to be similar or lower than at Grensasvegur measuring station for most events but in four events of nine it is higher. When looking at Figure 10 the reason for this is evident. Because Kaplakriki is further south than the Grensasvegur measuring station it detects different plumes, which is the plumes from Hellisheidi Power Plant (see Figures 9 and 10). The calculated plumes are not evenly distributed over the area but rather travel in clusters so the concentration at the two sites can be very different. The calculated plumes from the Nesjavellir and Hellisheidi power plants do not distribute evenly as can be seen by comparing Figures 9 and 10. The plumes can travel in clusters and/or change directions which increases the concentration locally. Therefore the hydrogen sulfide concentration can be very different from one place to another within the capital area.
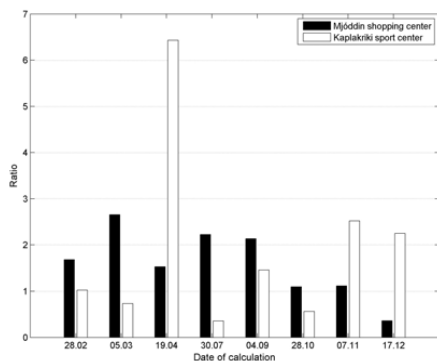

Figure 11. The ratio of the maximum 30 minute average concentration calculated for Mjoddin shopping center and Kaplakriki sport center and the maximum 30 minute average concentration calculated for Grensasvegur measuring station for each event.

Modification of the model

The model is based on a Gaussian plume model on top of particle tracking to calculate the distance from the center of the plume to the receptor. The plume can travel great distances before it arrives in Reykjavik and therefore the traveling time can vary greatly. Changes in weather can be significant during the event so the conditions used for the Gaussian calculations may vary during the event although this is not taken into account in the current model. For example the calculations of the dispersion parameters assume the air has the same stability during the event.

Other improvements might be:

- Include the Skalafell weather station in the particle tracking calculations. The weather station is located northeast of Reykjavik. This could not be done for the period presented as the wind direction meter was broken the whole year 2006.

- Represent the topography and roughness elements of the ground surface in the calculations, especially where weather measurements are lacking.

- The plume rise model, for unstable or neutral air, is sensitive to the wind speed, especially when the wind speed is around or below 1 m/s. The wind speed used in the plume rise calculations is measured at Middalsheidi highlands and the difference in wind speed at the highlands and at the Nesjavellir power plant, which is close to a mountain, are likely to be considerable in some cases. This could be taken into consideration.

Conclusions

Since the Hellisheidi Power Plant started production the H2S concentration in Reykjavik has increased. The emissions of H2S have increased but weather data suggest that weather is also a reason for increased concentration. Further analysis on weather data with emission data in underway.

The model is based on Gaussian approach with particle tracking to model hydrogen sulfide concentrations at the Grensasvegur measuring station in Reykjavik, that were compared to the measured concentrations at the station. For eight events out of nine analyzed the model calculated a rise in the concentration. This indicates that the model obtained can be used for calculating and predicting changes in hydrogen sulfide concentration in Reykjavik, although it would benefit from some modification.

By using the model the concentration at different locations in the capital area can be predicted. Hydrogen sulfide concentration was calculated at two other sites in the Reykjavik area and compared to the Grensasvegur measuring station calculations. These sites are Mjoddin shopping center in the Breidholt district and the Kaplakriki sport center in the town of Hafnarfjördur. The comparisons indicate that the maximum concentration at the three sites can be very different even though they are only a few kilometers apart. This is because the calculated plumes are not distributed evenly over the city. They often move in clusters which can result in different concentrations from one place to another, even inside the city.

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