A review of odour properties of H_2S - Odour Threshold Investigation 2012

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Cover Photo:
A Rotorua panellist entering his choice following the presentation of sample gas at the olfactometer ports.

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Executive Summary

H_2S is responsible for the characteristic 'rotten eggs' odour that most people would associate with geothermal areas. The odour can be detected at very low concentrations in air, and the level at which this first occurs is referred to as the odour threshold. This threshold varies from one person to the next, depending on individual sensitivities, age, state of health, and the conditions under which the odour is assessed.

This project aims to establish an odour threshold for hydrogen sulphide (H_2S) in air using local residents as the test subjects. This investigation looks at measuring and possibly refining the H_2S odour threshold value by using dynamic dilution olfactometry (DDO) and a sample panel of 60 people. Half of the sample panel (30) consists of Rotorua residents, as they represent a group of people that are regularly exposed to elevated concentrations of ambient H_2S. It is believed that this leads to a greater degree of tolerance of H_2S odours, but it is not known whether this is due to a reduced sensitivity to the odour (i.e. a higher odour threshold). The other panellists (30) were from Whakatāne and Tauranga, where there is no exposure to geothermal sources of H_2S.

The primary questions for this investigation were – (i) what was the H_2S detection threshold for a non-laboratory type screening panel and (ii) was there a difference in the results obtained for people living in an area with naturally high levels of H_2S (Rotorua) and those living elsewhere?

The threshold data calculations for this investigation have yielded a geometric mean concentration of 0.7 µg/m^3 when determined across the entire panel (n. = 59). The geometric means for the Rotorua and Whakatāne subgroups are 1.1 and 0.5 µg/m^3 respectively. These values are all well below the current New Zealand Ambient Air Quality guideline value of 7 µg/m^3. The geometric means are at the lower end of the summarised international threshold data. Discussion with olfactometry practitioners indicate that the results from this investigation are comparable with what they have recorded in laboratory type settings.

The current NZAAQ guideline value of 7 µg/m^3 which was first documented nationally nearly 20 years ago and discussed even earlier in a New Zealand context in the early 1980's is still widely used as a starting point for odour assessments. For geothermal affected areas the common approach has been to use a value of 70 µg/m^3, which was based on the historic New Zealand Health Department guideline. This value of 70 µg/m^3 meets the Good Practice Guide for Assessing Odour in New Zealand recommendation whereby for low sensitivity receiving environments the ambient concentrations can be in the order of 5-10 odour units (equivalent to 5 -10 times the odour threshold).

However, using the threshold determined in this investigation the acceptable low sensitivity receiving environment values would only be in the order of 3.5 to 7 µg/m^3, which as stated above is the value for non-geothermal (i.e. high sensitivity) areas. A guideline of 3.5 to 7 µg/m^3, is up to ten times lower than the value that is currently used for geothermal areas. However, based on community feedback and/or the lack of complaints about geothermal power plant emissions it appears these communities can tolerate 100 times the odour threshold determined in this study.

This tolerance may well be due not to physiological changes in these people, but more so the acceptance of their location (which is often characterised by having a number of active geothermal surface features) and the economic and societal benefits associated with the use of the geothermal features/resource.

In relation to the second question of this investigation the groups were spatially different, with one consisting of panellists from Whakatāne and Tauranga (non-geothermal areas) and one group from Rotorua, where the panellists are frequently exposed to concentrations well above the international literature odour thresholds. Other basic characteristics of the groups showed that they were generally similar in profiles when it came to the age and sex of the panellists. The residence time for the Rotorua panellists was also recorded. This was compared with threshold values for this group. The results showed no relationship with residence time and average measured threshold.

Several types of analysis of the grouped data showed that there was a statistically significant difference between the geometric mean odour threshold results for the two groups (1.1 µg/m^3 for Rotorua and 0.5 µg/m^3 for Whakatāne). The difference was small, but in the direction we would expect (Rotorua higher than non-geothermal locale). The results also showed that the human response to odour is highly variable.

The difference between the two groups is interesting in a purely theoretical sense. However, when taking into account – (i) the wide range of thresholds that have been published to date, (ii) inaccuracies in the methodologies used in these investigations, and (iii) the end use application of thresholds as a comparison point for modelled outputs, the difference shown between the two groups would be regarded as insignificant and largely treated as being the same for both. The analysis showed that the vast majority of the panellists were able to detect H_2S at the 7 µg/m^3 level.

In setting a guideline value it would be dependent on the receiving environments location, as both groups appear “equal” when it comes to detecting. Variations in odour response would be dependent on what is commonplace in their local environment. Communities that live in close proximity to existing or proposed developments or natural settings where H_2S emissions are present are equally adept at detecting the odour at low concentrations, when compared with the Whakatāne group, but more often than not would be accepting of the odour profile because of location.

In regard to Council air quality policy, the findings of this investigation will be used in the upcoming Bay of Plenty Regional Air Plan review process.

Contents

Tables and Figures

Part 1: Introduction

This project aims to establish an odour threshold for hydrogen sulphide (H_2S) in air using local residents as the test subjects. As part of this project a summary of international and national threshold information and regional ambient monitoring data has been compiled in order to give the project threshold data some context.

H_2S is responsible for the characteristic 'rotten eggs' odour that most people would associate with geothermal areas. The odour can be detected at very low concentrations in air, and the level at which this first occurs is referred to as the odour threshold. This threshold varies from one person to the next, depending on individual sensitivities, age, state of health, and the conditions under which the odour is assessed.

The odour threshold for H_2S is often used in determining the potential for odour nuisance to arise as a result of certain discharges to air. This is a key factor in assessing the air emissions from geothermal developments, for which there appears to be a growing demand within the Bay of Plenty region. The threshold value will also be relevant to the assessments for other potential odorous sources, such as wastewater treatment plants, waste transfer stations and composting operations.

The development of an odour threshold using local residents will help to ensure that the scientific and planning decisions around H_2S discharges are soundly based and directly relevant to the region.

Surprisingly, no work of this nature has been undertaken within New Zealand, even though in some areas H_2S is a prominent part of the natural environment, whether it be from geothermal features in or around Taupo, Rotorua and Kawerau, or decomposing sea lettuce in the Tauranga Harbour upper tidal zones.

National guidance documents have relied solely on international work when using the threshold values, and no locally-relevant thresholds have been formally determined. The need for local input is especially important for those areas that already experience a significant background H_2S signature.

There are a number of benefits of this investigation. Communities that live in close proximity to existing or proposed developments or natural settings where H_2S emissions are present will benefit most from the increased certainty around decision making. There may also be benefits to developers, because the current approach, based on published data, appears to be quite conservative, in that it is assumed that people are more sensitive to H_2S odour than suggested by actual experience.

The published values for the odour threshold of H_2S vary across a wide range of concentrations. These international and national values will be discussed in detail in Part 5.

This report looks at measuring and possibly refining the H_2S odour threshold value by using dynamic dilution olfactometry (DDO) and a sample panel of 60 people.

The standardisation of DDO in Australasia and Europe has only occurred in the past ten to twenty years. The variability in the measurement method before standardisation means that earlier data are not necessarily comparable to the current measurements[1]. The recommended method for DDO in New Zealand (and Australia) is AS/NZS 4323.3:2001[2], which was based on the European draft standard[3]. DDO and other techniques for odour measurement are described in detail in a central government technical report[4], along with other less commonly used techniques, such as electronic instruments and chemical measurement of odorous compounds.

This report follows the structure outlined below:

Part 2 – Background information relating to how the human olfactometry system detects odour.

Part 3 - A brief overview of H_2S health effects.

Part 4 - H_2S odour sources and monitoring data for ambient H_2S within the region.

Part 5 - A summary of international and national odour threshold data for H_2S.

Part 6 - A description of the methodology used for this investigation.

Part 7 - Statistical analysis of the measured data.

Part 8 - A discussion of results and conclusions from the investigation.

Data presented in this report will show different units. Quoted values will be as published, otherwise the unit convention will be to use µg/m^3. Conversion between ppb and µg/m^3 can be undertaken using the following equation, $H_2S(\mu g/m^3) = 1.52 * H_2S(ppb)$ at 0°C.

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[1] Victorian EPA, 2002, Comparison of EPA approved odour measurement methods, Publication SR1.

[2] Australian/New Zealand Standard, 2001, Stationary Source Emissions. Part 3: Determination of Odour Concentration by Dynamic Olfactometry.

[3] European Committee for Standardisation, 2003, Air quality - Determination of odour concentration by dynamic olfactometry, EN 13725.

[4] Ministry for the Environment, 2002c, Review of Odour Management in New Zealand: Technical Report. Air quality technical report no. 24. Ministry for the Environment, Wellington, New Zealand.

Part 2: What is odour?

2.1 The human response to odour

Odour is perceived by our brains in response to chemicals present in the air we breathe. Humans have the ability to detect odour even when chemicals are present in very low concentrations.

Most odours are a mixture of many chemicals that interact to produce what we detect as an odour. Fresh air is usually perceived as being air that contains no chemicals or contaminants that could cause harm, or air that smells ‘clean’. However, fresh air may contain some odorous chemicals, but these will either be pleasant in character or at concentrations too low to be detected by humans.

Different life experiences and natural variation in the population can result in different sensations and emotional responses by individuals to the same odorous compounds. Because the response to odour is synthesised in our brains, other senses such as sight and taste, and even our upbringing, can influence our perception of odour and whether we find it acceptable or objectionable and offensive.

2.2 Odour perception

A USEPA reference guide for odour thresholds states[5] that human odour perception has a few functional aspects of particular relevance: sensitivity and specificity. The close coupling of molecular odorant recognition events to neural signalling enables the nose to detect a few parts per trillion of some odorants[6]. The molecular nature of recognition permits the nose to distinguish between very similar molecules.

The initial events of odour recognition (Figure 2.1) occur in a mucous layer covering the nasal epithelium, which overlays the convoluted cartilage in the back of the nasal cavity. Each of the millions of olfactory neurons in the middle layer of this epithelium extends a small ciliated dendritic knob to the surface epithelial layer and into the overlaying mucus. The binding of a single odorant molecule to a receptor on this dendritic tip may be adequate to trigger a neural signal to the brain. On each tip dozens of cilia increase the surface area available for recognition events ·and may stir the local mucus, aiding in the rapid detection of small concentrations of odorants. Individual receptors desensitize with use, temporarily losing their ability to transduce signals.

The peripheral olfactory neurons project to the olfactory bulb from which signals are relayed to the olfactory cortex and more primitive brain structures such as the hippocampus and amygdala. This last structure affects whole brain-body emotive states. For further information on the olfactory system physiology, see Buck (2000)[7].

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[5] USEPA, 1992, Reference Guide to Odour Thresholds for Hazardous Air Pollutants Listed in the Clean Air Act Amendments of 1990, Office of Research and Development, EPA/600/R-92/047.

[6] Reed RR, 1990, How does the nose know? Cell 60, 1–2.

[7] Buck, L., 2000, Smell and taste: the chemical senses. In Principles of Neural Science, E.R. Kandel, J. H. Schwartz, and T. M. Jessell, eds. (New York, McGraw-Hill), pp. 625-652.

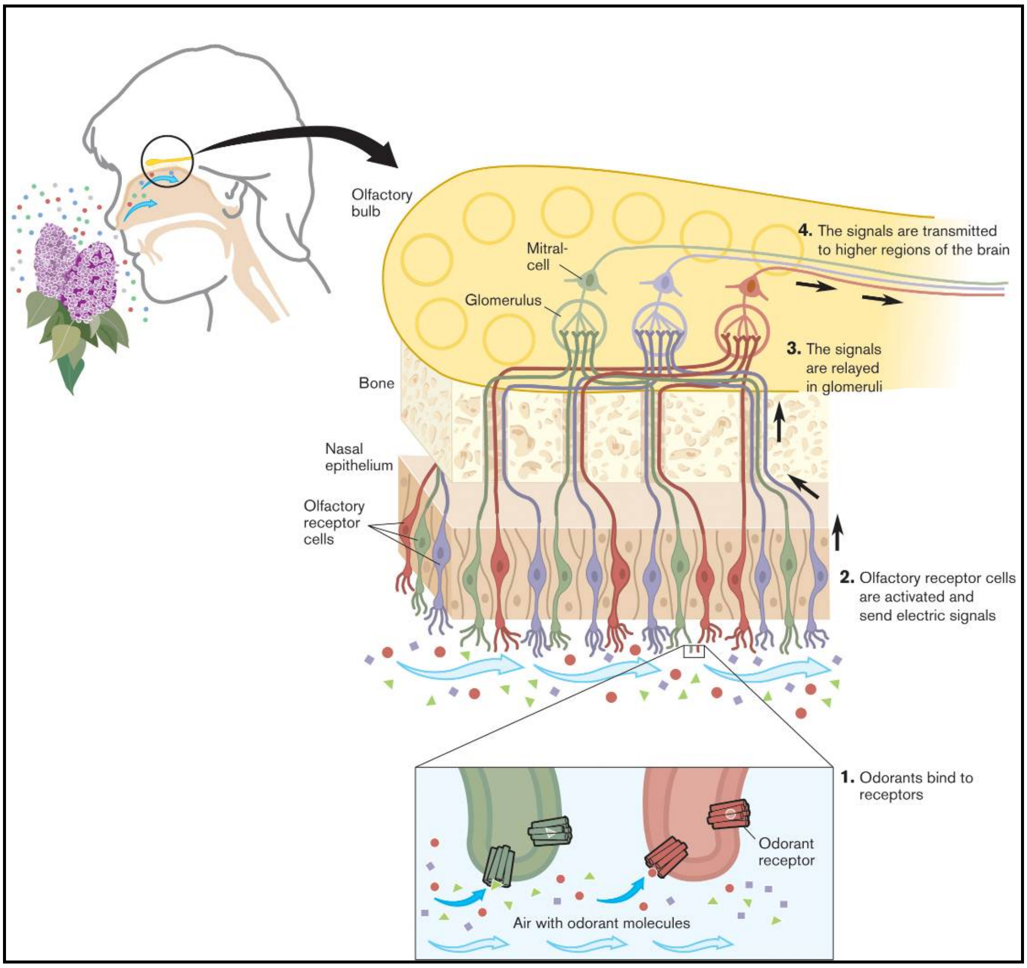

Figure 2.1 Odorant receptors and the organisation of the olfactometry system[8].

How an odour is perceived and its subsequent effects are not straightforward. The human perception of odour is governed by complex relationships, and its properties need to be considered when assessing potential odour effects.

2.3 Human sensitivity to odours

Our response to odours follows certain characteristic patterns common among most human sensory systems. For example, olfactory acuity in the population conforms to a normal distribution. Most people, assumed to be about 96% of the population, have a “normal” sense of smell as depicted in Figure 2.2. Two percent of the population are predictably hypersensitive and two percent insensitive. The insensitive range includes people who are anosmic (unable to smell) and hyposmic (partial smell loss). The sensitive range includes people who are hyperosmic (very sensitive) and people who are sensitised to a particular odour through repeated exposure. Another property of olfactory functioning includes adaptation to an odour, also known as olfactory fatigue. These terms describe a temporary desensitisation after being exposed to an odour[5].

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[8] Courtesy of www.nobelprize.org/nobel_prizes/medicine/laureates/2004/odorant_high_eng.jpg.

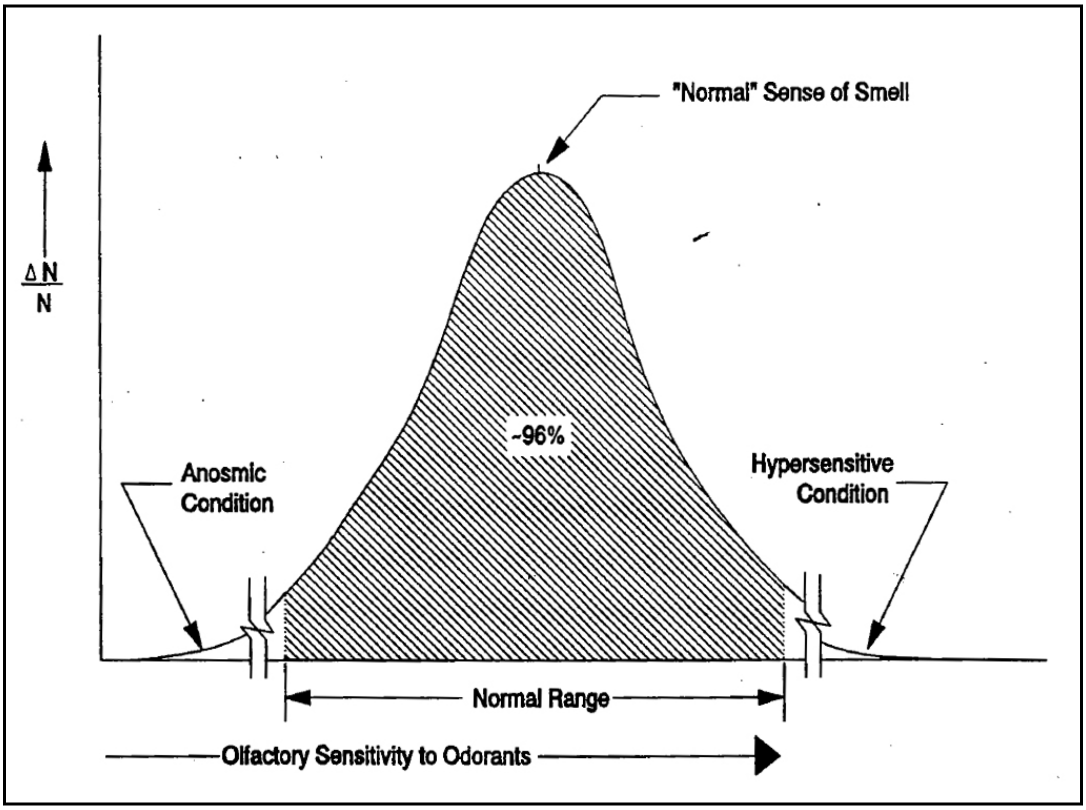

Figure 2.2 The normal range concept showing a potential population distribution of olfactory sensitivities to odorants[5].

Odour intensity refers to the perceived strength of the odour sensation. Intensity increases as a function of the concentration of the odorant chemical in the inhaled air. The relationship between perceived strength (intensity) and concentration can be expressed as a power function known as Stevens Law[3, 9]. In logarithmic coordinates Stevens Law becomes a linear function, the slope of which varies with the type of odorant over a range of about 0.2 to 0.7. In air pollution control this slope can be regarded as the “dose response” factor for odour effects. It also describes the degree of dilution necessary to decrease the intensity to ‘acceptable’ levels. A low slope value (such as H_2S) would indicate an odour that requires a greater relative dilution for the odour to become non-detectable. The relative slope of H_2S and ammonia are depicted schematically in Figure 2.3. The difference in slopes means that at high concentrations of both odorants the predominant odour will be that of ammonia, while at lower concentrations H_2S will be detected.

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[9] Australian/New Zealand Standard, 2001, Stationary Source Emissions, Part 3: Determination of odour concentration by dynamic olfactometry, AS/NZS 4323.3:2001.

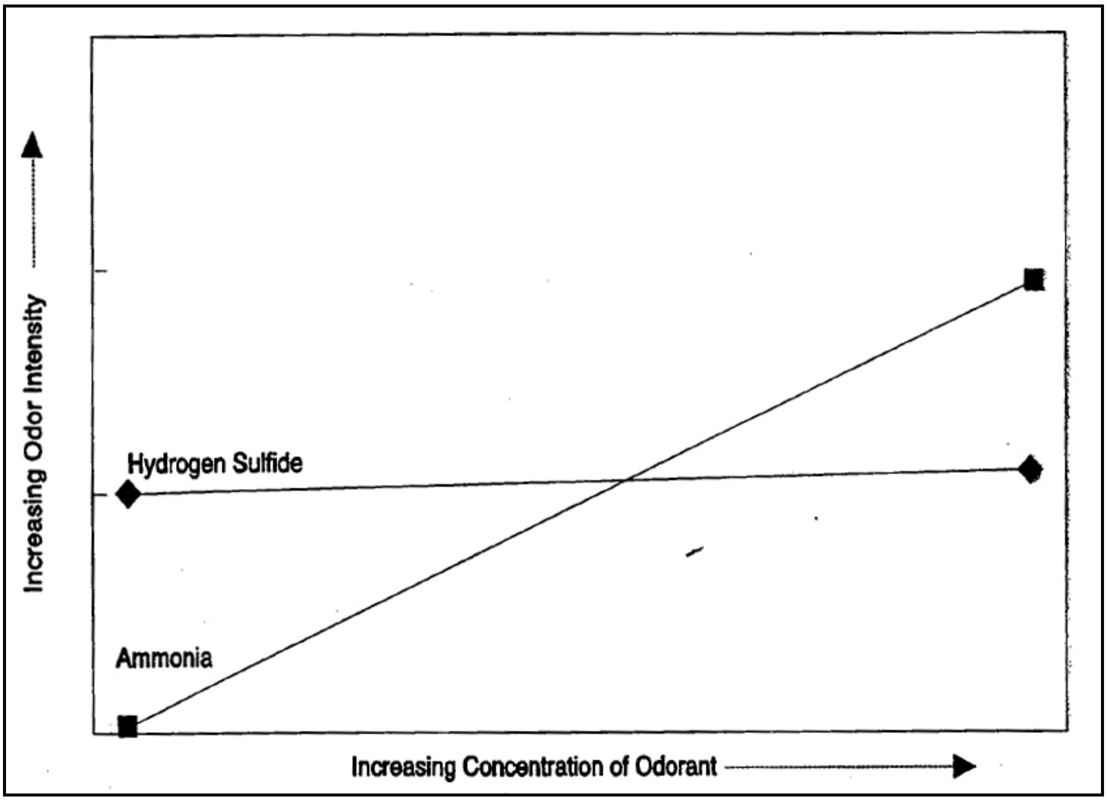

Figure 2.3 Relative slope of odour intensity for ammonia and hydrogen sulphide[5].

As indicated by Stevens' Law, the perception of the intensity of odour in relation to the odour concentration has a logarithmic relationship. The same relationship is known to occur for other human senses such as hearing and sensitivity to light. This means that if the concentration of an odour increases ten-fold, the perceived intensity will be approximately double (i.e. a two-fold increase).

2.4 Cumulative effects, desensitisation/adaption and recovery

In most situations a mixture of odorants, rather than just a single compound, will cause odour detection. One single compound may excite more than one type of olfactory receptor, while a different odorant is likely to excite a different subset of the 350 types of human olfactory receptor cells. Studies have been undertaken on the perceived intensity of odour mixtures by mixing two odorants, both above the detection threshold. The typical finding was that the perceived intensity of a mixture is less than the arithmetic sum (hypo-addition) of the individual intensities.

Interactions between mixtures of odorous compounds can also occur. An example is where one compound disguises or masks the presence of others. However, as the odour concentration reduces through dilution, the nature of the odour may change as different compounds dominate the effect; for example, mushroom-composting odour has been observed to have a distinctly different odour character at source than when diluted downwind.

Continued exposure to an odour can result in people becoming desensitised so that they can no longer detect the odour even though the odorous chemical is constantly present in the air. This is sometimes known as 'olfactory fatigue'. For example, people working in an environment with a persistent odour are often unaware of its presence and may not be aware that the odour is having an impact on the surrounding community.

With continuing exposure to a certain odour concentration, the sensation gradually decreases, and may even disappear. Olfactory fatigue from continued exposure to an odour may affect a person's sense of smell. This phenomenon is called adaptation[5, 10]. Adaptation begins to reduce perceived odour intensity and quality during the first inhalation. Adaptation may reduce both perceived odour intensity and perceived odour quality. Although adaptation takes some time to develop, recovery takes place more quickly.

Ruijten et.al reports that while sensitivity to an odour may decrease after sniffing a sample, 80 to 90% recovery generally occurs within a minute with complete recovery in several minutes[3, 10].

Due to the special olfactory nature of H_2S, during exposure, most subjects experienced an exponential decrease of intensity that dropped to a steady level within 2-5 minutes, and did not change appreciably up to 15 minutes later[11]. One of eight subjects indicated virtually complete loss of odour sensation and another substantial loss which is attributed to reversible paralysis of the olfactory nerve. The other six showed an approximately 50% decrease of perceived intensity, which corresponds to an apparent four-fold reduction in the H_2S concentration. After breathing pure air, the sensitivity recovered almost completely in about four minutes[12].

2.5 Odour effects

In New Zealand the nuisance effects of odour are commonly described by the term 'objectionable or offensive'. This concern with odour is regulated within the Resource Management Act (RMA)[13]. For some compounds, objectionable or offensive effects can occur at very low concentrations, usually far less than the concentrations associated with adverse health effects. However, other compounds only have objectionable or offensive effects at relatively high concentrations, at which point some of the contaminants in the odour may also be causing direct health effects such as skin, eye or nose irritation. Repeated or prolonged exposure to odour can lead to a high level of annoyance, and the receiver may become particularly sensitive to the presence of the odour.

The health effects that have been reported as being associated with odour exposures include nausea, headaches, retching, difficulty breathing, frustration, annoyance, depression, stress, tearfulness, reduced appetite, and being woken in the night . There are also social effects such as reduced enjoyment of the outdoors and embarrassment in front of visitors. All of these contribute to a reduced quality of life for the individuals who are exposed.

People can also develop physiological effects from odour even when their exposure is much lower than that normally associated with the reported health effects. This effect is sometimes termed 'odour worry' and is due to the perception that if there is a smell it must be doing physical harm.

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[10] Shusterman, D, 1992, Critical Review: The Health Significance of Environmental Odour Pollution. Arch. Environ. Hlth 47: 76-88.

[11] Ekman, G., B. Berglund, U. Berglund, 1967, Perceived intensity of odour as a function of time adaptation. Scand. J. Psychol. 8: 177-186.

[12] Ruijten, M., van Doorn, R. & van Harreveld, A, 2009, Assessment of odour annoyance in chemical emergency management, National Institute of Public Health and the Environment, RIVM Report 609200001/2009, The Netherlands.

[13] Resource Management Act (1991), Section 17 (3) (a) - *"require a person to cease, or prohibit a person from commencing, anything that, in the opinion of the Environment Court or an enforcement officer, is or is likely to be noxious, dangerous, offensive, or objectionable to such an extent that it has or is likely to have an adverse effect on the environment."*

Part 3: H_2S health effects

The primary focus of this report in on the odour threshold for H_2S but for completeness and context a brief summary of health effect information is given below. This has been extracted from the World Health Organisation Concise International Chemical Assessment Document 53[14].

Because hydrogen sulphide is a gas, inhalation is the major route of exposure to hydrogen sulphide. Most human data are derived from acute poisoning case reports, occupational exposures, and limited community studies. In confined spaces, human acute poisonings continue to occur. Single inhalation exposures to high concentrations of hydrogen sulphide cause health effects in many systems. Health effects that have been observed in humans following exposure to hydrogen sulphide include death and respiratory, ocular, neurological, cardiovascular, metabolic, and reproductive effects.

Respiratory, neurological, and ocular effects are the most sensitive end-points in humans following inhalation exposures. There are no adequate data on carcinogenicity.

A summary of human health effects resulting from exposure to H_2S is presented in Table 3.1.

Table 3.1 Human health effects at various hydrogen sulphide concentrations.

Exposure (mg/m^3)	Effect/observation	Reference
0.011	Odour threshold.	Amoore & Hautala, 1983
2.8	Bronchial constriction in asthmatic individuals.	Jappinen et al, 1990
5.0	Increased eye complaints.	Vanhoorne et al, 1995
7 or 14	Increased blood lactate concentration, decreased skeletal muscle citrate synthase activity, decreased oxygen uptake.	Bhambhani & Singh, 1991; Bhambhani et al., 1996b, 1997
5-29	Eye irritation.	IPCS, 1981
28	Fatigue, loss of appetite, headache, irritability, poor memory, dizziness.	Ahlhorg, 1951
>140	Olfactory paralysis.	Hirsch & Zavala, 1999
>560	Respiratory distress.	Spolyar, 1951
≥700	Death.	Beauchamp et al, 1984

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[14] WHO, 2003, Hydrogen Sulphide: Human Health Aspects. World Health Organisation, Geneva. Concise International Chemical Assessment Document (CICAD) No.53.

Part 4: Sources of H_2S in the Bay of Plenty

4.1 Sources of H_2S within the Bay of Plenty

There is a wide range of possible odour sources in the Bay of Plenty region, some of which are associated with the numerous odour complaints received each year by the Bay of Plenty Regional Council (BOPRC) (see Figure 4.1). Total quantities of H_2S emissions have not been determined for the Bay of Plenty, although some of the more major industrial sources have been documented. However, the spatial extent and variability of natural sources make this an unachievable task.

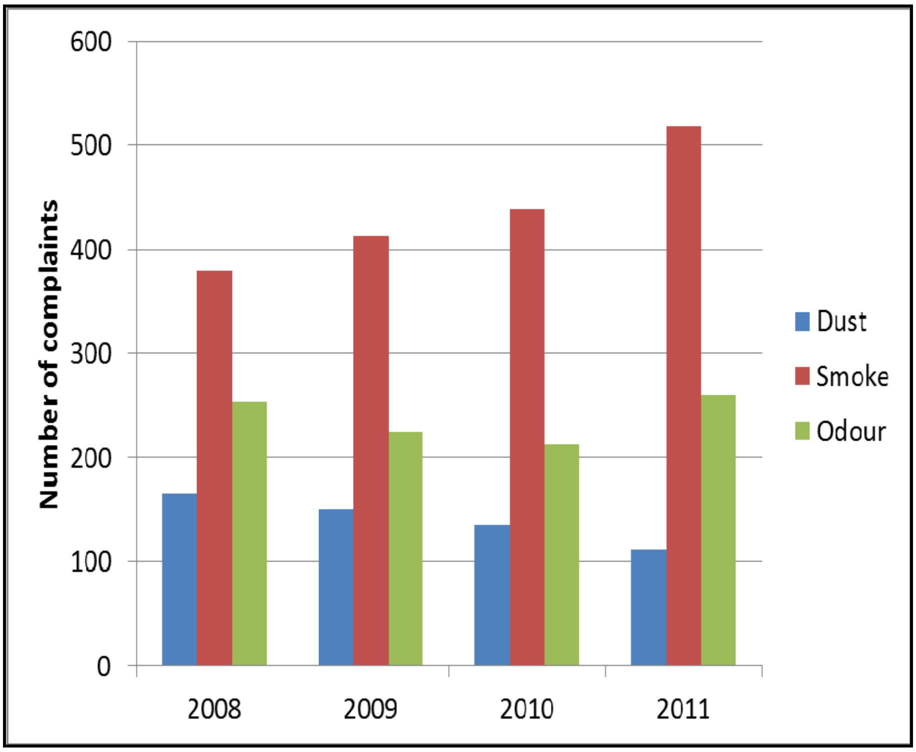

Figure 4.1 BOPRC complaints database output based on air complaint categories.

Geothermal activity is one of the most common natural sources of H_2S in the region (biogenic emissions[15] would be the most wide-spread) and occurs at a number of locations. Geothermal surface features extend from the northern boundaries of the Tauranga Harbour in the west, through to Manaohau springs located in Te Urewera National Park in the east. The northern extent of these features includes the offshore islands of Tuhua, Motuhora and Whakaari. Another significant natural source of H_2S is decomposing sea lettuce in estuarine environments, particularly Tauranga Harbour.

Anthropogenic sources within the Bay of Plenty include a number of industrial processes (which typically require air discharge permits[16]) such as pulp mills, wastewater treatment plants, geothermal power generation, meat processing works, commercial composting operations and refuse transfer facilities. Domestic sources

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[15] For example - coastal marine sediments.

[16] These permits may require ambient monitoring (Mighty River Power Ltd - 63298 and Carter Holt Harvey - 65725) or odour surveys (Tauranga City Wastewater Treatment plant - 62722 & 62723) to be undertaken depending on the scale of the operation.

such as composting can provide very localised issues along with human flatulence[17] (18ppm (~27mg/m^3) for humans on a normal diet). Internationally investigations into vehicular H_2S sources have also been undertaken at several overseas locations, with an hourly maximum[18] of 54µg/m^3 and peaks[19] up to 150µg/m^3 being recorded.

Rather that attempting to measure particular emission rates within the Bay of Plenty, ambient monitoring has been undertaken in various forms over the last 40 years at a number of locations within the region. This information is summarised below in order to provide an indication of the levels the population can be exposed to as they go about their daily activities and as context for the odour threshold studies.

4.2 Ambient H_2S levels within the Bay of Plenty

Documentation of ambient levels varies in detail, ranging from a simple (but quantitative) categorisation of areas[20] to semi and fully quantitative H_2S measurements. Odour surveys have also been undertaken at different times within the region[21, 22, 23]. These surveys are a consent requirement for some of the more substantial odour producing industrial activities. They do not require any H_2S measurements as such, but are a qualitative way of determining odour influence and significance within a specific area of interest.

4.2.1 Rotorua area

Ambient monitoring of H_2S has occurred in proximity to both natural and industrial sources. The Regional Council has monitored ambient H_2S levels in Rotorua since the mid 1990's[24]. Recorded levels for two of the longer periods of monitoring (at Ti Street and Arawa Street) show peak (one hour average) levels of up to about 4000 µg/m^3, and annual average concentrations of between 75 and 150 µg/m^3 respectively. The data show clear diurnal patterns (Figure 4.2) which are most likely determined by meteorological factors such as wind speed and direction, atmospheric stability and rainfall.

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[17] ATSDR, 2006, Agency for Toxic Substances and Disease Registry ToxGuide for Hydrogen Sulfide, CAS#7783-06-4, July 2006.

[18] Kourtidis, K., Kelesis, A., Petrakakis, M., 2008, Hydrogen sulphide in urban air, Atmospheric Environment, vol 42, 7476 - 7482.

[19] Deuchar, C. N., 2002, The Detection and Measurement of Hydrogen Sulphide, A thesis submitted to the University of Nottingham for the degree of Doctor of Philosophy in the School of Life and Environmental Sciences.

[20] Bates, M. N., Garrett, N., Shoemack, P., 2002, Investigation of health effects of hydrogen sulphide from a geothermal source, Arch. Environ. Health, 57(5), 405-411.

[21] Tauranga City Council, 2012, Tauranga Biannual Community Odour Survey 2012, A requirement of the Resource Consents for the Chapel Street and Te Maunga Wastewater Treatment Plant, September 2012.

[22] Mighty River Power, 2009, Mighty River Power Kawerau Geothermal Power Station Odour Survey Report, prepared for Mighty River Power by Beca Infrastructure Limited.

[23] Carter Holt Harvey Tasman Limited, 2007, Carter Holt Harvey Tasman Kraft Pulp Mill Odour Survey Report 2007, Prepared for Carter Holt Harvey Tasman Limited by Beca AMEC Limited, March 2007.

[24] Iremonger S, 2004. NERM Air Monitoring Review. Environment BOP, Whakatane. Environmental Publication No. 2004/03.

City wide measurements were also undertaken by Horwell[25] using a novel qualitative passive sampler approach. A method involving the reaction of H_2S with the silver halide contained in treated photographic paper was developed and tested. Based on the analysis of the results Rotorua city was divided into three regions, an area of low concentrations in the west of the city, a corridor of high concentrations in the centre of the city, and an area of medium concentrations in the east of the city. During the project continuous gas detector measurements were also undertaken with a paper tape toxic gas detector[26] at three locations, Jervis Street located approximately 1 km northwest of the Arikikapakapa geothermal area, Ruihi Street, central city 1 km northwest of the racecourse and a lake front location. All deployments were for periods of several months.

For Jervis Street the average concentration was ~5 ppb with occasional spikes reaching 90 ppb, with concentrations in the range of 20-30 ppb commonly being recorded during the night. The lake front site was monitored for a period between August 1997 and November 1997, and the 90 ppb instrument limit was exceeded about 40 times during the deployment. The average concentration from September to November was 1.3 ppb. The Ruihi Street deployment collected 15 days of record, 4.2% of the time values were above the instrument maximum of 90 ppb. An average over the 15 days was 11 ppb. Approximately 50% of the time values were <3 ppb.

In conjunction with Howell's project and also independently, NIWA have undertaken ambient H_2S measurement throughout the city which has been summarised by Hinz[27] and in several NIWA reports[28, 29, 30, 31]. The monitoring was conducted at seven sites – at Whakarewarewa Village, Sunset Road, Te Ngae Road, Ōwhata, Jervis Street, Arawa Road and at the Lake front. Monitoring did not occur concurrently, but lasted for one to three months per site. Therefore concentrations cannot be compared directly as they might be affected by daily and seasonal variation, but patterns in the distribution of H_2S are detectable. The NIWA readings at Te Ngae Road, which is in proximity to Ti Street (the BOPRC site), showed the highest H_2S concentrations with an overall mean value range between 72 and 108 ppb. Whakarewarewa Village and Arawa Street also had relatively high concentrations with an overall mean value range of 66 to 100 ppb and 7 to 54 ppb respectively. In contrast, at Jervis Street, Owhata, Lake Front and Sunset Road observations were relatively low, with concentrations of 4, 4, 3 and 0.3 ppb respectively.

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[25] Horwell, C., 1998, Geothermal hydrogen sulphide mapping across Rotorua, New Zealand: Implication for the Assessment of Public Health, Victoria University, Wellington.

[26] Honeywell Analytics Chemkey TLD portable toxic gas detector, https://www.honeywellanalytics.com/.

[27] Hinz, R., 2011, Hydrogen Sulphide in Rotorua, New Zealand: Personal Exposure Assessment and Health Effects, Master of Science in Earth Science thesis, Massey University, New Zealand.

[28] Peterson, J., Fisher, G.W., Timpany, G, 1996 Survey of Background Hydrogen Sulphide in Rotorua – 1996, AK96058, NIWA.

[29] Peterson, J., Fisher, G.W., Timpany, G, 1998 Survey of Background Hydrogen Sulphide in Rotorua – 1996/1997, AK98013, NIWA.

[30] Wegmuller, M & Peterson, J., 1998, Method to quantify the H_2S exposure for the urban area of Rotorua, AK98024, NIWA.

[31] Fisher, G, 1999, Natural Levels of Hydrogen Sulphide in New Zealand, Atmos. Environ. 33(18), 3078-3079.

Seigel et al[32] undertook measurement of H_2S at 32 sites within Rotorua City. “Metronics Rotorod Colortec” asbestos pads treated with lead acetate were used to obtain hourly spot measurements over a 12 hour daily measurement window. Values ranged from <5ppb for sites in the western areas to 1900 ppb in the southern Fenton/ Amohau Street area. Central city sites measured values in the 30-100 ppb range with values in a 5-30 ppb range on the periphery of this central area.

Siegel et al.[33] also investigated H_2S concentrations along the lake shore and found a noticeable increase in concentrations from the north of Sulphur Bay at Ōhinemutu towards the south of Sulphur Bay at Ngāpuna. The average level north of Ōhinemutu was 5 ppb, while from Ōhinemutu to the north tip of Sulphur Bay most sites gave concentrations in the range of 3 to 115 ppb, apart from one which was in the range of 15 to 290 ppb. The lower Sulphur Bay sites had a range from 1200 ppb to 2700 ppb. The results of this study should be taken as purely indicative, as measurements were taken on just one to three occasions per site, and exposure times of the samplers varied between 10 and 60 minutes.

Monitoring for H_2S in air was carried out by the Department of Health[34, 35] on various occasions during the 1970’s and this indicated that levels within the geothermal area including the central business district, could be up to $1mg/m^3$ or above. The most reliable data[36], from a three month monitoring exercise in 1978, indicated a median concentration of about 30 $\mu g/m^3$, with 35% of the results in excess of 70 $\mu g/m^3$, and 10% above 400 $\mu g/m^3$. A similar range of measurements was also reported for some earlier measurements taken using a less reliable method[37].

A current research program[38] is looking at developing a longitudinal H_2S exposure profile for each of the 1,800 Rotorua residents participating. Mapping and modelling[39] the distribution of H_2S concentrations across the geothermal field and how these concentrations vary seasonally and across the course of a day is being undertaken in order to develop the exposure profile.

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[32] Seigel, S. M., Seigel, B. Z., Penny, P, Penny, E., 1984, Geothermal Hydrogen Sulphide and Health in Rotorua, New Zealand, A preliminary report prepared for the Hawaii Natural Energy Institute’s Environmental Quality Study, University of Hawaii.

[33] Seigel, S. M., Penny, P., Seigel, B.Z. and Penny, D., 1986 Atmospheric Hydrogen Sulphide levels at the Sulphur Bay Wildlife Area, Lake Rotorua, New Zealand, Water, Air and Soil Pollution, 28(3):385-391.

[34] Graham, B. W and Edmunds, C. J., 1978, Hydrogen sulphide levels in Rotorua, unpublished monitoring data, Department of Health, Environmental Laboratory, Auckland.

[35] Graham, B. W. and Narsey, H., 1994, Air pollution monitoring in New Zealand, 1960 -1992., Institute of Environmental Science and Research, Report No. MESC 94/27.

[36] Rolfe, K.A., 1980, The air pollution aspects of geothermal power stations, The New Zealand Energy Journal, Vol. 53, No. 3, p.51-58.

[37] Thom, N.G. & Douglas, R. T., 1977. A study of hydrogen sulphide levels in the geothermal areas of Rotorua, New Zealand, In Proceedings, 4th International Clean Air Congress, International Union of Air Pollution Associations (Brighton).

[38] Bates, M. N., 2006, Effects of Long Term Low Level Hydrogen Sulphide Exposure, National Institute of Environmental Health Sciences, Research Summary Document Grant Number R01ES014038.

[39] Barclay, J. (2010). Preliminary findings of hydrogen sulphide in Rotorua, New Zealand, and where to next. In: Eccles, J.D., Grigor, M.R., Hoskin, P.W.O., Hikuroa, D.C.H. (eds). Abstract Volume, GeoNZ 2010 Conference, Auckland, New Zealand. Geoscience Society of New Zealand Miscellaneous Publication 129A: p.20.

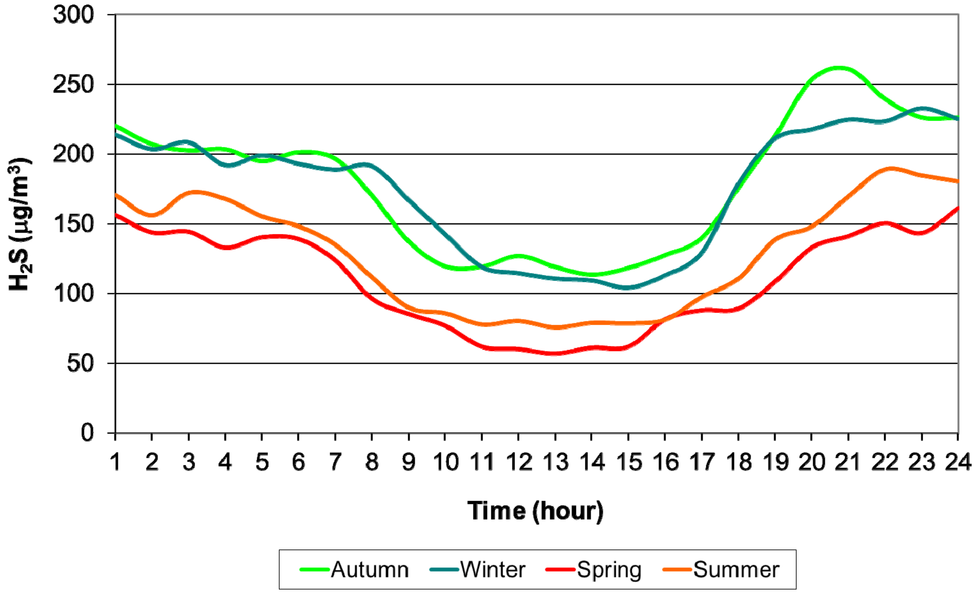

Figure 4.2 Seasonal diurnal patterns recorded at Ti Street, Rotorua

Source or near source measurements

In Rotorua there have been a number of projects looking at levels of H_2S. Finlayson[40] investigated soil gas levels which showed an isolated but significant concentration zone at Arikikapakapa and a north/south alignment of zones of higher concentration (20,000 – 200,000 ppm), that starts at the edge of Whakarewarewa, proceeds north with increasing concentrations and a greater area of significant gas emissions, terminating at Government Gardens.

Indoor H_2S measurements were undertaken by Durand & Scott[41]. The primary means of gas entry was directly from the ground through the floors, walls, and subsurface pipes. Indoor vents were located and found emitting up to approximately 200 ppm H_2S, concentrations high enough to present an acute respiratory hazard to persons close to the vent (e.g. children playing at floor level). These confined space levels are significantly higher than ambient levels.

Smid et. al[42] reported on direct source measurements from 38 geothermal features including fumaroles, acid pools, alkaline springs, collapsed craters, mud pools, mud cones, and warm ground. H_2S gas concentrations in parts per million (ppm) were recorded using a personal H_2S monitor, the Dräger Pac 7000[43], calibrated with a data logger interval set at 10 seconds. H_2S gas readings were taken at the surface/entry of the feature, 0.5 meters above the surface/entry, and 1 m above the surface/entry. Overall, features emitted concentrations of H_2S gas from 0 to 100+ ppm at the feature entries. At a height of 0.5 m above feature surface/entry, H_2S readings ranged from 0 to 57 ppm. At 1 m above feature surface/entry, the H_2S measurements ranged from 0 to 20 ppm.

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[40] Finlayson, J.B., 1992, A soil gas survey over Rotorua Geothermal Field, Rotorua, New Zealand, Geothermics, Vol. 21 No. 1/2, ISSN 0375-65058.

[41] Durand, M. & Scott, 2005, Geothermal ground gas emissions and indoor air pollution in Rotorua, New Zealand, Sci. Total Environ, 345, 69-80.

[42] Smid, E. R., Howe, T. M. & Lynne, B. Y.,2010, H_2S Pilot Study, Rotorua, New Zealand, Institute of Earth Science and Engineering, New Zealand, Report 11-2010.1, April 2010.

[43] Electrochemical diffusion device.

Rotorua District Council also undertakes regular monitoring of H_2S levels within Rotorua. This monitoring typically has an indoor or enclosed space focus. The Council administers the Geothermal Safety Bylaw[44] and provides an advisory role, which includes testing for the presence of H_2S gas to ensure as far as possible, the safety of public from geothermal activity. The levels monitored can be as high as several hundred ppm on occasions[45].

4.2.2 Kawerau area

Carter Holt Harvey Pulp and Paper Limited at the Tasman Mill continuously monitor ambient TRS[46] at Edgecumbe[47] (and also historically at Awakaponga[48]) (see Figures 4.3 and 4.4 respectively). This monitoring builds on earlier investigative monitoring undertaken during 1992 which looked at total sulphur levels[49] where a H_2S guideline value of 7µg/m^3 was exceeded for 4.8 percent of the time over the seven month (mainly winter time) monitoring period.[68]

A key issue relating to the Rangitāiki Plains ambient monitoring is that the data records TRS. These measurements therefore include H_2S emissions from the Norske Skog Turbo Alternator 3 electricity generator stack, a number of the Carter Holt Harvey pulp mill stacks, and the geothermal surface features located in the Kawerau township and the hills to the west. The percentage contribution made by H_2S to the TRS readings is unknown, and may vary from hour to hour depending on both natural and industrial geothermal emissions.

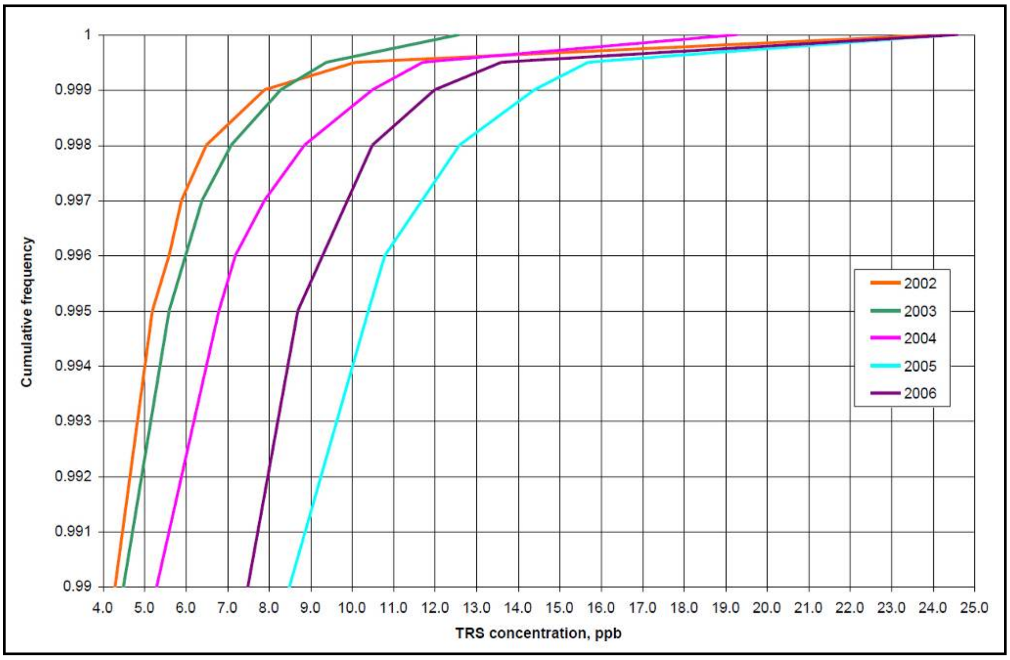

Figure 4.3 Ambient TRS data frequency from Awakaponga site[50].

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[44] Rotorua District Council, 2008, Geothermal Safety Bylaw, Doc No: IT-621891.

[45] Pers. Comms Peter Brownbridge, RDC Geothermal Inspector.

[46] Total Reduced Sulphur - includes hydrogen sulphide, mercaptans, dimethyl sulphide, dimethyl disulphide and other sulphur compounds.

[47] Resource Consent 60725

[48] Resource Consent 61435

[49] Bingham, A.G. et al, 1992, Ambient Air Quality Monitoring – Edgecumbe, 1992. Institute of Environmental Health & Forensic Sciences, NECAL Report S92/837C, 5 August 1992, 27p.

[50] Resource Consent 65720 Assessment of Environmental Effects, Chapter 4.

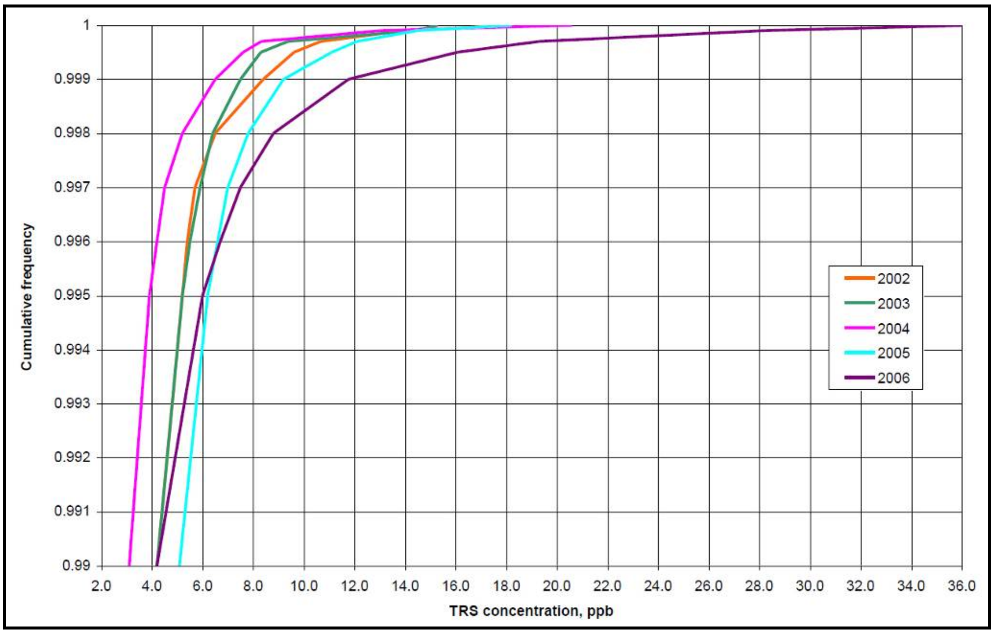

Figure 4.4 Ambient TRS data frequency from Edgecumbe site[50].

Mighty River Power Ltd – Kawerau Geothermal Power Station has also undertaken limited ambient monitoring as required by their air discharge consent[51] at a location at the adjacent Tasman Mill, and at the three nearby townships of Kawerau, Edgecumbe and TeTeko.

The results[52] show that short term (10-15 minute average) concentrations of H_2S can reach 924 μg/m^3 at the Mill site, over 120 μg/m^3 at the Kawerau site[53], up to 30 μg/m^3 at the TeTeko site, and up to 70 μg/m^3 at the Edgecumbe site. The longer term concentrations, indicated by the annual averages, can reach 7.0 μg/m^3 at the Mill site, over 3.8 μg/m^3 at the Kawerau site, 0.3 μg/m^3 at the Te Teko site, and 0.9 μg/m^3 at the Edgecumbe site.

Under a consent change Mighty River Power Ltd are now required to undertake ambient H_2S monitoring[54] for a period of not less than 24 months in relation to the operation of their geothermal plant near Kawerau township. The gas analyser monitoring equipment is currently being installed at monitoring sites at the north end of the Kawerau Township, Edgecumbe and Te Teko.

4.2.3 Rotomā area

Kingston Morrison[55] also reports on H_2S monitoring carried out at Rotomā. On 3 April 1995 the monitoring equipment was located at Rotomā School for several months. H_2S levels were frequently above 7 μg/m^3 and up to approximately 22 μg/m^3 were reported. These higher concentrations mostly occurred at night.

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[51] Resource Consent 63298 Assessment of Environmental Effects, Air Quality documentation.

[52] Fisher, G.W., 2009, Ambient Monitoring Analysis, Assessment of Effects of the Discharges from the Proposed Kawerau Geothermal Power Station, prepared for Mighty River Power, 5 August 2009, 26p.

[53] Although probably high concentrations since the instrument has exceeded its scale.

[54] BOPRC Air discharge consent 63298.

[55] Kingston Morrison, 1995, Rotomā Geothermal Field Chemistry of Discharge Fluids from Well RM1 for Power NZ, Works Geothermal Report P164703.

Kevern[56] undertook several surveys (20/8/93, 10/9/93 and 17/9/93) using a Jerome Model 621 sensor with a H_2S detection range of 0-50 ppb. Measurement points were at irregular intervals along the State Highway from Kawerau to Rotorua. Results showed that the H_2S level around Rotoehu/Rotoma were below 5 ppb. Kevern noted that samples taken at the Waitangi Soda Springs on 10 September were high (up to 45 ppb) compared to the values recorded on 17 September and attributed this to possibly a contamination of the measurement cell from high readings recorded in Rotorua earlier in the day. Elevated levels were found in the Kawerau, Tikitere and Rotorua areas (15->50 ppb).

4.2.4 Tauranga Harbour

Monitoring of ambient H_2S associated with decomposing sea lettuce[57] has shown concentrations that are at adverse human health effect levels. Two sites in Tauranga Harbour, Ongare Point and Ngakautuakina Point, were selected for monitoring of H_2S based on reported odour issues and health concerns raised by local residents. When the material was disturbed, both sites recorded values greater than ~288,000 μg/m^3. Values recorded ~1 m above the surface ranged from 2.88 mg/m^3 to 14.4 mg/m^3.

A summary of the ambient values from this section are shown in Table 4.1. For the purposes of comparison all H_2S volume measurements have been converted to weight-based measurements (see Section 1). It should be noted that the results obtained by different measurement methods may not be directly comparable (sampling inlet position has been noted where known). No allowance has been made for the different measurement sampling and averaging times.

The summary table shows that a wide range of concentrations can be experienced depending on location. Also at any given location there can be variations of several orders of magnitude in the values monitored, most likely due to variations in emissions and/or meteorological conditions.

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[56] Kevern, R., 1993, BOPRC Internal memorandum, Ambient Hydrogen Sulphide Monitoring around Lake Rotoma, File Reference 1370 03 0077, 5p.

[57] BOPRC, 8 December 2009, Tauranga Harbour sea lettuce - hydrogen sulphide monitoring, Agenda Report to Regulation Monitoring & Operations Committee.

Table 4.1 Ambient recorded data summary for the Bay of Plenty.

Ambient recorded data summary for the Bay of Plenty ($\mu g/m^3$).							
	Data interval				**Data interval**		
Location	**Peak**	**Hourly**	**Annual**	Location	**Peak**	**Hourly**	**Annual**
Tasman Mill, Kawerau[51]	924		7	Rotorua central	1000[34]	150[32]	
Te Teko[51]	30		0.3	Rotorua western[32]		<8	
Kawerau[51]	120		3.8	Rotorua southern[32]		2900	
Edgecumbe[50, 51]	54 - 70	24	0.9 - 2	Ohinemutu[33]		8	
Awakaponga[50]	38	27	1.5	Lake Front – Ōhinemutu to Sulphur Bay[33]	140+[29]	23 - 440	
Arawa Street, Rotorua[24]		4200	150	Sulphur Bay[33]		1800 - 4100	
Ti Street, Rotorua[24]		3900	75	Rotorua geothermal features[42]	150000+		
Jervis Street, Rotorua[28]	140+			Rotomā area[56,55]	<8 - 22		
Ruihi Street, Rotorua[28]	140+			Decomposing sea lettuce, Tauranga Harbour[57]	288000 (surface) 2880 (at 1 m)		

Part 5: H_2S threshold information

Odour threshold literature for a particular chemical can provide a wide range of threshold values and, as highlighted within this section, this is certainly the case for H_2S. Often the disparity stems, in part, from inter-individual differences in sensitivities to odours, and in part, from methodological differences[58,59]. Warner[60] has also stated that the widely varying odour thresholds for H_2S, some three orders of magnitude, are generally ascribed to olfactory desensitisation, which is a characteristic of the gas.

The Good Practice Guide for Assessing and Managing Odour in New Zealand[61] states that published odour threshold data should be used with caution because many different methods have been used and there is a wide variation reported in the literature, often by four orders of magnitude. As an example, when using dilution dynamic olfactometry methods the odour threshold is usually taken as the value at which 50 percent of the panel are able to detect or recognise the odour, but some historical data are based on a range of different percentages. Most odour threshold reference data appear to have been developed before dilution dynamic olfactometry was standardised, so the data may not be directly applicable to assessments where odour guidelines have been developed based on the standard olfactometry techniques.

Both detection and certainty, or recognition, odour thresholds for compounds are reported in the literature. The detection threshold is the lowest concentration of a compound that can just be detected by a certain percentage of the population, while the certainty or recognition threshold is the lowest concentration of a compound that can be recognised with certainty as having a characteristic odour quality. In general, recognition thresholds are approximately three to five times the detection threshold. When using odour threshold data it is important to be clear about which type of threshold is being reported.

This section lists references for H_2S threshold data. The majority of the information is from international publications, while the information from local sources relates mainly to the use of threshold data in establishing air quality guidelines.

5.1 International information

Van Gemert[62] provides a compilation of published odour threshold data for a wide range of chemical substances. The data for H_2S is summarised in Figure 5.1, and covers studies from as far back as 1848. The data are given chronologically for each compound with the original data source identified, but no attempt is made by the author (van Gemert) to critically evaluate the data. Van Gemert's publication is an update of similar previous compilations, such as Devos et al [63]. In addition to van Gemert's data, data points (shown in red) have been added as a result of a literature search undertaken during the production of this report.

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[58] van Harreveld, A.P., Heeres, P. & Harssema, H., 1999, A Review of 20 Years of Standardization of Odour Concentration Measurement by Dynamic Olfactometry in Europe, J. Air & Waste Manage. Assoc., 49:705-715.

[59] Ramsdale, S.L. and Baillie, C.P, 1996, Inter laboratory Test Program: Odour Detection Threshold for Hydrogen Sulphide, Journal of the Clean Air Society of Australia and New Zealand, Vol. 30 No. 1, 36-37.

[60] Warner, P., 1976, Analysis of Air Pollutants, Environmental Science and Technology Series, John Wiley & Sons Inc, ISBN 9780471921073.

[61] Ministry for the Environment, 2003, Good Practice Guide for Assessing and Managing Odour in New Zealand, Air Quality Report 36, ISBN: 0-478-24090-2, ME: 473, Wellington, New Zealand.

[62] van Gemert LJ, 2011. Compilations of Odour Threshold Values in Air and Water. ISBN/EAN: 978-90-810894-0-1.

[63] Devos, M., Patte, F., Rouault, J., Laffort, P. van Gemert, L., 1990, Standardized Human Olfactory Thresholds, IRL Press at Oxford University Press.

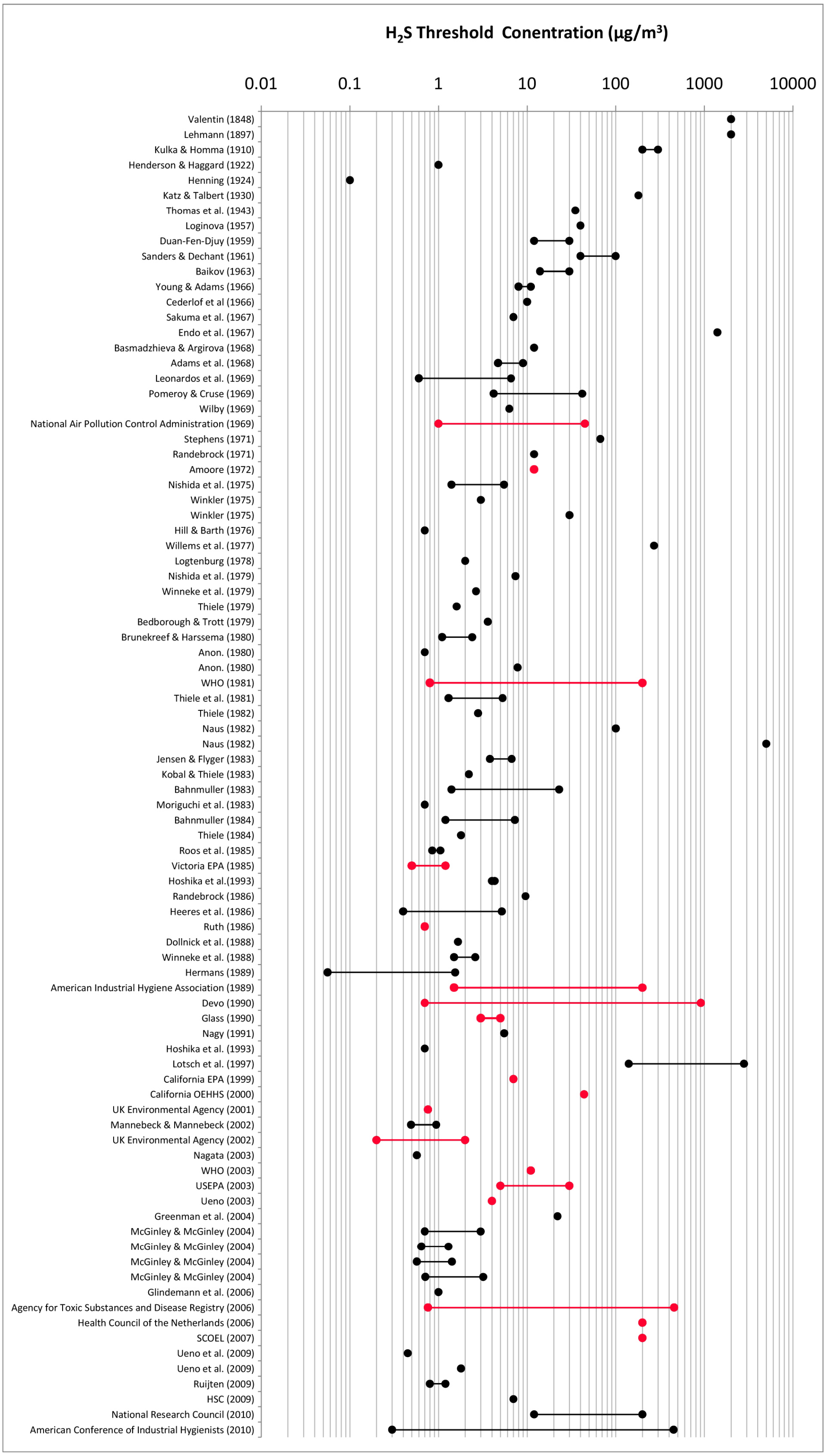

Figure 5.1 *H_2S threshold values plotted from van Gemert (2011) data (Note: data in red are additions which were sourced during the production of this report).*

The American Industrial Hygiene Association[64] produced a report in 1989 which was intended to serve as a chemical odour threshold reference document. The reported mean estimates of odour thresholds were developed from acceptable data sources. These sources were drawn from two compilations of odour threshold values[65, 66]. A two phase review was conducted on the sources. The review consisted of first determining if the source was a primary odour experimental paper. If so, the data was critiqued according to the following criteria – panel size, panel selection, panel calibration, presentation mode that minimises additional dilution at the intake, threshold type, potential for olfactory fatigue, number of repeated trials, concentration steps increasing by a factor of two or three. The range of 'acceptable' threshold results for H_2S determined through this process was 0.001 to 0.13 ppm.

From the information presented in this section it can be seen that the refinement in technology and method has resulted in quoted H_2S threshold figures frequently below the 1 µg/m^3 level.

5.2 National air quality criteria

There has been no published research in New Zealand to determine detection thresholds for H_2S. Rather the focus of this section is on the use of published odour threshold data to derive ambient air quality guidelines.

The New Zealand Air Quality Guidelines include H_2S as one of the contaminants. The first guidelines were published in 1994, but prior to that a discussion paper[67] was released by Ministry for the Environment (MfE) with proposed values of 7 µg/m^3 (one hour average) and 70 µg/m^3 (one hour average). The 70 µg/m^3 was intended to be applied in areas of significant natural emissions of H_2S (e.g. Rotorua) and a level of 7 µg/m^3 in areas unaffected by natural emissions. The paper included a comparative table of other air quality guidelines with the following entries for H_2S.

New Zealand Department of Health Guidelines	70 µg/m^3 (one hour mean) and 7 µg/m^3 (24 hour mean).
Victoria EPA	0.14 µg/m^3.
WHO	7 µg/m^3 (30 minute mean).
Canada	Maximum desirable 1 µg/m^3 (one hour mean) and maximum acceptable 15 µg/m^3 (one hour mean) 5 µg/m^3 (24 hour mean).
Netherlands	2.5 µg/m^3 (one hour mean).

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[64] AIHA, 1989. Odour Thresholds for Chemicals with Established Occupational Health Standards. American Industrial Hygiene Association, Fairfax, Virginia.

[65] van Gemert, L. J. & Nettenbreijer, A.H., 1977, Compilation of Odour Threshold Values in Air and Water, The Netherlands Central Institute for Nutrition and Food Research TNO (CIVO-TNO), National Institute for Water Supply (RID).

[66] van Gemert, L. J., 1982, Compilation of Odour Threshold Values in Air. Supplement IV, The Netherlands Central Institute for Nutrition and Food Research TNO (CIVO-TNO).

[67] MfE, 1993, Air Quality Guidelines, A discussion paper on proposed ambient air quality guidelines in New Zealand, Ministry for the Environment, Wellington.

The first guidelines[68] were published in 1994, with a level of 7 µg/m^3 (30 minute average[69]) for H_2S. This was based on the WHO guideline which recommends a value of 7 µg/m^3 to avoid "substantial complaints about odour annoyance". It was noted that this value was above the recognised odour threshold (0.2 to 2 µg/m^3) and could therefore result in some level of complaint from the most sensitive parts of the population. The 70 µg/m^3 level (based on the old Health Department Guideline) was discarded, because it appeared to be based on simply scaling up from the 'normal' level (i.e. with no real scientific basis). Rather than setting a level which could be exceeded because of naturally occurring circumstances, the Ministry recommended that H_2S monitoring networks be setup where H_2S was a concern.

The 7 µg/m^3 (one hour average) value of for H_2S has been retained in the latest (2002) version of the Air Quality Guidelines[70] with a footnote stating that the value is based on odour nuisance and may be unsuitable for use in geothermal areas.

A specific guideline for use in geothermal areas was developed by Graham (2008), who submitted the following summary and analysis of the threshold information for the Board of Inquiry for the Te Mihi Geothermal development near Taupo[71]:

Hydrogen sulphide has a characteristic 'rotten eggs' odour, which can be detected at very low concentrations in air. The level at which this first occurs is referred to as the odour threshold. This threshold varies from one person to the next, depending on individual sensitivities, age, state of health, and the conditions under which the odour is assessed. Published values for odour thresholds are normally based on the level at which 50% of a selected group of people can detect the odour, under controlled conditions.

The published values for the odour threshold of hydrogen sulphide vary across a wide range of concentrations, as illustrated by the following examples:

Ministry for the Environment (2002):	*0.2 to 2 µg/m^3*
UK Health & Safety Commission (2000):	*180 µg/m^3*
UK Environment Agency (2002):	*0.76 µg/m^3*
World Health Organisation (2003):	*11 µg/m^3*

More extensive reviews of the published data have reported values ranging between about 1 and 300 µg/m^3, and sometimes even higher. However, the average of all of the studies appears to be around 11 µg/m^3. This is reasonably consistent with the guideline level of 7 µg/m^3 that was recommended by the World Health Organisation "to avoid substantial complaints about odour annoyance". This level is also specified in the Ambient Air Quality Guidelines for New Zealand.

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[68] MfE, 1994, Ambient Air Quality Guidelines, Ministry for the Environment, Wellington.

[69] The discussion document cited a 1 hour averaging time, the correct averaging time is 30 minutes.

[70] MfE, 2002, Ambient Air Quality Guidelines, Ministry for the Environment, Wellington.

[71] Graham, B. W., 2008, Brief of Evidence in Chief by Bruce William Lang Graham – Before the Board of Inquiry, Te Mihi Power Station Proposal, New Zealand.

Earlier summaries of data in relation to a suitable guideline value had been undertaken by Rolfe[72] who made the following observations:

“the threshold of detection for hydrogen sulphide odour in laboratory studies has been variously reported between 0.0007 – 0.2 mg/m^3. No information is available on the odour threshold concentration in non-laboratory (field) situations. Air quality guidelines should be based on odour nuisance considerations. Because of the approximately logarithmic-normal relationship between concentrations of odours and their degree of intensity, multiples of the odour threshold concentration are appropriate. It is suggested the 24 hour average concentration not exceed 7 ug/m^3, and short term (say one hour maximum) concentrations not exceed 70 ug/m^3. These concentrations are proposed as guidelines for use in geothermal areas, which often have natural source of hydrogen sulphide, and are probably ten times higher than ambient air concentrations that would be appropriate for pristine areas with no history of hydrogen sulphide odour”.

The New Zealand Department of Labour geothermal guide[73] lists a minimal perceptible odour of 0.13 ppm.

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[72] Rolfe, K. 1983, Air Pollutants Associated with Geothermal Energy, Department of Health, Auckland, New Zealand, 8p.

[73] Department of Labour, 1999, The ABC’s of Hydrogen Sulphide in Geothermal Bores, Occupational Safety and Health Service, New Zealand.

Part 6: Determination of an odour threshold value for hydrogen sulphide in the Bay of Plenty

6.1 Outline

This part of the project aims to establish an odour threshold for H_2S in air using local residents as the test subjects. This investigation looks at measuring and possibly refining the H_2S odour threshold value by using dynamic dilution olfactometry (DDO) and a sample panel of 60 people. Half of the sample panel (30) consists of Rotorua residents, as they represent a group of people that are regularly exposed to elevated concentrations of ambient H_2S. It is believed that this leads to a greater degree of tolerance of H_2S odours, but it is not known whether this is due to a reduced sensitivity to the odour (i.e. a higher odour threshold). The other panellists (30) were from Whakatāne and Tauranga, where there is no exposure to geothermal sources of H_2S.

The primary questions for this investigation were – (i) what was the H_2S detection threshold for a non-laboratory type screening panel and (ii) was there a difference in the results obtained for people living in an area with naturally high levels of H_2S (Rotorua) and those living elsewhere?

6.2 Overview of the study methodology

Note: Some of the information presented in this section has been sourced from the "Hydrogen sulphide odour detection threshold olfactometry investigation, Final Report, June 2012" produced by The Odour Unit Pty Limited.

An Australian company - The Odour Unit (TOU) was engaged by the BOPRC to assist with this study. The TOU's portable odour laboratory is designed and operated to the Australian Standard for odour measurement, and was used at sites in Whakatane and Rotorua from 19 to 30 March 2012.

The TOU odour laboratory uses the technique known as dynamic dilution olfactometry. Dynamic dilution olfactometry involves the repeated presentation of two sample gas streams consisting of diluted gaseous odour sample and an odour-free air stream, to a panel of qualified assessors through two adjacent ports on an olfactometer. The use of this method ensures a high degree of confidence in the accuracy, repeatability and reproducibility of results[9].

For the purpose of the Bay of Plenty study, six (6) untrained panellists were used per three (3) hour session. Three (3) sessions were carried out daily, equivalent to eighteen (18) panellists per day. A total of 59 panellists were tested, 29 in Rotorua and 30 in Whakatane.

The method involved the odorous gas (H_2S or n-butanol) sample initially being diluted to the point where it could not be detected by any member of the panel. The assessors stepped up to the olfactometer in turn, took a sniff from each port, then chose which port contained the odour and entered their response via an integrated laptop (this approach is described as the forced choice mode). At each stage of the testing process, the concentration of the odorous gas was systematically doubled and represented to the panellists. A round was completed when all assessors had correctly detected the presence of the odour with certainty.

The results generated by the olfactometer provide an odour measurement in odour units (ou), based on the extent of dilution that resulted in 50% of the panel being able to positively identify an odour. Dividing the known volume concentration of the odorous gas by its measured odour concentration (ou), gives the odour threshold in parts per billion (ppb).

6.3 Specific aspects of the methodology relevant to this study

The following aspects of the standard methodology were specifically adopted and/or modified for this study:

- AS/NZS4323.3 was followed, except in the areas of assessor selection and calibration, and testing room air quality.
- Assessors of all ages and both sexes were used in the study.
- The assessors received minimal training only, sufficient to participate in the olfactometry testing. They were not pre-screened using n-butanol over a three non-consecutive day period, and nor were any people eliminated from the study on the basis of abnormal sensitivity (or non-sensitivity) to odour, as required by AS/NZS4323.3.
- Competitive behaviour within each assessor panel was strongly discouraged. A relaxed environment in the lab was encouraged, and assessors were encouraged to talk freely (except about the testing) and not necessarily focus entirely on the testing.
- H_2S samples were interspersed with n-butanol samples, so as to minimise repetition and prevent the assessors ‘looking’ specifically for H_2S.
- The air quality in the testing room was not treated in any way to remove odours. This was driven largely by practical considerations but has special significance for some of the Rotorua results (see section 7.1.2).
- As required by the Standard, the TOU olfactometer is calibrated annually. This calibration was last done in August 2011.
- A Jerome 631-X H_2S analyser[74] capable of quantifying H_2S in the range 2 to 50 ppm was used to measure concentration in every sample tested and for monitoring ambient concentrations throughout this study.

6.4 Study locations

The Whakatāne session was held between 19 – 23 March using the West Wing of the BOPRC Whakatāne office (NZMG 2861631E 6353571N). Testing in Rotorua was initially in Scott Street at the old Department of Conservation Offices (NZMG 2795999E 6333462N) on 26 March, but due to elevated room temperatures and ingress of ambient H_2S, the testing was transferred to the Rotorua District Council Redwood Information Centre located in the Redwood Reserve on the edge of the city (NZMG 2796903E 6333228N). Testing in this latter location ran from 27 to 30 March.

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[74] http://www.azic.com/downloads/brochures/Jerome®%20631%20Brochure.pdf

6.5 Equipment

6.5.1 Olfactometer

The TOU olfactometer, an Odourmat™ V04, is a twin-port, forced-choice design, in which panellists sequentially presented to the machine, made their assessment and returned to their seats. The odour sample is presented through one sniffing port, and clean odour-free air is presented through the other port. The panellist was required to choose which port has the odour. The panellist selection is qualified in terms of whether they are “Guessing”, “Inkling” or “Certain” of their selection. Only the “Certain and Correct” response is used in the subsequent data processing.

The presentation of the sample to the ports was random, with neither the operator nor the panellist knowing which port contains the odour sample. The sample was presented in reducing order of dilution (i.e. increasing strength) in which each ‘sniff’ was at twice the odour concentration as the previous one. Normally, with the TOU olfactometer, a panellist is excused from further sniffing in a given round of testing once he/she achieves two consecutive certain and correct detection results. Cleaning cycles were carried out as required, to avoid residual contamination from previous testing sessions.

The repeatability and odour measurement accuracy of the olfactometer is determined by its deviation from statistical reference values specified in AS/NZS4323.3:2001. This includes calculation of instrumental repeatability (r), where r must be less than 0.477 to comply with the standard criterion for repeatability. Its accuracy (A) is also tested against the 95th percentile confidence interval, where A must be less than 0.217 to comply with the Standard. The olfactometer was last calibrated in August 2011 and complied with all requirements set out in the Standard (see Appendix 1 for Calibration Certificate). The calibration gas used was 50 ppm n-butanol in nitrogen gas.

6.6 Requirements of the panellist

The method used by TOU to analyse samples comprises the repeated presentation of both a diluted odour sample and an odour-free air stream to each of the panellists in turn, through two adjacent ports on the olfactometer.

The odorous gas sample is initially diluted to the point where it cannot be detected by any member of the panel. The panellists step up to the olfactometer in turn, take a sniff from each port, then chose which port contains the odour and enter their response. The Odourmat™ software operates to a forced choice method and provides a choice of guessing, inkling or certain from the left and right sniffing ports. The assessor chooses a response for each port and the response for the ‘sample’ port is recorded using one of the following options:

1. “Wrong” and “Guess”
2. “Wrong” and “Inkling”
3. “Wrong” and “Certain”
4. “Correct” and “Guess”
5. “Correct” and “Inkling”
6. “Correct” and “Certain”

At each round of the testing process the concentration of the odorous gas is systematically increased (doubled) and re-presented to the panellists. A round is completed when all panellists have correctly detected the presence of the odour with certainty. The odour is presented to the panel for three rounds.

6.7 Calculation of odour concentration

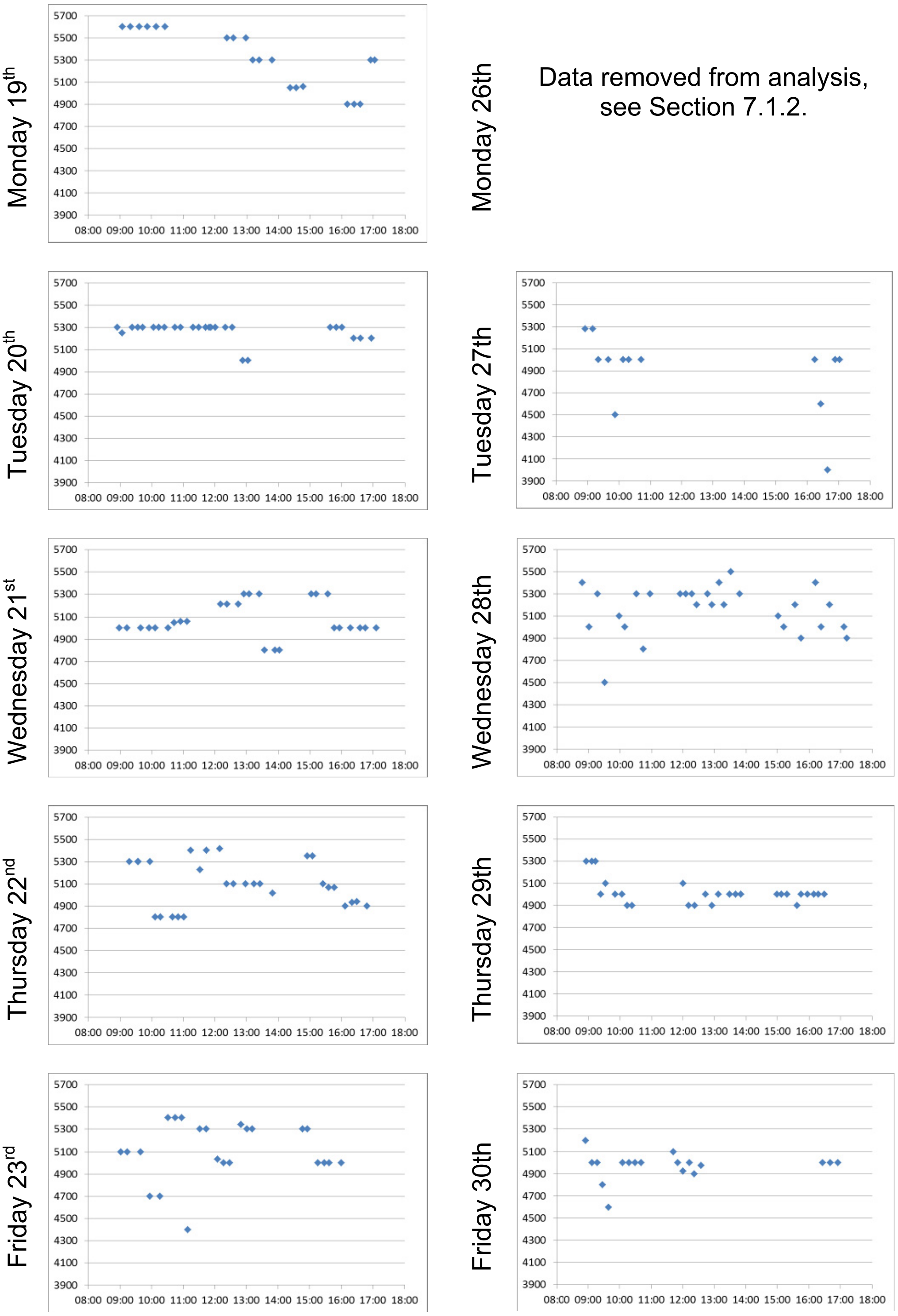
The method used to determine odour concentration as calculated by the Odourmat™ software is as follows. The individual threshold estimate (ITE) for a panellist is calculated as the geometric mean of the first threshold estimate in a series of two where the panellist correctly and with certainty, detected the odorant; and the previous threshold estimate (see Figure 7.7 for an example of the collected information and calculated output).

A detailed explanation of ITE calculations can be found in Sections 11 and 12 of AS/NZS 4323.3:2001.

6.7.1 H_2S calibration gas

A certified D-size cylinder of 5 ppm H_2S in nitrogen gas (see Appendix 2) was used at both locations. Each sample of H_2S was drawn directly from the cylinder into a Nalophan sample bag. This concentration was checked regularly using the Jerome H_2S monitor. The Jerome documentation states that for the concentration range 1 to 9 ppm a standard deviation of ± 0.3 ppm at the 5 ppm midpoint can be expected, Figure 6.1 shows this to be the case with a deviation of this order being experienced. The Jerome is also subject to thermal drift but this effect didn't appear to be strongly evident in the two weeks of testing.

For the purpose of calculating the final threshold the measured Jerome values were used rather than a set value based on the gas bottle certification.



Data removed from analysis, see Section 7.1.2.

Figure 6.1 *Nalophan sample bag H_2S concentrations (µg/m^3) measured with the Jerome during each day of testing, before and after rounds and as new bags were introduced to the testing.*

6.7.2 n-Butanol vapour

The standard reference substance for calibrating panellists is n-butanol in nitrogen. The recommended concentration of n-butanol has not been defined in AS/NZS 4323.3:2001, however, TOU uses a nominal concentration of 50 ppm n-butanol in nitrogen.

A certified cylinder of n-butanol in nitrogen was not available for this study so an alternate method was used which involved injecting n-butanol liquid into a bag of clean dry air. The air was obtained from the oil-free compressor which supplied clean air to the olfactometer and included a carbon filter for removal of organic contaminants.

The concentration of 50 ppm n-butanol was achieved by injecting a volume of 3.73 µL n-butanol into 20L of dry air. The bags were left for at least 30 minutes to equilibrate before initial use.

Part 7: Analysis of the results

A review of statistical methods was undertaken at the start of the data analysis, and discussions were also held with Drs Ray Littler[75] of the University of Waikato and Alastair Suren[76] of BOPRC, regarding the most appropriate statistical techniques. Dr Littler also undertook selected analysis on an early non quality assured dataset and his report can be found in Appendix 3. The approach taken by Dr Littler provided valuable guidance and has been mirrored (with appropriate additions) in this section with the final quality assured dataset.

7.1 Testing room parameters

7.1.1 Temperature and humidity

An attempt was made to keep room conditions comfortable for the panellists. No strict air conditioning regime was enforced and windows were often opened to provide suitable working conditions.

Temperature and humidity were monitored (Figure 7.1) at both locations. The Rotorua temperature plot shows the challenging environment encountered at the first location on Day 1, which was one of the reasons for moving to the second site (also see 7.1.2). No further analysis of the room parameters and test results have been undertaken at this time, but it can be seen that generally the conditions were relatively stable (per location) during the days of testing, with typically a 5°C band of temperature being recorded at both locations. It was also noted that Rotorua was on average about 5°C cooler than Whakatane.

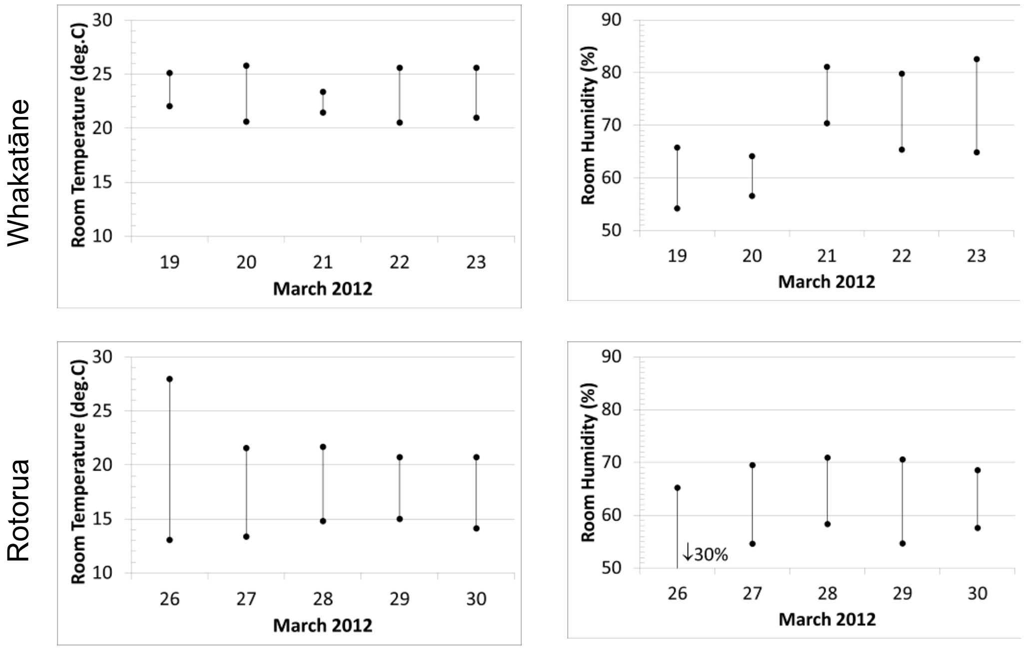


Figure 7.1 Room parameters for both locations during testing.

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[75] Dr R A (Ray) Littler MSc *Auck,* PhD *Monash* (applied probability theory). Pro Dean for the School of Computing and Mathematical Sciences at Waikato University.

[76] BOPRC Environmental Scientist (ex. NIWA) who has 20 years' experience as a freshwater ecologist and has experience in working with large biological datasets.

7.1.2 Ambient H_2S levels

No H_2S was detected by the Jerome instrument within the Whakatāne test room.

During testing in Rotorua a number of sessions were affected by the ingress of ambient H_2S into the testing room. Figure 7.2 shows the indoor levels recorded by the Jerome analyser, and the significant ingress experienced on the first day prompted the move to a second location. Because of this contamination, the following data values were removed from the Rotorua H_2S dataset prior to the main analysis:

- 26/3/2012 all data points.
- 27/3/2012 12:00 – 16:00.
- 30/3/2012 13:00 – 16:30.

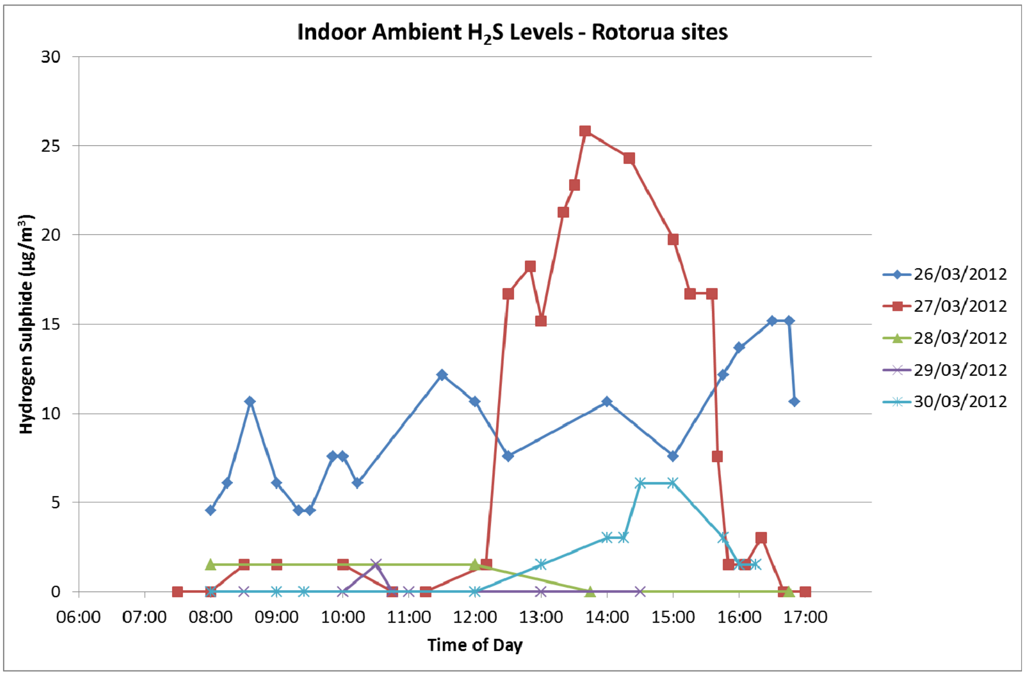


Figure 7.2 Indoor H_2S levels during testing in Rotorua.

The effect of this elevated background level of H_2S in the testing room can be seen in the following two graphs (Figure 7.3). A desensitising effect can be seen per panellist, with high threshold values being recorded.

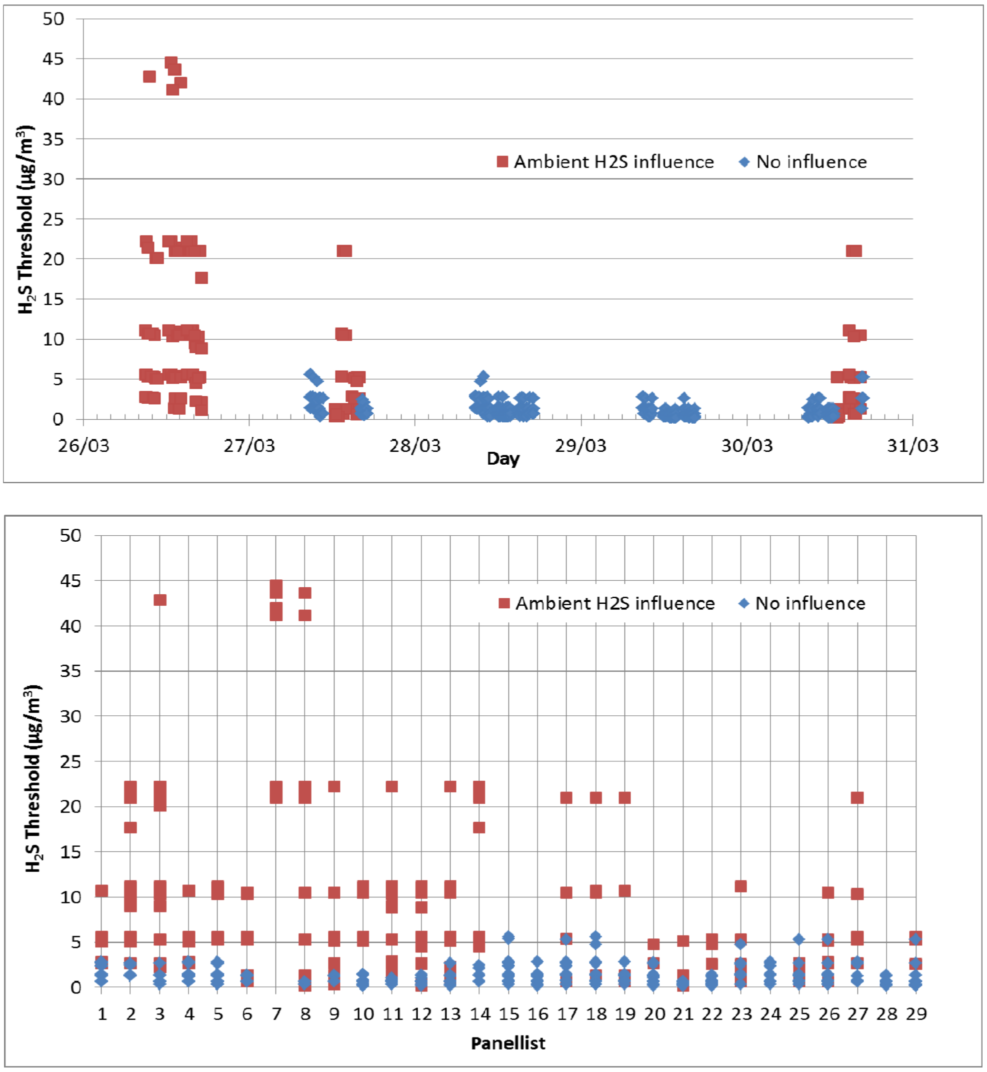


Figure 7.3 Effect of elevated ambient H_2S level during testing.

7.2 Panel characteristics

The following two sections give some background information about the character of each group. Sex and age are the two main parameters recorded along with the amount of time each Rotorua panellist had lived in Rotorua (Figure 7.4). Details regarding smoking were also noted but all panellists except Panellist #1 were non-smokers.

Sex was evenly split for both groups with a slight dominance of females in the Rotorua group. Age spread was also generally common for both groups; the Whakatāne group had a median age of 43, with a minimum of 22 (Panellist #46) and maximum of 60 (Panellist #59). Rotorua had a median age of 42, with a minimum of 21 (Panellist #27) and maximum of 58 (Panellist #8).

Residence time for Rotorua panellists showed a median of 16 years, and a wide range with a minimum of one month (Panellist #18) and a maximum of 44 years (Panellist #21).

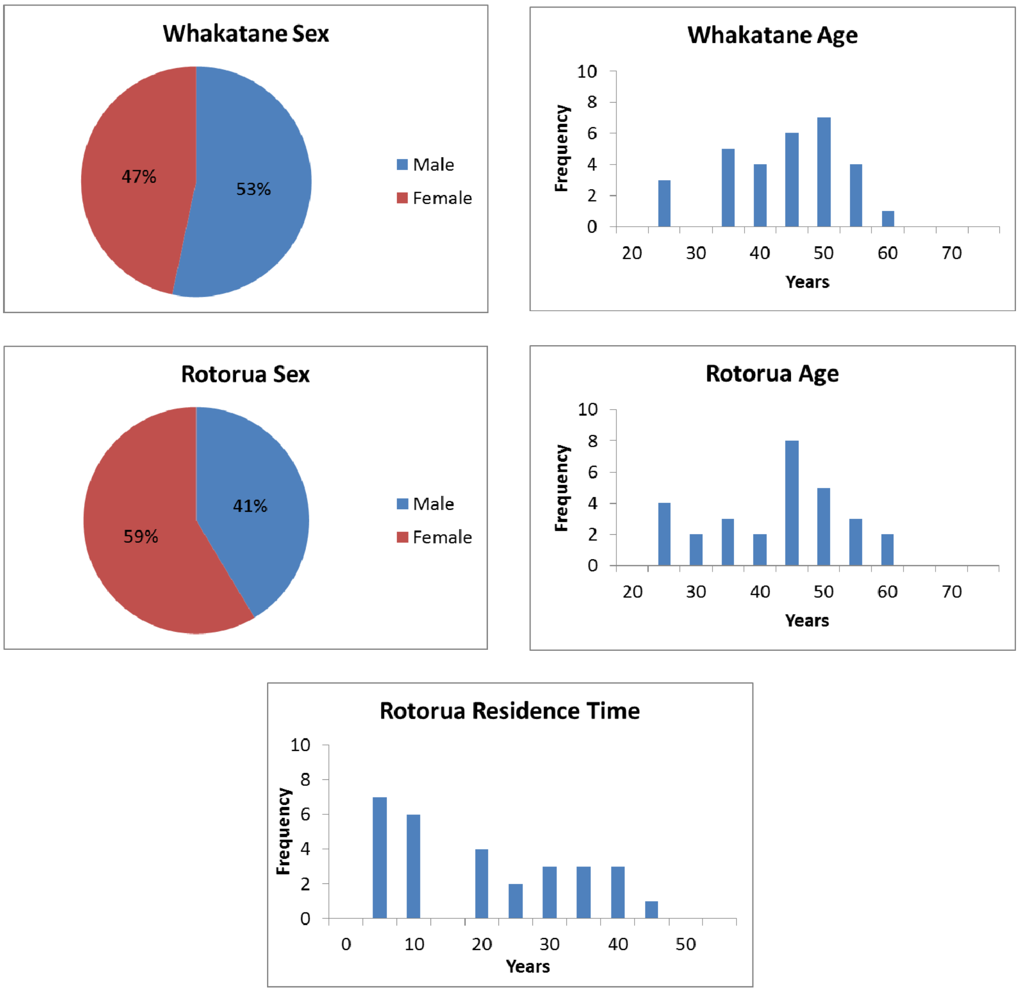


Figure 7.4 Graphical summaries of panellist characteristics.

7.3 Result structure

The testing programme was arranged so that ideally each panellist would sit in on three sessions, each session being approximately three hours in duration. Within that session each panellist would be exposed to three H_2S samples (and also some n-butanol samples). For each sample there would be three rounds. So in theory each panellist would have 27 threshold values determined (Figure 7.5) at the completion of testing. As the testing program evolved no panellists recorded 27 values for a range of logistical reasons (Figure 7.6).

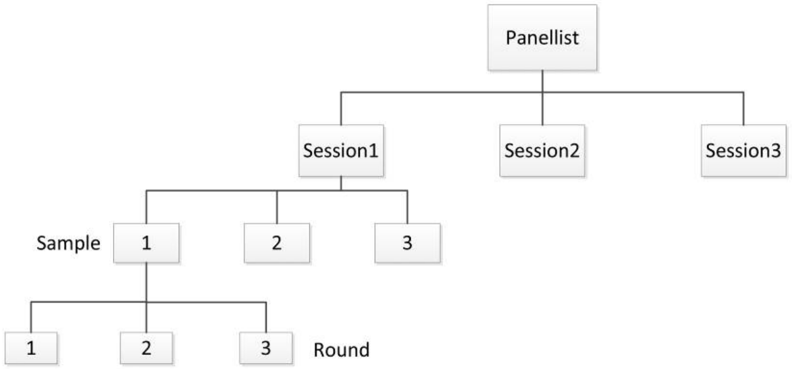


Figure 7.5 Ideal testing structure per panellist.

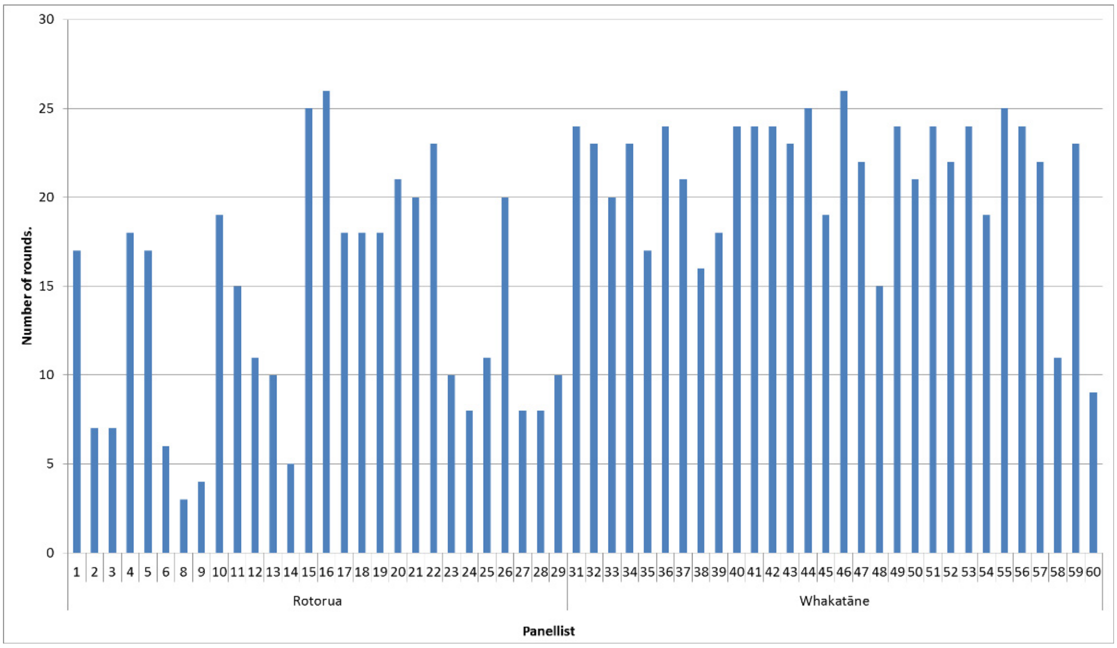
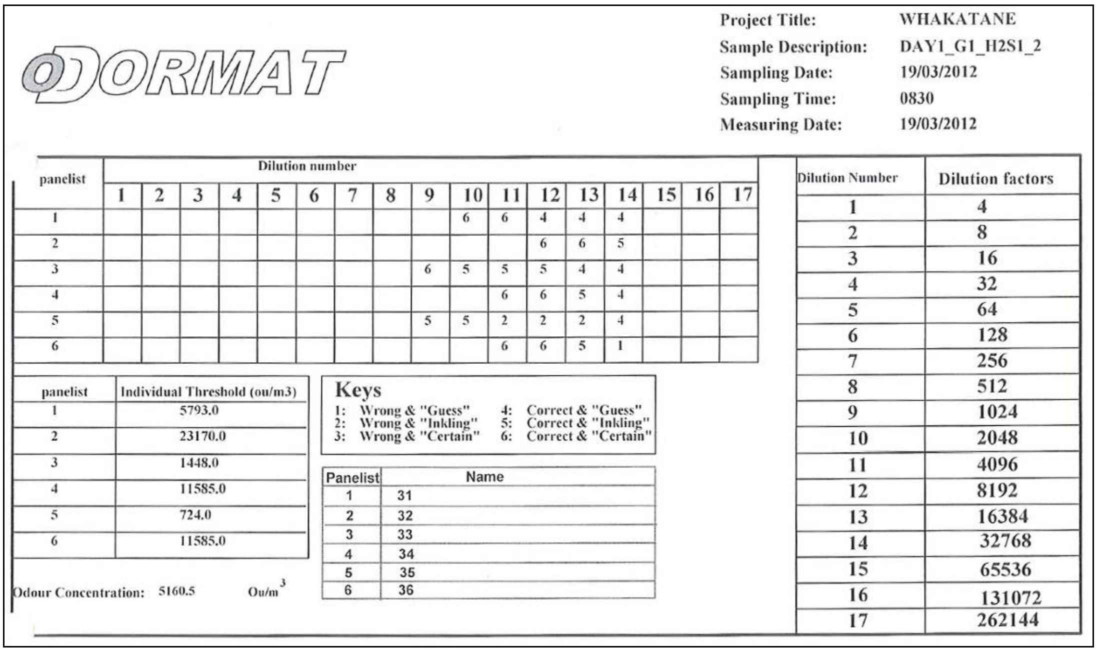


Figure 7.6 Number of rounds recorded per panellist.

7.4 Incomplete rounds

It should be noted that within the raw dataset there are data points which were derived from a situation whereby the panellist was not able to complete a round (two “Corrects” recorded) due to software limitations. An example of such a situation is shown in Figure 7.7 for panellists 3 and 5.



ODORMAT

Project Title: WHAKATANE
Sample Description: DAY1_G1_H2S1_2
Sampling Date: 19/03/2012
Sampling Time: 0830
Measuring Date: 19/03/2012

panelist	Dilution number																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1										6	6	4	4	4			
2												6	6	5			
3									6	5	5	5	4	4			
4											6	6	5	4			
5									5	5	2	2	2	4			
6											6	6	5	1			

panelist	Individual Threshold (ou/m3)
1	5793.0
2	23170.0
3	1448.0
4	11585.0
5	724.0
6	11585.0

Keys

1: Wrong & "Guess"
2: Wrong & "Inkling"
3: Wrong & "Certain"
4: Correct & "Guess"
5: Correct & "Inkling"
6: Correct & "Certain"

Panelist	Name
1	31
2	32
3	33
4	34
5	35
6	36

Odour Concentration: 5160.5 Ou/m^3

Dilution Number	Dilution factors
1	4
2	8
3	16
4	32
5	64
6	128
7	256
8	512
9	1024
10	2048
11	4096
12	8192
13	16384
14	32768
15	65536
16	131072
17	262144

Figure 7.7 Example of incomplete rounds (Panellists 3 and 5) with individual thresholds still being determined upon "completion" of the round.

It can be seen from the top left portion of the datasheet that Panellist #3 had attained a single 6 entry when the test was stopped, and it would be reasonable to expect him/her to follow up with another 6, based on the prior inkling/certain pattern recorded. However for Panellist #5 the situation is less obvious. It was decided to exclude these types of results from the analysis. For untrained panellists two correct inklings indicates that they detect it but still lack some confidence.

To remove conservatism, panellists that finished the round with either of the two scenarios discussed above have been excluded from the following analysis (Figure 7.8). 79% of the Rotorua panellists showed results whereby the round didn't finish with two correct identifications of the presented gas hence showing a high level of insensitivity. For the Whakatāne group, 43% of the panellists showed this pattern of not being able to successfully finish a round.

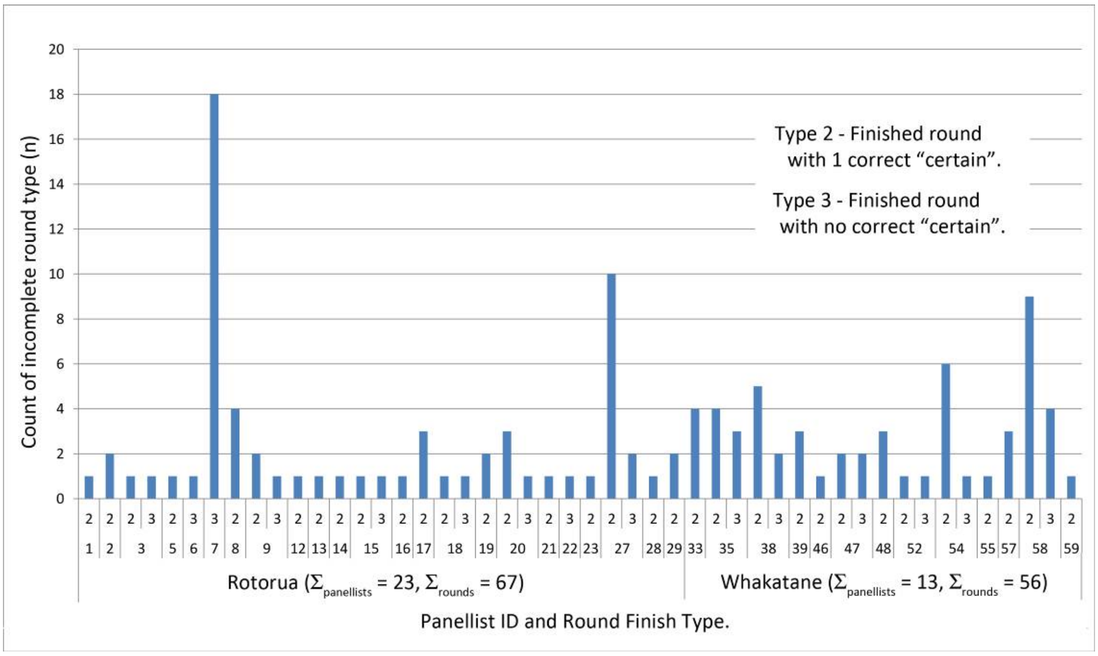


Figure 7.8 Graphic of incomplete rounds and hence removed data points.

7.5 Hydrogen sulphide

7.5.1 Raw data profile

A total of 1,169 raw threshold values were recorded during the two week period. 692 of these were in Whakatāne and the remaining 477 were in Rotorua. Following the above mentioned data screening, the number of data points used in the subsequent analysis were 636 and 383, for Whakatāne and Rotorua respectively.

Counts of threshold values are shown in Figure 7.8. The grouping of the data into discrete concentration steps is a function of the stepwise dilution process in the olfactometer. The highest threshold value (21 µg/m^3) was recorded in Rotorua.

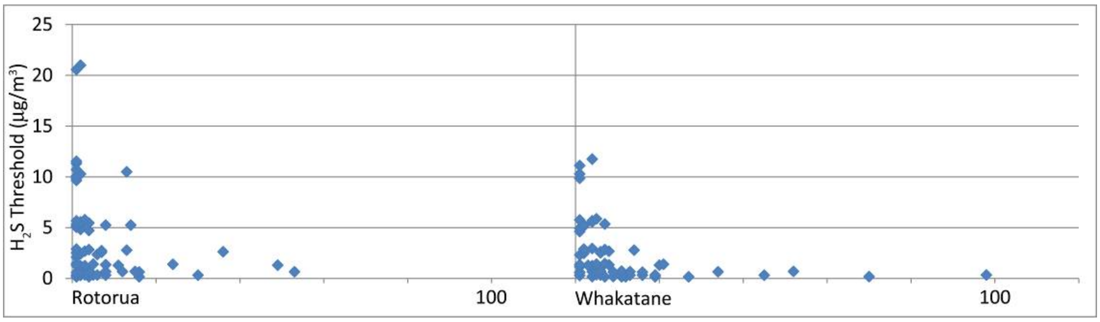


Figure 7.8 Counts of threshold concentrations.

7.5.2 Data aggregation

The data structure tree shown in Section 7.3 allows for levels of data simplification to occur.

A display of the "round" values shows (Figure 7.9) a skewed histogram which is quite normal for data of this type. The Panellist session mean data has been chosen as the primary dataset (Figure 7.10) used in the following analysis as it provides a suitably smoothed distribution and it is all that is required to see if there is a difference between the two locations.

Lower level averages or the base level round data would be suitable for testing aspects of the methodology but are beyond the scope and ability of this investigation. Some analysis of these finer datasets is briefly investigated in the following sections as a means of potentially identifying additional investigations. Any deviations from the session mean analysis will be noted at the time.

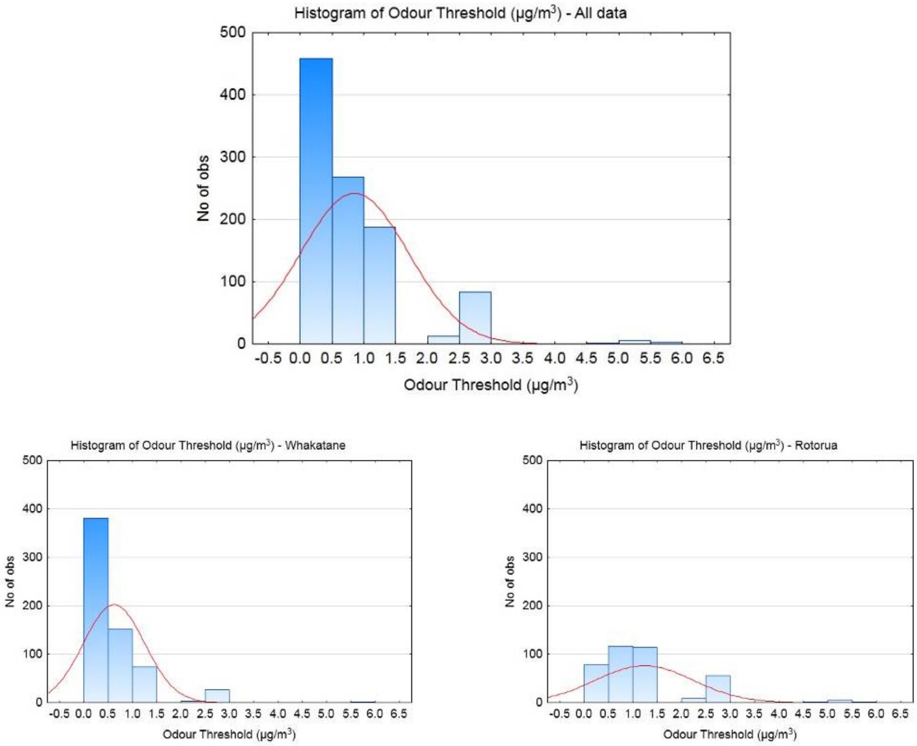


Figure 7.9 Graphical summary of the "round" data.

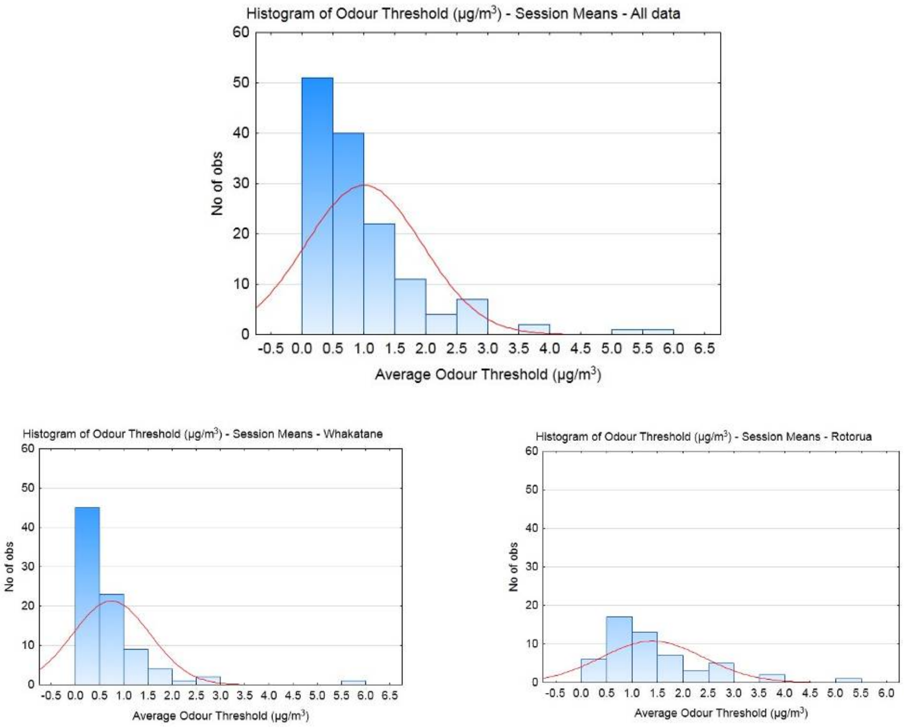


Figure 7.10 Graphical summary of the "session mean" unconditioned data.

7.5.3 Transforming the data

Analysis of variance (ANOVA) is a convenient method to quantify the variability of threshold values between sessions, panellists and locations. ANOVA works well if underlying variation is approximately normally distributed and if the standard deviations of the applied normal curves are roughly equal. Otherwise the ANOVA estimates are likely to be unreliable. The detection threshold data in untransformed scale does not satisfy this requirement (Figure 7.9 and 7.10). Working with the log-based data, however, improves the "diagnostics" a great deal as shown in (Figure 7.11).

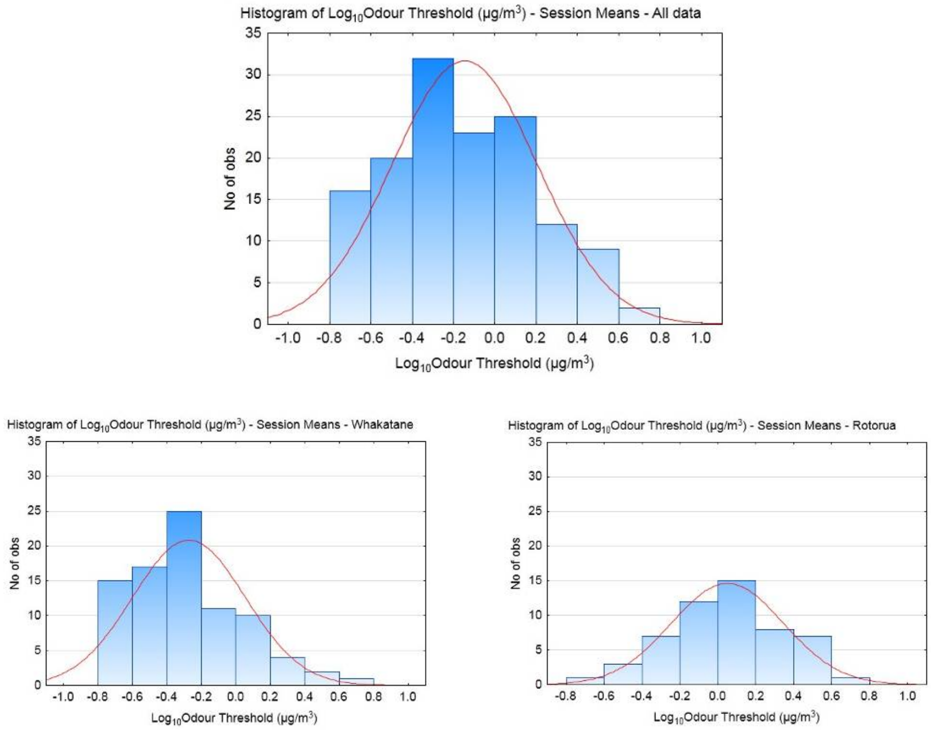


Figure 7.11 Log_{10} mean session data for the entire group and locations.

Box-Cox transformations[77] were also investigated and similarly showed improvements in the normality of the resulting dataset. A lambda value of -0.15 was derived which is positioned between the natural log and reciprocal square root transformation families. For the analysis in this project the log-transformed data above has been chosen due to this supporting output from several different statistical methods of transforming datasets.

7.5.4 Mean H_2S threshold calculations for the dataset

Table 7.1 show a statistical summary of the dataset grouped by location as well as the entire dataset. The geometric mean was determined by taking the logarithms of the original data values, calculating the mean of the log values, and then converting that back to a non-log form (i.e. exponentiating or back-transforming e.g. 10^x). As expected for this type of skewed data, the geometric mean is approximately equal to the median value.

Table 7.1 Mean threshold values (µg/m^3) for all data and by location.

Statistic summary	All data (µg/m^3)	Rotorua (µg/m^3)	Whakatāne (µg/m^3)
Mean	0.99	1.39	0.73
Median	0.67	1.12	0.49
Geometric mean	0.71	1.11	0.53

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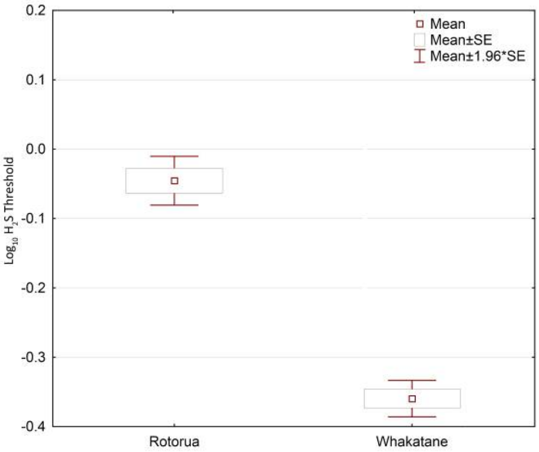
[77] Osborne, J.W., 2010, Improving your data transformations: Applying the Box-Cox transformation, Practical Assessment, Research & Evaluation, Volume 15, Number 12. http://pareonline.net/pdf/v15n12.pdf

7.5.5 Two sample t-test for location

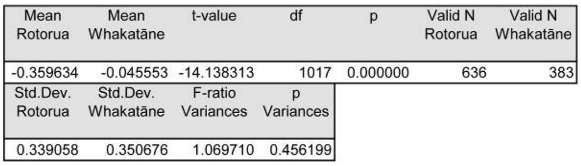
The t-test was used to determine if there were statistically significant differences between the results obtained for Whakatane and Rotorua. This analysis was done for the geometric means of the full (screened) dataset, the session means, and the panellist means at the 95% confidence interval. The p-level reported with each of the t-test represents the probability of error involved in accepting our research hypothesis about the existence of a difference. Technically speaking, this is the probability of error associated with rejecting the hypothesis of no difference between the two categories of observations (corresponding to the groups) in the population when, in fact, the hypothesis is true[78].

For all three levels of data averaging it was found that p-levels were such that there was very strong evidence that the geometric means threshold were higher in Rotorua than in Whakatāne (Figure 7.12).

All round data



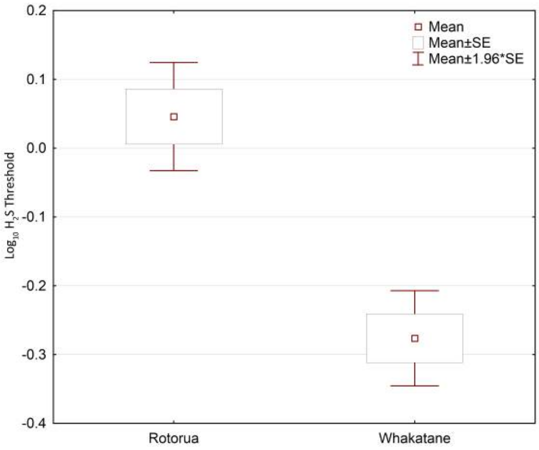
t-test output

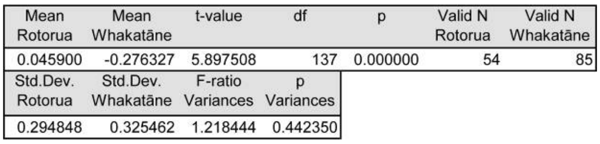


Mean Rotorua	Mean Whakatāne	t-value	df	p	Valid N Rotorua	Valid N Whakatāne
-0.359634	-0.045553	-14.138313	1017	0.000000	636	383

Std.Dev. Rotorua	Std.Dev. Whakatāne	F-ratio Variances	p Variances
0.339058	0.350676	1.069710	0.456199

Panellist session means





Mean Rotorua	Mean Whakatāne	t-value	df	p	Valid N Rotorua	Valid N Whakatāne
0.045900	-0.276327	5.897508	137	0.000000	54	85

Std.Dev. Rotorua	Std.Dev. Whakatāne	F-ratio Variances	p Variances
0.294848	0.325462	1.218444	0.442350

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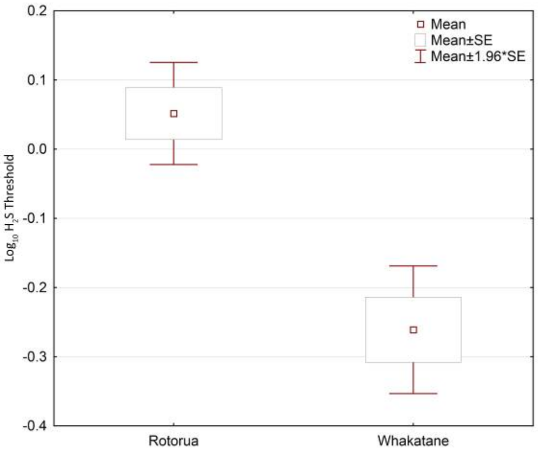
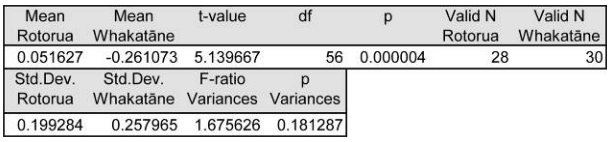
[78] StatSoft Inc, Statistica10® Electronic Manual.

Panellist means





Mean Rotorua	Mean Whakatāne	t-value	df	p	Valid N Rotorua	Valid N Whakatāne
0.051627	-0.261073	5.139667	56	0.000004	28	30

Std.Dev. Rotorua	Std.Dev. Whakatāne	F-ratio Variances	p Variances
0.199284	0.257965	1.675626	0.181287

Figure 7.12 t-test results (with box plots) for a range of averaging levels and locations.

7.5.6 Other relationships and data characteristics

Trends over sessions

Determining a trend over sessions for individual panellists was outside the initial brief of this project and is ultimately focussed more on the methodology aspect of the investigation rather than the determination of odour thresholds. Figure 7.13 shows the pattern of test results per panellist per session to see if a dominant pattern existed which could warrant further investigation.

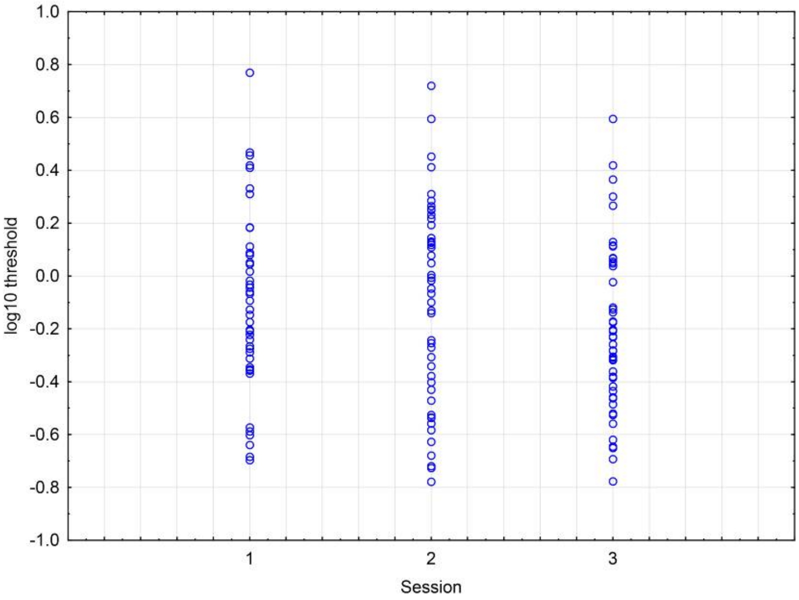


Figure 7.13 H_2S threshold range per session, all panellists.

Figure 7.13 shows a wide range of values recorded per session. Linear best fit analysis results in a negative slope relationship which would suggest a reduction over sessions, but the range of values per session overshadows this relationship.

Preliminary investigation of session trends are shown in Figure 7.14 where individual graphs per panellist are presented. These show the wide variability in trends and a number of cases where only 1 or 2 data points are available, thus undermining the credibility of such an exercise.

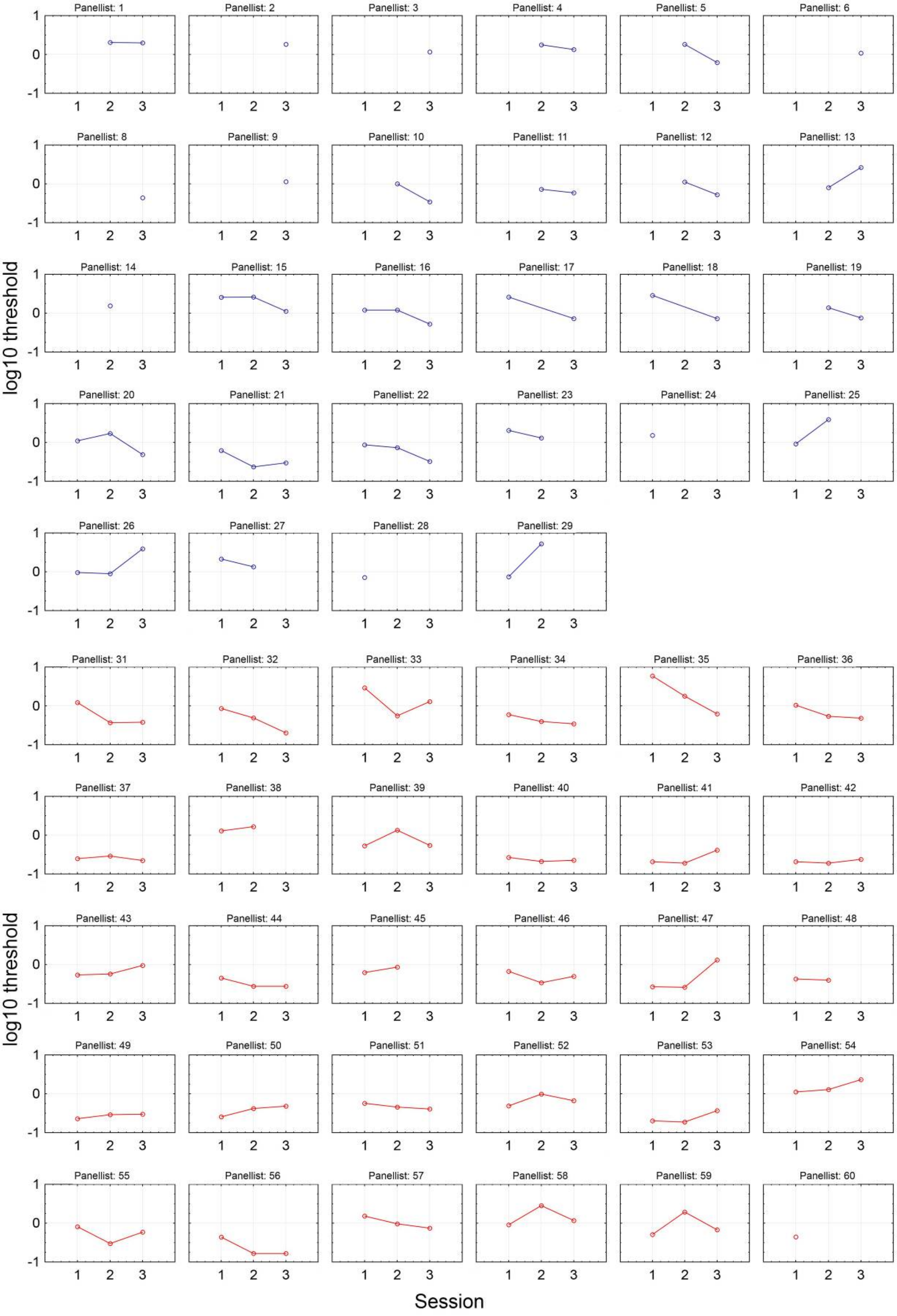


Figure 7.14 Trends per panellist per session (blue – Rotorua, red – Whakatāne).

The original concept behind the testing methodology was one of using an untrained panel of participants. However as the tests progressed panellists became well aware of what was required and the random nature of the presentation of gas along with the appropriate conditioning of the gas (e.g. no obvious temperature difference between the two ports etc.) at each olfactometer port was critical. It is reasonable to assume that during the testing the threshold value per panellist may have decreased as panellists become more attuned to the odour. In Figure 7.15 first and last round results are presented for a number of the Whakatāne panellists (where each panellist attended three sessions) there is visual evidence that some of the panellists are exhibiting this downward trend. There are however a number that show a trend in the opposite direction. No further analysis of panellist behaviour over sessions is undertaken at this time as a more rigorous and tailored methodology would be required to check the hypothesis of changes per panellist over sessions.

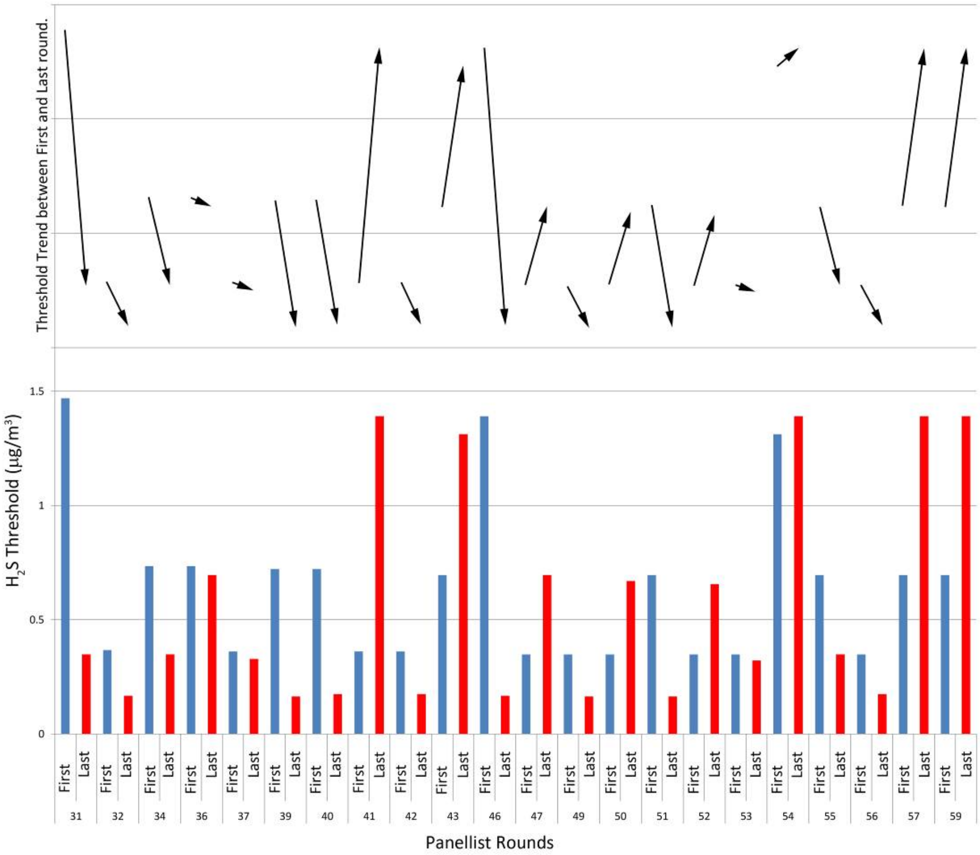


Figure 7.15 Trends per panellist by comparing first and last round results.

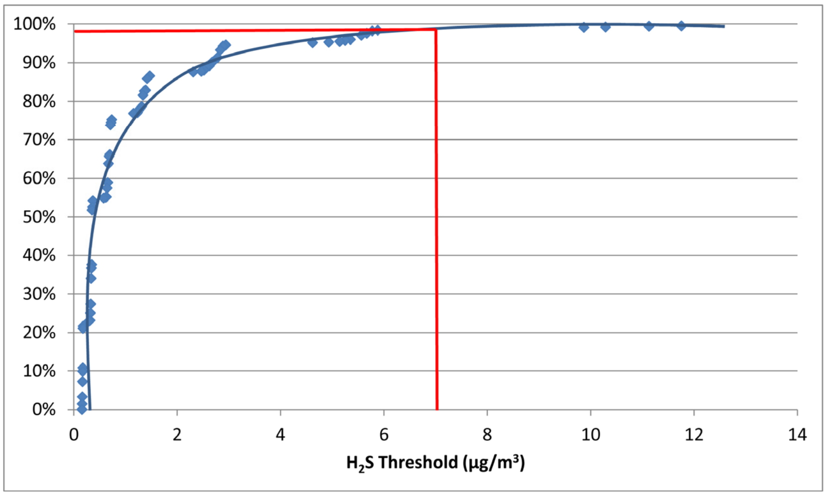
NZAAQ 7 µg/m^3 guideline analysis

There is also the ability to investigate the percentages of the dataset which are below or above a value(s) of interest. For this exercise a value of 7 µg/m^3 has been chosen. With the plots shown in Figure 7.16 percentage results for any value of interest can be easily obtained. The chosen 7 µg/m^3 represents the current MfE guideline for odour annoyance.

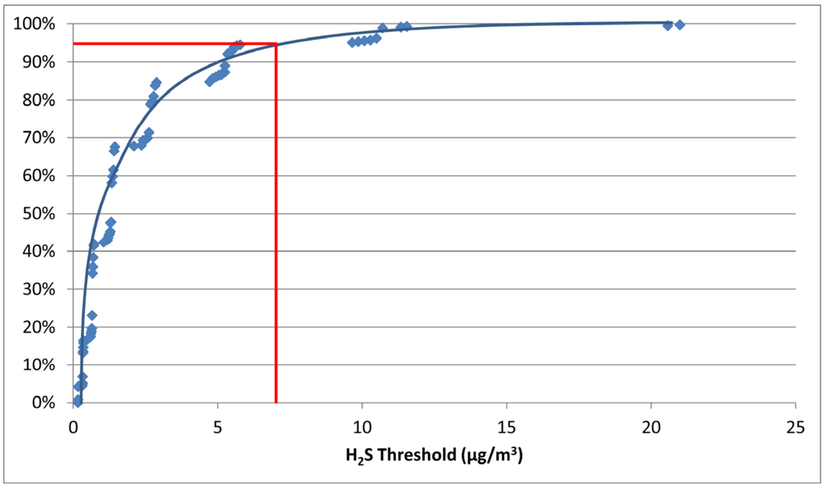
The percentage detection results show that most panellists in the Whakatāne and Rotorua groups are able to recognise the 7 µg/m^3 concentration, with >95% of the recorded detection values below this guideline. The Rotorua plot shows a slightly lower percentage of values at which this guideline was met. The third plot shows the results for the periods of testing in Rotorua where elevated ambient H_2S

concentrations were recorded within the testing room. These data points were removed from the earlier analysis (see Section 7.1.2). They show a pattern of a lower level of sensitivity whereby only 58% of the values were at or below the guideline.

Whakatāne Group – round data



Rotorua Group – round data



Rotorua removed data

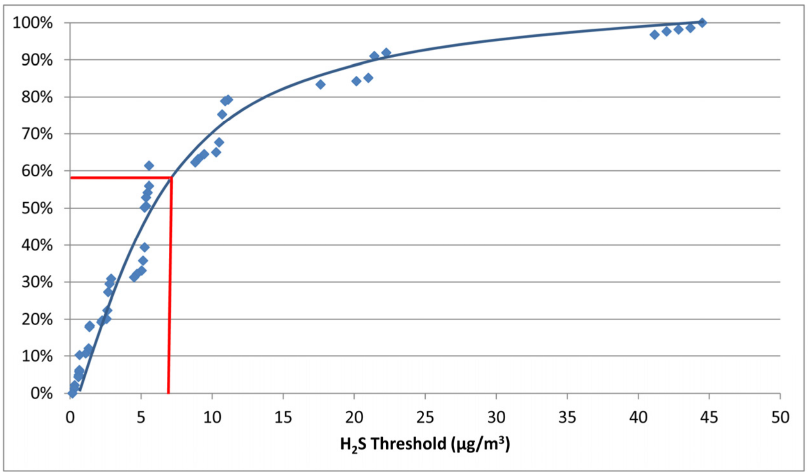
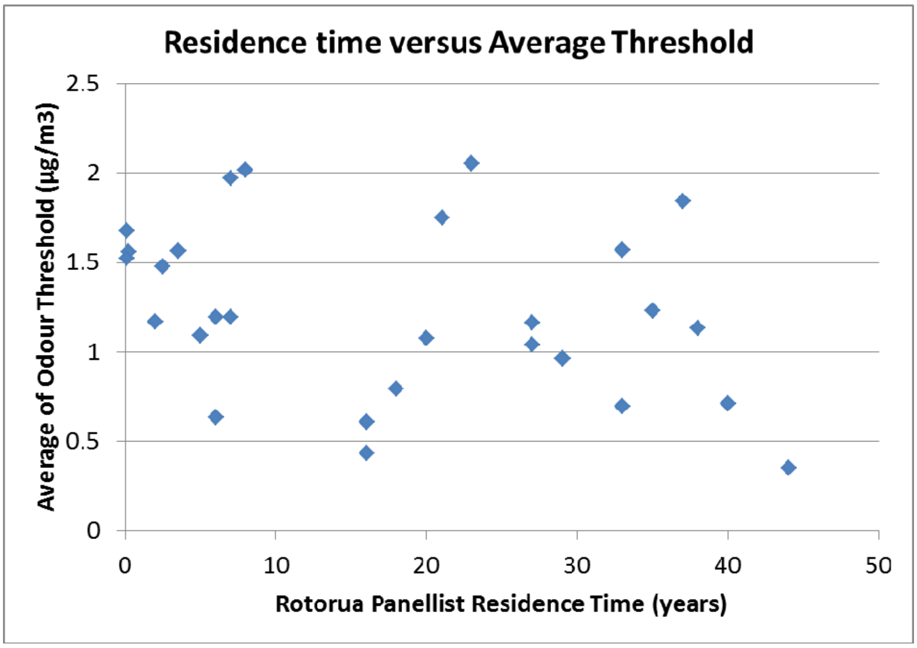


Figure 7.16 Frequency plots - percentage of data points in relation to 7 µg/m^3.

Residence time versus threshold

The residence time of the Rotorua panellists was also recorded. As shown below, there was a wide level of 'historical' exposure (this was not manipulated in any way as a real life snapshot of the population was required for this non laboratory type investigation), but no pattern as to a relationship with average measured threshold was found.



7.6 n-butanol results

n-butanol is normally used as a screening gas for identifying suitable panellists for laboratory based olfactometry exercises. AS/NZS 4323.3:2001 requires that each panellists' threshold for n-butanol has to fall within 0.5 and 2 times the accepted reference value (132 µg/m^{3}or 40 ppb), therefore within the range of 66 to 264 µg/m^3.

The calculated geometric means for the n-butanol results obtained in this study are 138 and 167 µg/m^3 for the Whakatāne and Rotorua groups respectively. The relationship with the standard requirements was not investigated on an individual panellist basis as the theory behind this project was to use a non-screened panel which would provide a more realistic real world scenario.

A quick summary of the n-butanol results are shown in the histograms in Figure 7.16. Once again a negatively skewed raw dataset was obtained which was normalised by performing a log normal transformation. The relationship between the two gases used in this investigation per panellist (Figure 7.17) shows no strong relationship and thus highlights the complex nature of odour recognition and interplay of contaminants on an individual by individual basis.

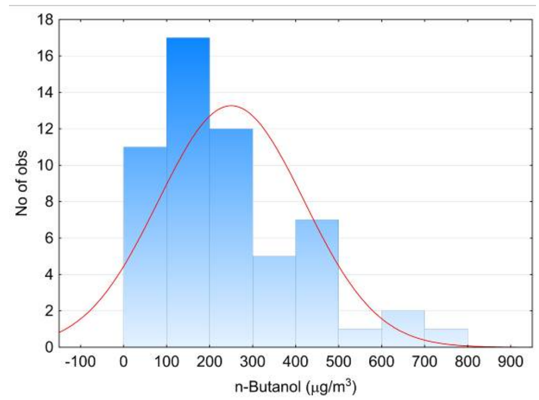
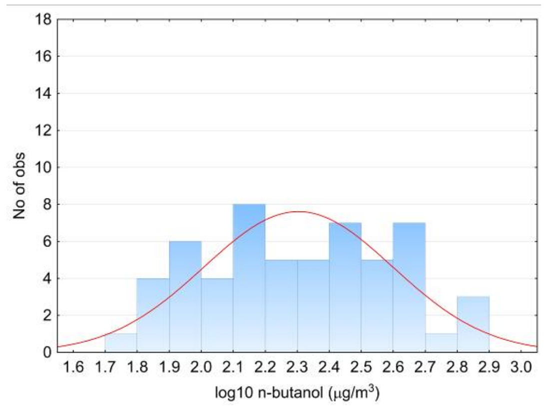
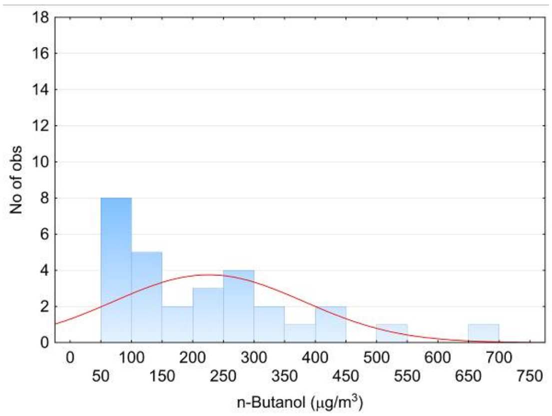
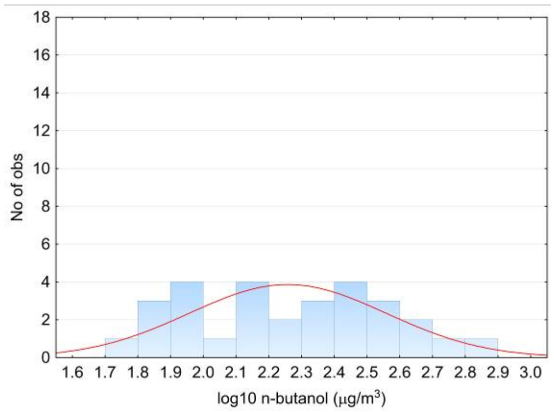
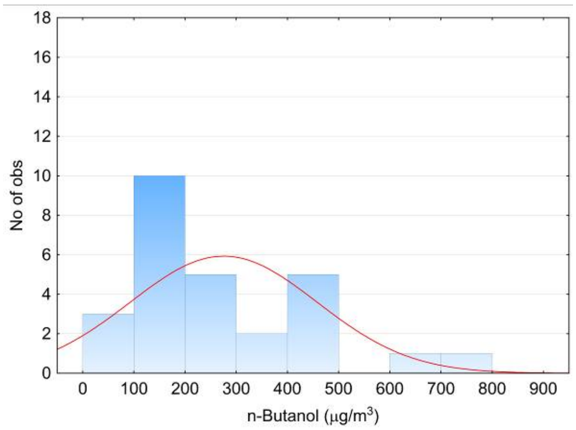
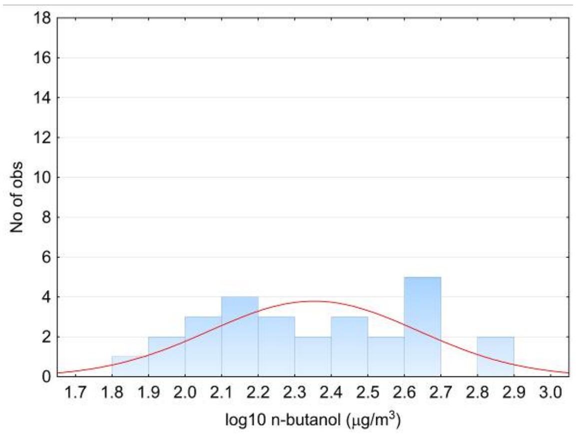
<table>
<tr><th>Untransformed</th><th>Log 10 Transformed</th></tr>
<tr><th colspan="2">All data</th></tr>
<tr><td>
</td><td>
</td></tr>
<tr><th colspan="2">Whakatāne</th></tr>
<tr><td>
</td><td>
</td></tr>
<tr><th colspan="2">Rotorua</th></tr>
<tr><td>
</td><td>
</td></tr>
</table>

Figure 7.16 Distribution patterns for n-butanol.

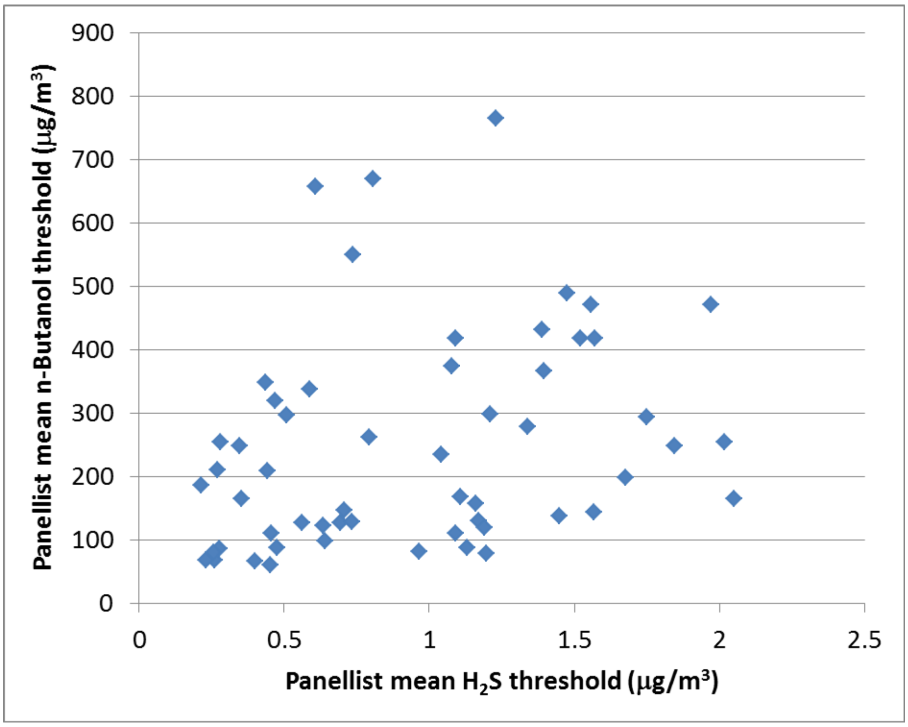


Figure 7.17 Scatterplot showing n-butanol and H_2S relationship.

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Part 8: Discussion and conclusion

8.1 Discussion

The primary questions for this investigation were – (i) what was the H_2S detection threshold for a non-laboratory type screening panel? and (ii) was there a difference in the results obtained for people living in an area with naturally high levels of H_2S (Rotorua) and those living elsewhere? The concept of developing an odour threshold using local residents was to ensure that the scientific and planning decisions around H_2S discharges are soundly based and directly relevant to the region.

The threshold data calculations for this investigation have yielded a geometric mean concentration of 0.7 $\mu g/m^3$ when determined across the entire panel (n. = 59). The geometric means for the Rotorua and Whakatāne subgroups are 1.1 and 0.5 $\mu g/m^3$ respectively. These values are all well below the current NZAAQ guideline value of 7 $\mu g/m^3$. The geometric means are at the lower end of international threshold data summarised in Figure 8.1 (which is a repeat of Figure 5.1 but with the current results added at the bottom). Discussion with olfactometry practitioners indicate that the results from this investigation are comparable with what they have recorded in laboratory type settings[79].

The current NZAAQ guideline value of 7 $\mu g/m^3$ which was first documented nationally nearly 20 years ago[67] and discussed even earlier in a New Zealand context in the early 1980's[72] is still widely used as a starting point for odour assessments. For geothermal affected areas the common approach has been to use a value of 70 $\mu g/m^3$, which was based on the historic New Zealand Health Department guideline. This value of 70 $\mu g/m^3$ meets the Good Practice Guide for Assessing Odour in New Zealand[61] recommendation whereby for low sensitivity receiving environments the ambient concentrations can be in the order of 5-10 odour units (equivalent to 5 -10 times the odour threshold).

However, using the threshold determined in this investigation the acceptable low sensitivity receiving environment values would only be in the order of 3.5 to 7 $\mu g/m^3$, which as stated above is the value for non-geothermal (i.e. high sensitivity) areas. A guideline of 3.5 to 7 $\mu g/m^3$, is up to ten times lower than the value that is currently used for geothermal areas. However, based on community feedback and/or the lack of complaints about geothermal power plant emissions it appears these communities can tolerate 100 times the odour threshold determined in this study.

This tolerance may well be due not to physiological changes in these people, but more so the acceptance of their location (which is often characterised by having a number of active geothermal surface features) and the economic and societal benefits associated with the use of the geothermal features/resource.

In relation to the second question of this investigation the groups were spatially different, with one consisting of panellists from Whakatāne and Tauranga (non-geothermal areas) and one group from Rotorua, where the panellists are frequently exposed to concentrations well above the international literature odour thresholds. Other basic characteristics of the groups showed that they were generally similar in profiles when it came to the age and sex of the panellists. The residence time for the Rotorua panellists was also recorded. This was compared with threshold values for this group. The results showed no relationship with residence time and average measured threshold.

---

[79] Pers comms with Terry Schulz during testing in Whakatāne, March 2012.

Several types of analysis of the grouped data showed that there was a statistically significant difference between the geometric mean odour threshold results for the two groups (1.1 µg/m^3 for Rotorua and 0.5 µg/m^3 for Whakatāne). The difference was small, but in the direction we would expect (Rotorua higher than non-geothermal locale). The results also showed that the human response to odour is highly variable.

The difference between the two groups is interesting in a purely theoretical sense. However, when taking into account – (i) the wide range of thresholds that have been published to date, (ii) inaccuracies in the methodologies used in these investigations, and (iii) the end use application of thresholds as a comparison point for modelled outputs, the difference shown between the two groups would be regarded as insignificant and largely treated as being the same for both. The analysis showed that the vast majority of the panellists were able to detect H_2S at the 7 µg/m^3 level.

In setting a guideline value it would be dependent on the receiving environments location, as both groups appear “equal” when it comes to detecting. Variations in odour response would be dependent on what is commonplace in their local environment. Communities that live in close proximity to existing or proposed developments or natural settings where H_2S emissions are present are equally adept at detecting the odour at low concentrations, when compared with the Whakatāne group, but more often than not would be accepting of the odour profile because of location.

Public annoyance from H_2S odour may have little to do with the odour threshold, but the environment which people accept or are accustomed to, for example in Rotorua locals appear not to worry about the H_2S odour until it gets particularly high. This approach may be fine for H_2S but if you put a different odour source (e.g. chemical processing plant) in the middle of Rotorua then the response would be quite different.

Given the ambient values regularly measured in Rotorua the threshold values we have recorded are somewhat irrelevant, however it is interesting that Rotorua people can detect these low values and the variation within.

The analysis of the Rotorua group showed that there was an effect on threshold values when the testing environment was affected by elevated ambient H_2S levels. It appeared to have a temporary desensitising effect on the panellists. Because this ambient exposure was not controlled in any way, it would be difficult to determine the exact effect in a quantitative sense, but results showed that the measured thresholds increased, up to a factor of 10, during these periods (See Figure 7.3). Once again this would support the use of a higher threshold value for these areas which are regularly or constantly exposed to the contaminant.

In the context of a non-geothermal impact assessment the value of 7 µg/m^3 seems quite conservative for sensitive receiving environments. However where natural emissions are present, current and historical situations seem to show that 70 µg/m^3 is an acceptable limit whereby nuisance effects will not be experienced by most residents.

In regard to Council air quality policy, the findings of this investigation will be used in the upcoming Bay of Plenty Regional Air Plan review process.

8.2 Conclusion

The primary questions for this investigation were – (i) what was the H_2S detection threshold for a non-laboratory type screening panel? and, (ii) was there a difference in the results obtained for people living in an area with naturally high levels of H_2S (Rotorua) and those living elsewhere?

The H_2S detection threshold for the entire 59 panellists was 0.7 µg/m^3. For the Whakatāne sub-group the H_2S detection threshold was 0.5 µg/m^3. For the Rotorua subgroup the H_2S detection threshold was 1.1 µg/m^3.

Statistically there is a difference in threshold values for the subgroups. However in a real world situation this difference would be regarded as being insignificant.

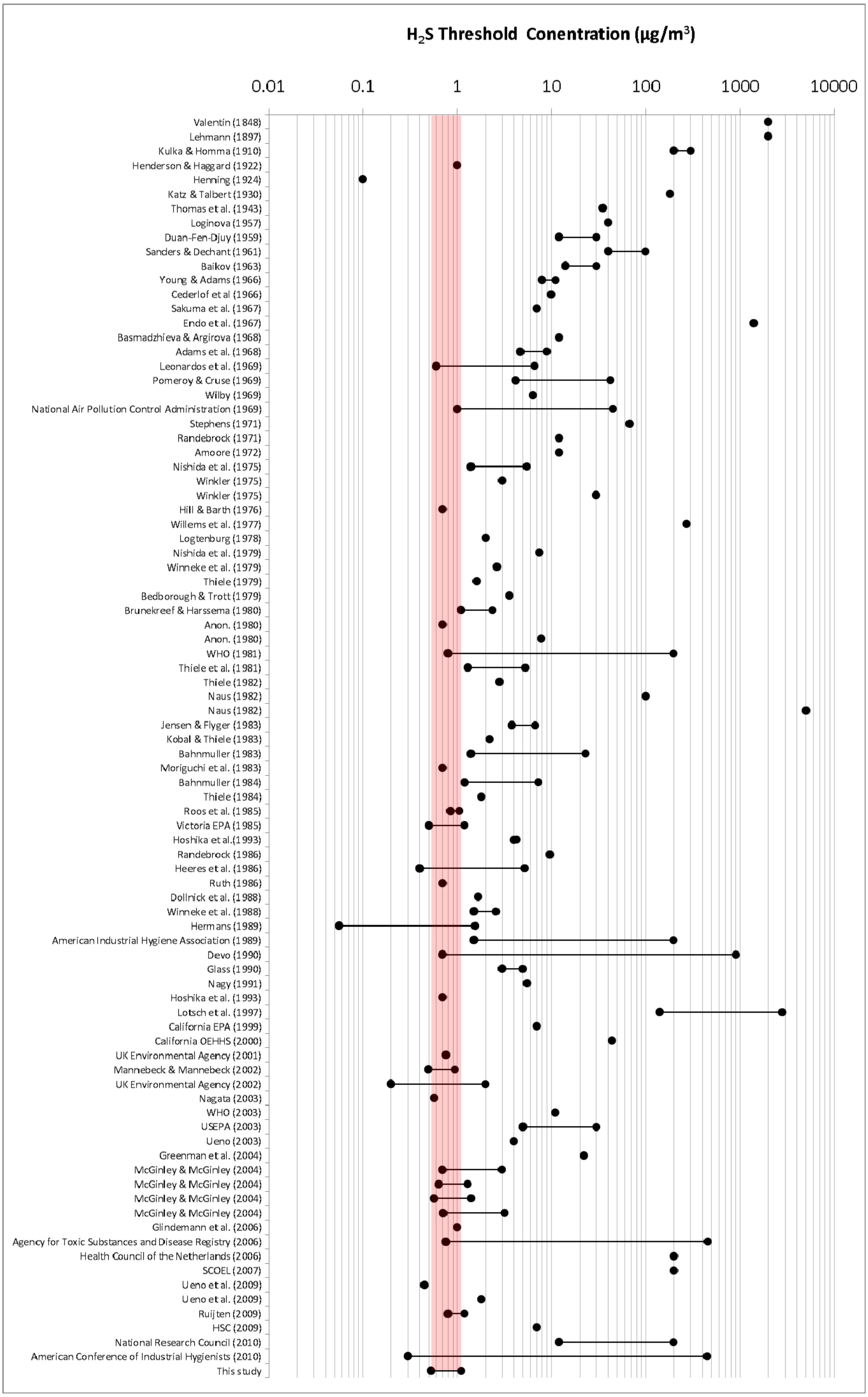
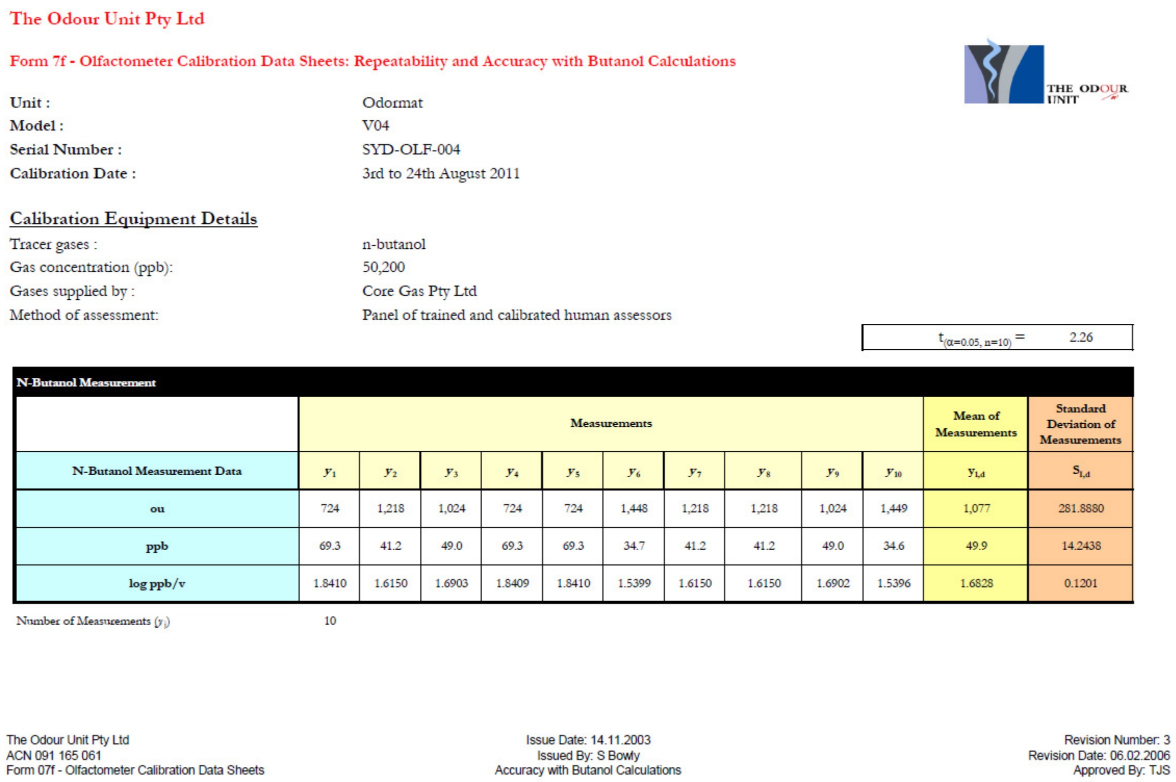


Figure 8.1 Updated H_2S threshold summary graph (adapted from Figure 5.1).

Appendices

Appendix 1 – Olfactometer calibration sheet



The Odour Unit Pty Ltd

Form 7f - Olfactometer Calibration Data Sheets: Repeatability and Accuracy with Butanol Calculations

THE ODOUR UNIT

Unit :	Odormat
Model :	V04
Serial Number :	SYD-OLF-004
Calibration Date :	3rd to 24th August 2011

Calibration Equipment Details

Tracer gases :	n-butanol
Gas concentration (ppb):	50,200
Gases supplied by :	Core Gas Pty Ltd
Method of assessment:	Panel of trained and calibrated human assessors

$t_{(\alpha=0.05,\ n=10)} =$ 2.26

N-Butanol Measurement

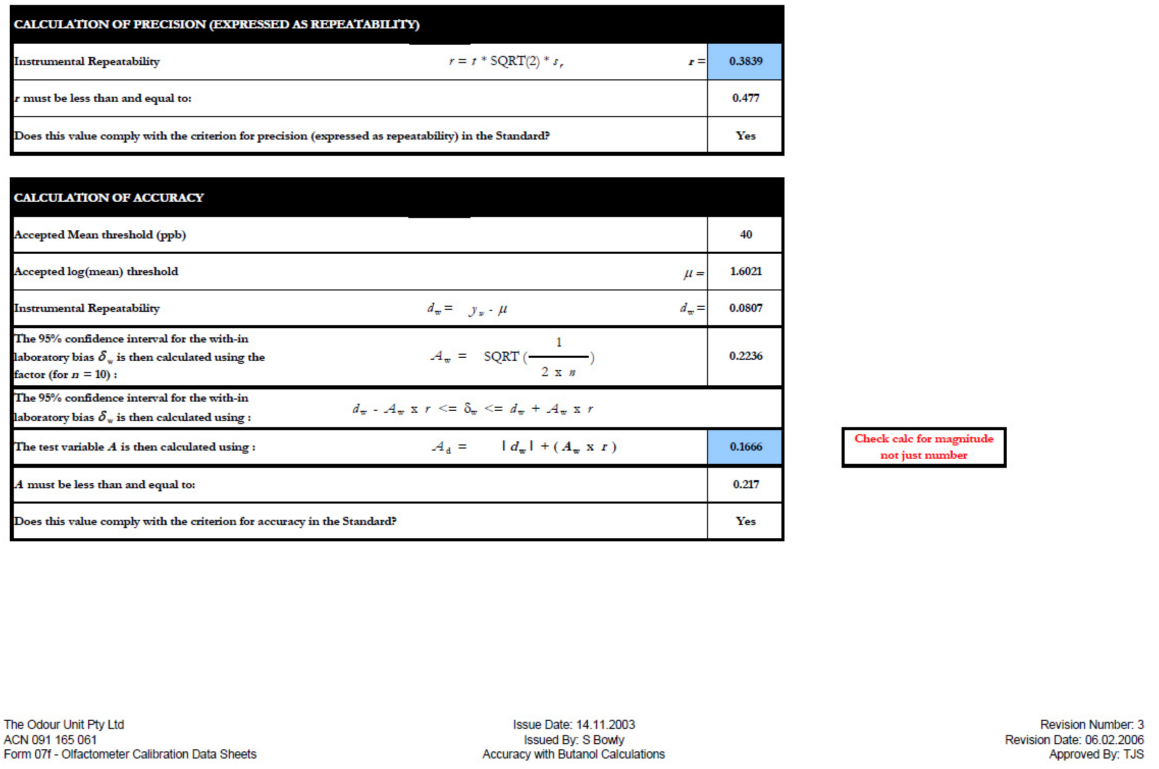
	Measurements										Mean of Measurements	Standard Deviation of Measurements
N-Butanol Measurement Data	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	y_{10}	$y_{I,d}$	$S_{I,d}$
ou	724	1,218	1,024	724	724	1,448	1,218	1,218	1,024	1,449	1,077	281.8880
ppb	69.3	41.2	49.0	69.3	69.3	34.7	41.2	41.2	49.0	34.6	49.9	14.2438
log ppb/v	1.8410	1.6150	1.6903	1.8409	1.8410	1.5399	1.6150	1.6150	1.6902	1.5396	1.6828	0.1201

Number of Measurements (y_i) 10

The Odour Unit Pty Ltd
ACN 091 165 061
Form 07f - Olfactometer Calibration Data Sheets

Issue Date: 14.11.2003
Issued By: S Bowly
Accuracy with Butanol Calculations

Revision Number: 3
Revision Date: 06.02.2006
Approved By: TJS



CALCULATION OF PRECISION (EXPRESSED AS REPEATABILITY)			
Instrumental Repeatability	$r = t * \mathrm{SQRT}(2) * s_r$	$r =$	**0.3839**
***r* must be less than and equal to:**			**0.477**
Does this value comply with the criterion for precision (expressed as repeatability) in the Standard?			**Yes**

CALCULATION OF ACCURACY			
Accepted Mean threshold (ppb)			**40**
Accepted log(mean) threshold		$\mu =$	**1.6021**
Instrumental Repeatability	$d_w = y_w - \mu$	$d_w =$	**0.0807**
The 95% confidence interval for the with-in laboratory bias δ_w is then calculated using the factor (for $n = 10$) :	$A_w = \mathrm{SQRT}\left(\frac{1}{2 \times n}\right)$		**0.2236**
The 95% confidence interval for the with-in laboratory bias δ_w is then calculated using :	$d_w - A_w \times r <= \delta_w <= d_w + A_w \times r$		
The test variable *A* is then calculated using :	$A_d = \lvert d_w \rvert + (A_w \times r)$		**0.1666**
***A* must be less than and equal to:**			**0.217**
Does this value comply with the criterion for accuracy in the Standard?			**Yes**

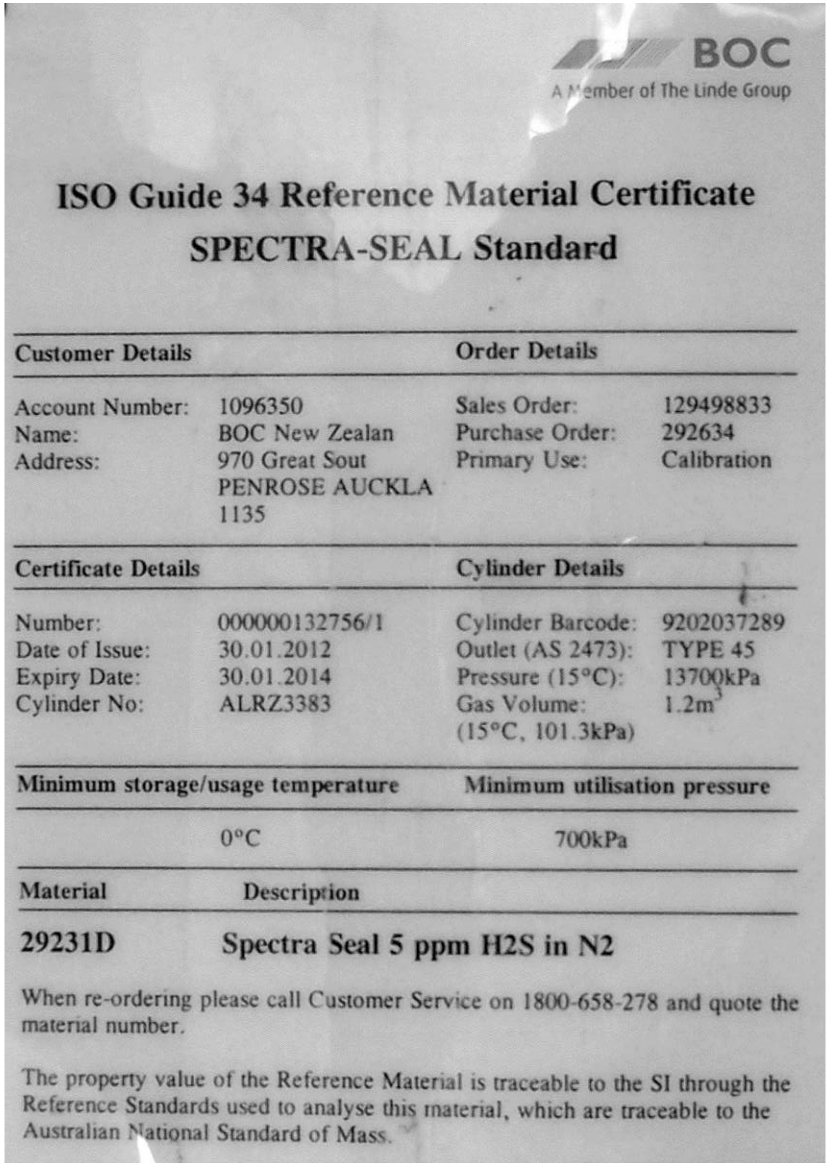
Check calc for magnitude not just number

The Odour Unit Pty Ltd
ACN 091 165 061
Form 07f - Olfactometer Calibration Data Sheets

Issue Date: 14.11.2003
Issued By: S Bowly
Accuracy with Butanol Calculations

Revision Number: 3
Revision Date: 06.02.2006
Approved By: TJS

Appendix 2 – Calibration gas certification



BOC
A Member of The Linde Group

ISO Guide 34 Reference Material Certificate
SPECTRA-SEAL Standard

Customer Details		Order Details	
Account Number:	1096350	Sales Order:	129498833
Name:	BOC New Zealan	Purchase Order:	292634
Address:	970 Great Sout PENROSE AUCKLA 1135	Primary Use:	Calibration

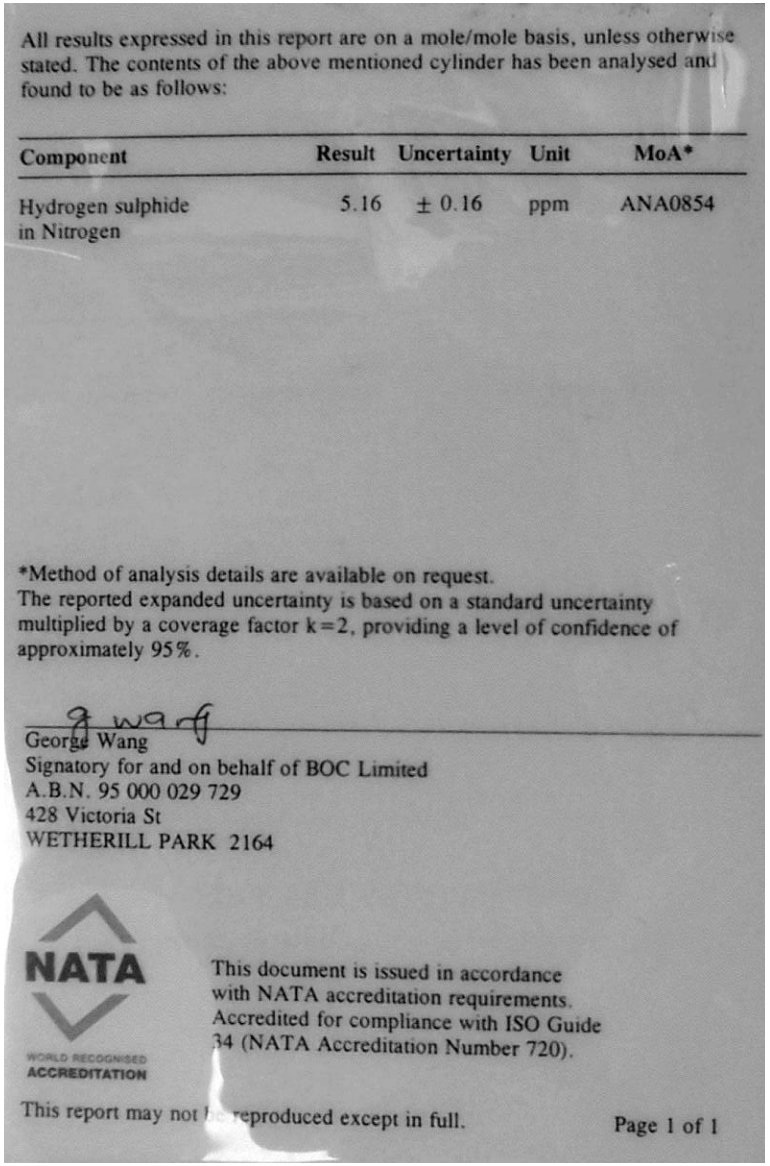
Certificate Details		Cylinder Details	
Number:	000000132756/1	Cylinder Barcode:	9202037289
Date of Issue:	30.01.2012	Outlet (AS 2473):	TYPE 45
Expiry Date:	30.01.2014	Pressure (15°C):	13700kPa
Cylinder No:	ALRZ3383	Gas Volume: (15°C, 101.3kPa)	1.2m^3

Minimum storage/usage temperature	Minimum utilisation pressure
0°C	700kPa

Material	Description
29231D	**Spectra Seal 5 ppm H2S in N2**

When re-ordering please call Customer Service on 1800-658-278 and quote the material number.

The property value of the Reference Material is traceable to the SI through the Reference Standards used to analyse this material, which are traceable to the Australian National Standard of Mass.



All results expressed in this report are on a mole/mole basis, unless otherwise stated. The contents of the above mentioned cylinder has been analysed and found to be as follows:

Component	Result	Uncertainty	Unit	MoA*
Hydrogen sulphide in Nitrogen	5.16	± 0.16	ppm	ANA0854

*Method of analysis details are available on request.
The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor k=2, providing a level of confidence of approximately 95%.

g wang
George Wang
Signatory for and on behalf of BOC Limited
A.B.N. 95 000 029 729
428 Victoria St
WETHERILL PARK 2164

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Page 1 of 1

Appendix 3 – Dr Ray Littler analysis report

Brief report on H_2S Detection Threshold Study

Ray Littler

Waikato Applied Statistics Unit

University of Waikato

The main statistical task is to characterise the distribution of the 1371 H_2S detection threshold results collected from 59 subjects, residents of either Rotorua or Whakatane. We are particularly interested in whether the fact that Rotorua residents are accustomed to higher ambient H_2S levels affects their detection thresholds in comparison to those for Whakatane residents. Untrained panellists were used as subjects because of the context of the study, and tests were structured so that subjects evaluated samples from a dilution series repeatedly at each of three test sessions. Subsidiary questions relate to the repeatability of test results, and the possible effects of some demographic variables on the thresholds. Thresholds determined for n-butanol in the study have also been analysed.

Data aggregation

Because of the dilution series nature of the study, the raw results are necessarily rather discrete (see Figure 1), and it is sensible to take as the primary unit for analysis the mean threshold per session per panellist. In addition the steps between possible values are wider for high thresholds, so we may find absolute measurement error greater for high threshold values.

Because of the number of tests per session we expect session means to have approximately continuous distributions. So most of our analyses are actually based on either Panellist.Session means or Panellist means. The Panellist.Session means are averaged over about eight individual test results (each result the outcome of a series of dilution responses).

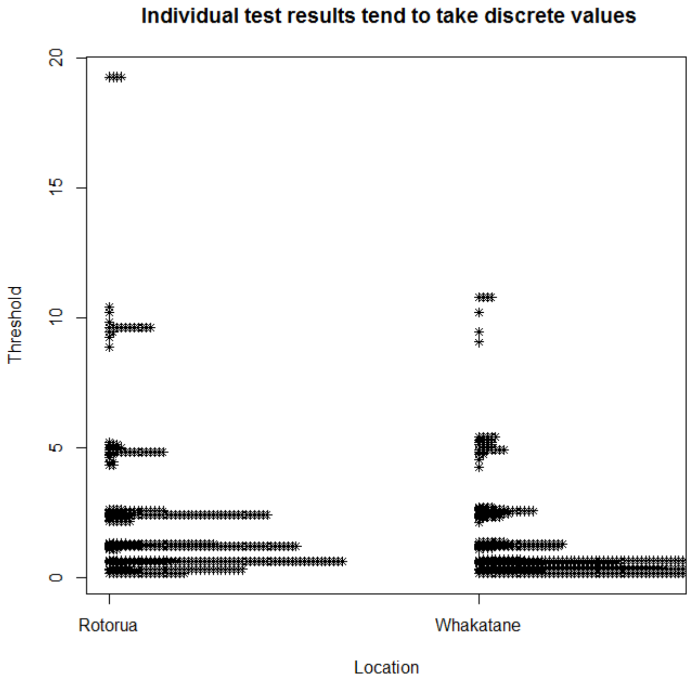


Figure 1 (Data for this plot excludes Rotorua data with elevated ambient H_2S).

Effect of elevated ambient H_2S

On 26 and 27 March, some testing was carried out at Rotorua when ambient H_2S levels were unusually high for the testing location. It has been proposed that the data from these periods be removed. Figures 2 and 3 demonstrate that the affected period did show markedly elevated detection thresholds in comparison to other results at about the same time, even those for the same panellist. It is therefore justifiable to remove the data as proposed. Unfortunately 31% (209/678) of the Rotorua data is lost. From now on our analyses are based on the consequently “trimmed’ data set.

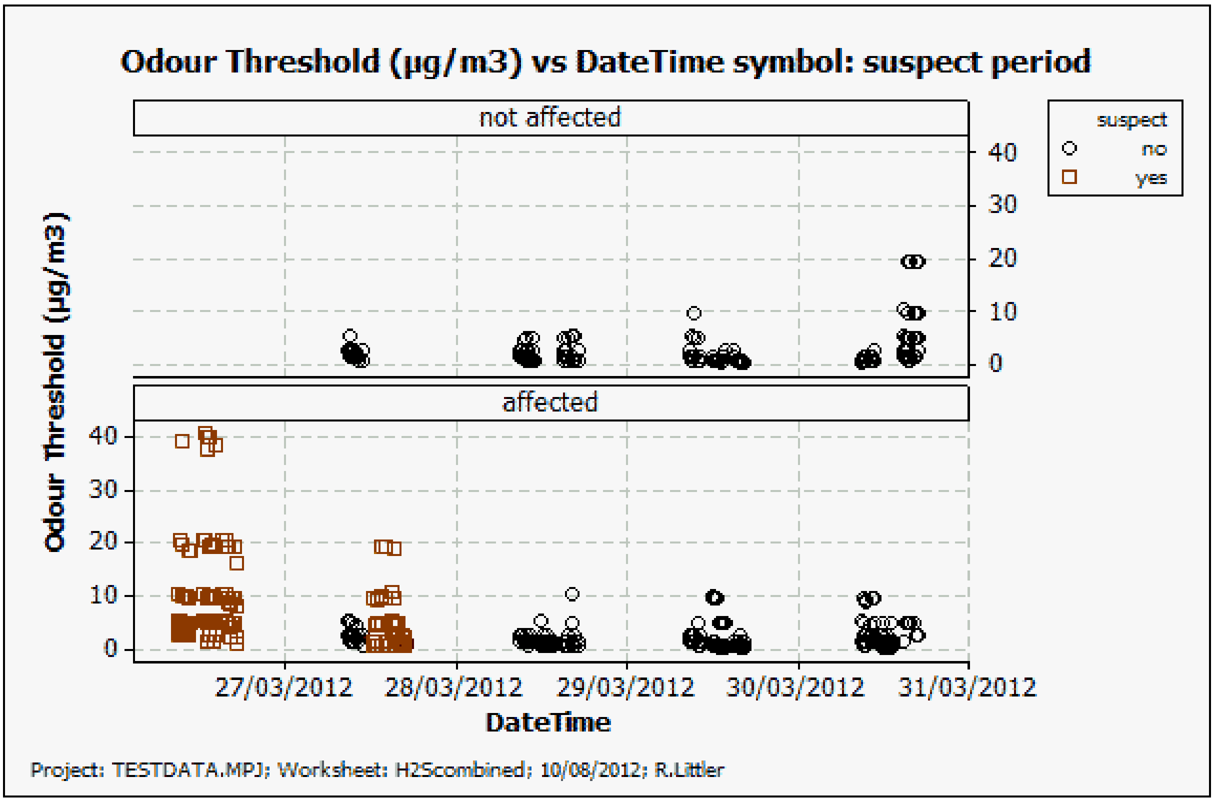


Figure 2 “affected” panellists have at least one result in the “suspect” period.

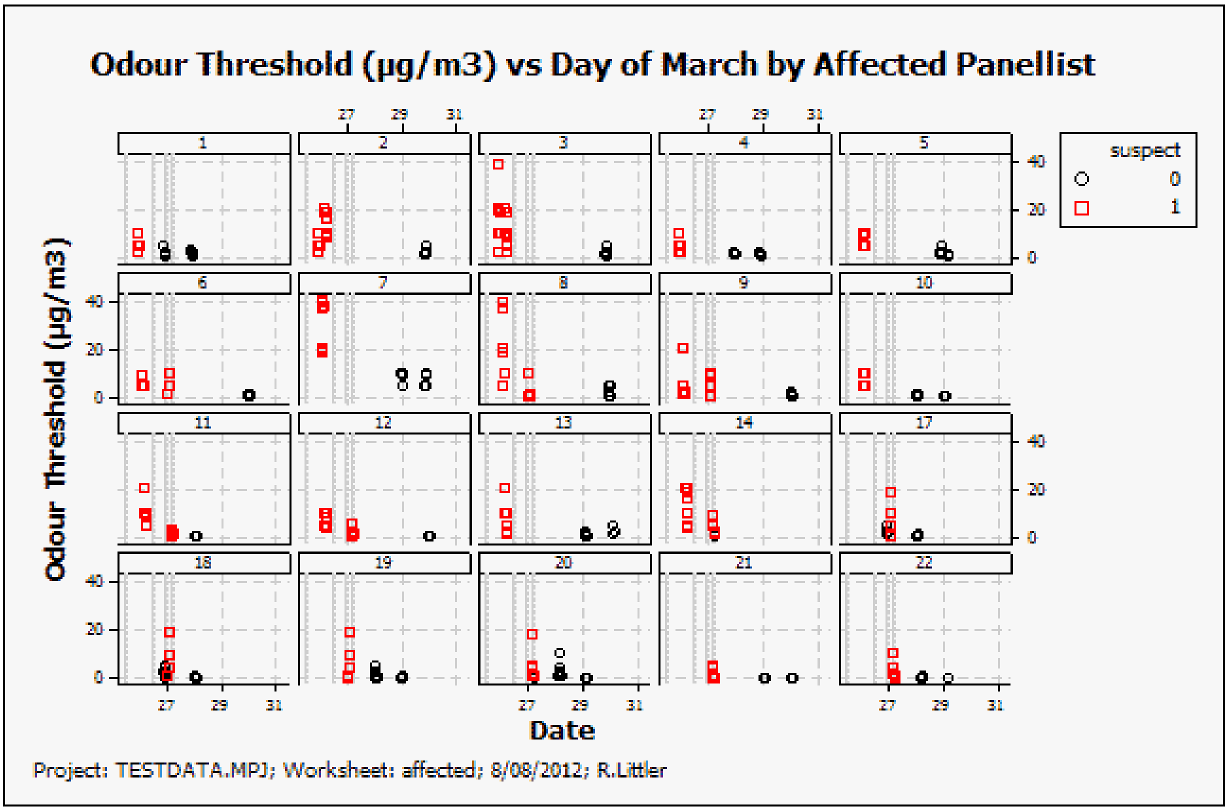


Figure 3 Effects by panellist.

Transforming the data

It is convenient to use analysis of variance (ANOVA) to quantify the variability of threshold values between sessions, panellists and locations. Anova works well if underlying variation is approximately normally distributed and if the standard deviations of the approximating normal curves are roughly equal. Otherwise the anova estimates are likely to be unreliable. The detection threshold data in untransformed scale does not satisfy this requirement, which is common for this sort of measurement. Working with logged data, however, improves the “diagnostics” a great deal as shown in the rather technical figs 4 and 5. They show “residual analysis” for the raw data and then the logged data. The skewed shape and variable SD is corrected. We can still draw conclusions (with care) about the problem in the original scale.

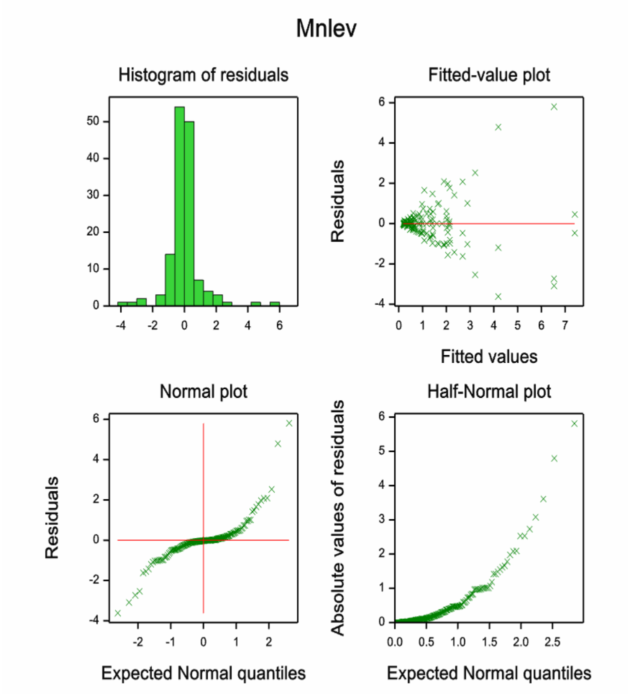


Figure 4 Untransformed is non-normal, increasing SD

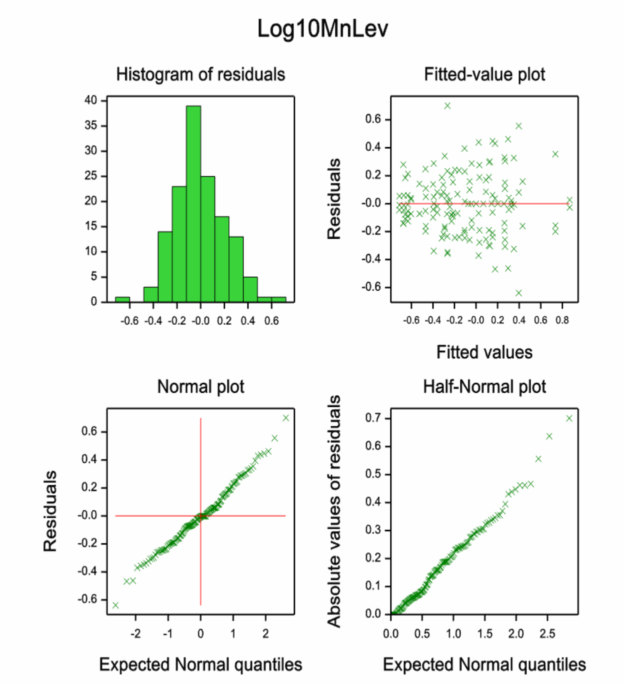


Figure 5 Transformed is-normal, uniform SD

Is there a trend over sessions?

It would appear plausible that panellists might become better at detecting H_2S over three sessions leading to a negative trend in threshold. Working in the log scale we show in Figure 6 (using the trimmed data) that we can readily “see” a trend over the three sessions for many individual panellists. However a number of them are in the “wrong” direction. A formal non-parametric test gives some support to the existence of a reduction in mean threshold over sessions.

Figure 6 also gives some guidance as to the between-session variation in threshold for a subject, whether it be due to trend or “random” variation. A more careful analysis of the variation between sessions provides the following prediction. If we collect **untransformed** mean threshold values for a subject for three sessions, then we expect the **ratio** of the maximum value to the minimum (of the three) to be about 2.78. (This is based on an estimate of the between-session standard deviation for $\log_{10}$(mean threshold) of 0.283).

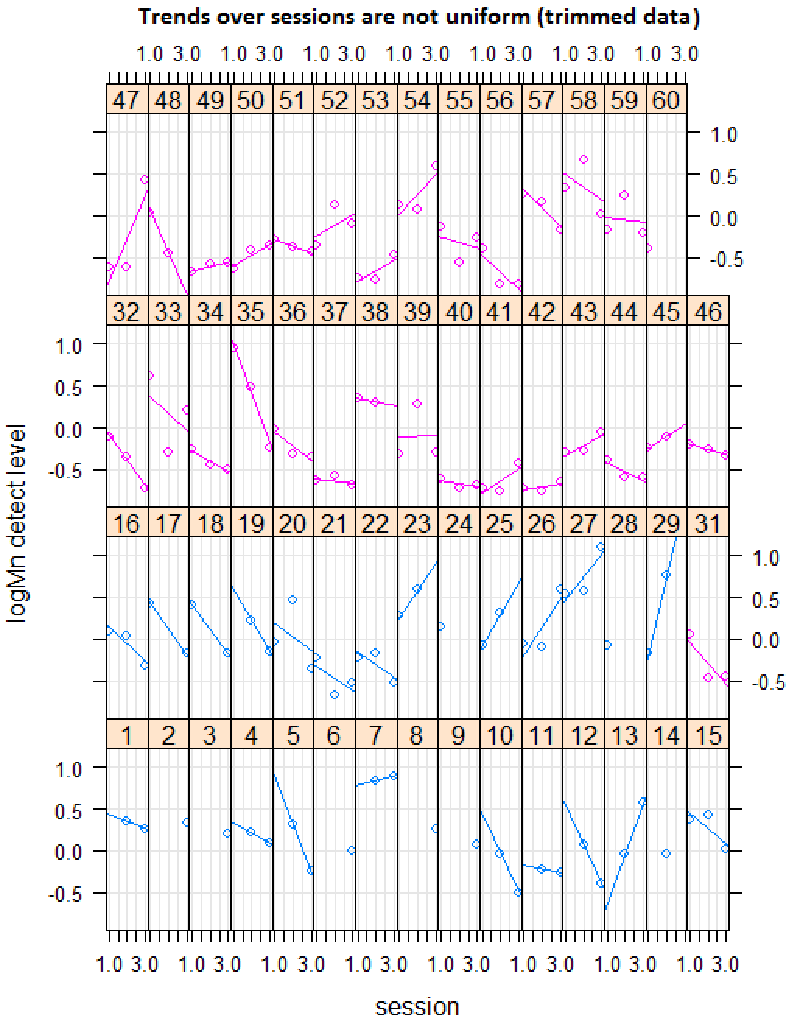


Figure 6 Between session trends in log scale.

Comparing geometric means of threshold for two locations

Here are "average" summaries for the untransformed threshold data for the two locations.

statistic	Rotorua	Whakatane
mean	1.83	0.89
median	1.44	0.57
geometric mean	1.44	0.62

If we log the data, find the mean and then back-transform to the original scale we get the geometric mean. We can conclude that, for skewed data of the shape we have, the geometric mean is approximately equal to the median of the data.

Figure 7 with the Whakatane per-panellist data illustrates the point.

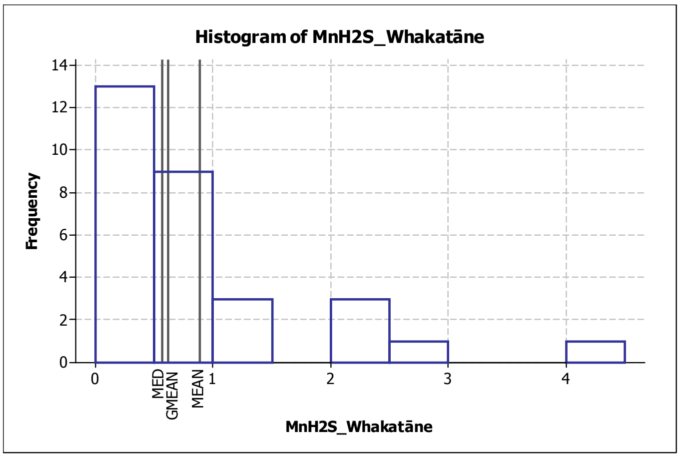


Figure 7 Distribution of Whakatāne thresholds.

We now (finally) give the results of useful analyses comparing locations which show the clear difference in average thresholds between the locations. Although our full analysis used data with all results per session per panellist, it is sufficient to simply compare the log thresholds at the two locations using a two-sample *t*-test. The test is justified by the approximate normality of the logged form of the data. And given that there are only two locations it is also simple to allow the variability at the locations to be different.

Two-sample T for log10MnH$_2$S

Location	N	Mean	StDev	SE Mean
Rotorua	29	0.159	0.291	0.054
Whakatāne	30	-0.208	0.362	0.066

Difference = mu (Rotorua) - mu (Whakatāne).

Estimate for difference: 0.3671.

95% CI for difference: (0.1960, 0.5381).

T-Test of difference = 0 (vs not =): T-Value = 4.30 P-Value < 0.0005 DF = 55.

We have shown there is very strong evidence that the geometric mean thresholds at Rotorua are higher than at Whakatane. Our point estimate of the difference in the log scale is 0.3671 which corresponds to a ratio in geometric means of $10^{0.367}$ = 2.3. We are 95% sure that the ratio is somewhere between $10^{.196}$ and $10^{.538}$ i.e. between 1.6 and 3.5. Note that the estimated geometric means are $10^{-.208}$=0.62 and $10^{.159}$ = 1.44 as listed previously.

Estimating other useful characteristics of the threshold distributions

As an alternative to using transformations, some statistical software offers alternative approaches to leaving the data in the untransformed state and estimating various percentiles (such as the median), the mean, and also the proportion of the data in various data ranges. The results below used such a procedure and included fitting the threshold data with a three-parameter lognormal distribution (equivalent to the data transformation Y = $\log_e$ (threshold – 0.16)).

Whakatane		
statistic	**estimate** (µg/m^3)	**confidence interval**
Mean	1.02	(.59, 1.77)
Median	0.53	(.39, .73)
% detecting 2 µg/m^3	89%	(77%, 96%)
% detecting 7 µg/m^3	99%	(94%, 100%)
Rotorua		
statistic	**estimate (µg/m^3)**	**confidence interval**
Mean	1.85	(1.35, 2.54)
Median	1.4	(.72, 3.44)
% detecting 2 µg/m^3	69%	(54%, 81%)
% detecting 7 µg/m^3	98%	(90%, 100%)

Location effects on butanol threshold

Analysis of the butanol data using similar methods to those used above showed that the location difference in geometric means was not statistically significant. However the **variation** in the Rotorua data was significantly greater than that for Whakatane.

The *t*-test results for $\log_e$ (butanol threshold) were as follows:

Two-sample T for lnMnbut

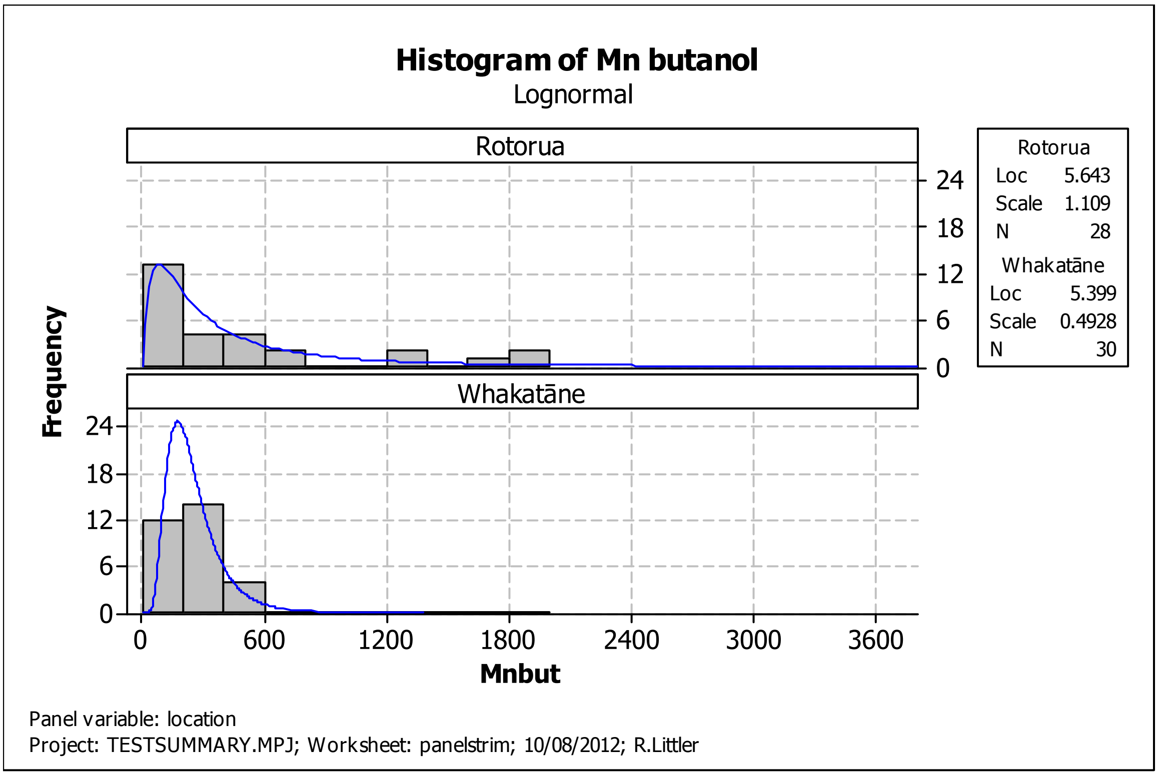
Location	N	Mean	StDev	SE Mean	Median	Est Geometric Mean
Rotorua	29	0.159	0.291	0.054	**238**	**281.5**
Whakatāne	30	-0.208	0.362	0.066	**237**	**221.2**

Difference = mu (Rotorua) - mu (Whakatāne).

Estimate for difference: 0.244.

95% CI for difference: (-0.218, 0.707).

T-Test of difference = 0 (vs not =): T-Value = 1.07 P-Value = 0.291 DF = 36.



Panel variable: location
Project: TESTSUMMARY.MPJ; Worksheet: panelstrim; 10/08/2012; R.Littler