



Monitoring and mapping of hydrogen sulphide emissions across an active geothermal field: Rotorua, New Zealand

C.J. Horwell^{a,*}, J.E. Patterson^b, J.A. Gamble^c, A.G. Allen^d

^aDepartment of Earth Sciences, University of Bristol, Bristol, BS8 1RJ, UK

^bSchool of Earth Sciences, Victoria University of Wellington, Wellington, New Zealand

^cDepartment of Geology, National University of Ireland, University College, Cork, Ireland

^dSchool of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, UK

Received 26 January 2004; accepted 20 August 2004

Abstract

Hydrogen sulphide (H₂S) is one of a number of gaseous species associated with geothermal activity in the Taupo Volcanic Zone (TVZ), New Zealand. The city of Rotorua is located within Rotorua Caldera in the TVZ and is one of the few urban areas in the world where a large population (>60,000 people) is frequently exposed to geothermal emissions. In order to evaluate the health hazard from long-term exposure to H₂S being emitted from the Rotorua geothermal field, a passive sampler has been developed to measure concentrations of H₂S at many locations across the city simultaneously. In contrast to other passive or pump-based samplers, the sampler is inexpensive, easily mass-manufactured, and involves the reaction of H₂S with silver halide contained in treated photographic paper. H₂S-exposed paper shows a distinct colour change from white to dark brown as H₂S concentrations increase and is sensitive to concentrations between $\ll 30$ and around 1000 ppb. Rotorua city can be divided into three regions—an area of low H₂S concentration in the west, a ‘corridor’ of high concentrations running north–south through the city centre where H₂S is being emitted, and an area of medium concentration to the east which is influenced by the prevailing wind direction, creating a plume from the central corridor. The data give new insight into the subsurface routes of degassing in the Rotorua geothermal field, by showing the surface expression of the main upflow zone and the direction of the conjectured faulting below.

© 2004 Elsevier B.V. All rights reserved.

Keywords: hydrogen sulphide; geothermal; Rotorua; air quality; monitoring; passive sampler

1. Introduction

Hydrogen sulphide (H₂S) is a corrosive gas known to be acutely toxic in high concentrations. It is one of a number of gaseous species (including HCl, SO₂, CO₂ and H₂O) associated with geothermal activity in the

* Corresponding author. Tel.: +44 117 954 5243; fax: +44 117 925 3385.

E-mail address: claire.horwell@bristol.ac.uk (C.J. Horwell).

Taupo Volcanic Zone, New Zealand. The city of Rotorua is located within the active Taupo Volcanic Zone, and is one of the few urban areas in the world where a large population (>60,000 people) is frequently exposed to geothermal emissions. The geysers, hot pools and warm ground have been exploited for centuries and are a world-renowned tourist attraction.

Little is known about the chronic long-term health effects of breathing low concentrations of H₂S. A medical study carried out in 1998 by a local health authority, Eastbay Health, for the New Zealand Ministry of Health, on the long-term health effects of H₂S on the Rotorua population required a map of H₂S concentrations across the city. In this paper, we give details of a year-long study established to map H₂S concentrations across Rotorua city. The results

give valuable insight into the subsurface routes of degassing in the Rotorua geothermal field.

1.1. Geological setting

The Taupo Volcanic Zone (TVZ) in the central North Island, New Zealand (Fig. 1), is the continental margin segment of the Tonga–Kermadec–New Zealand subduction system associated with subduction of the Pacific Plate beneath the Australian Plate. The region is distinguished by anomalously high heat flow (4200 ± 500 MW, Bibby et al., 1995), some 20 mapped geothermal systems (Giggenbach, 1995) and eruption of voluminous rhyolite ignimbrites from at least eight calderas over a 2-Ma time span (Houghton et al., 1995; Wilson et al., 1995).

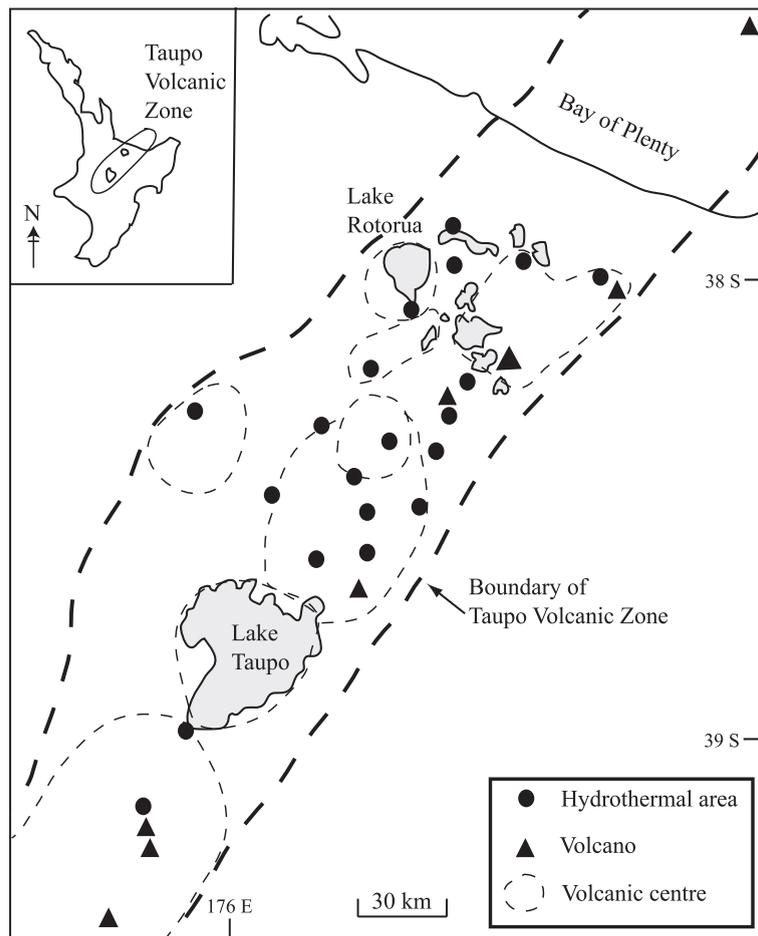


Fig. 1. Map of Taupo Volcanic Zone showing volcanic centres and geothermal areas.

Eruption of the $>145 \text{ km}^3$ Mamaku Ignimbrite at $0.22 \pm 0.01 \text{ Ma}$ (Houghton et al., 1995; Wilson et al., 1995; Milner et al., 2003) resulted in the formation of the Rotorua Caldera. Following caldera collapse, extrusion of rhyolite around the caldera rim gave rise to a number of dome complexes (Houghton, 1982; Wood, 1992) and these, together with the ignimbrite, are the host rocks to the Rotorua geothermal system (Fig. 2).

Surface flow of geothermal fluids in the Rotorua geothermal field results from the coincidence of a zone of upwelling with the caldera-bounding fractures

and a series of NE–SW-trending faults associated with extension across the entire TVZ. As a result, the main area of upwelling is a roughly elliptical zone ($5 \times 3.5 \text{ km}$) extending from the caldera bounding fault in the south to the shore of Lake Rotorua in the north. A smaller zone is associated with the Kuirau Fault, 1 km to the west (Fig. 2).

1.2. The Rotorua geothermal field

The geothermal field centred on Rotorua city is recognised as a low sulphidation geothermal system.

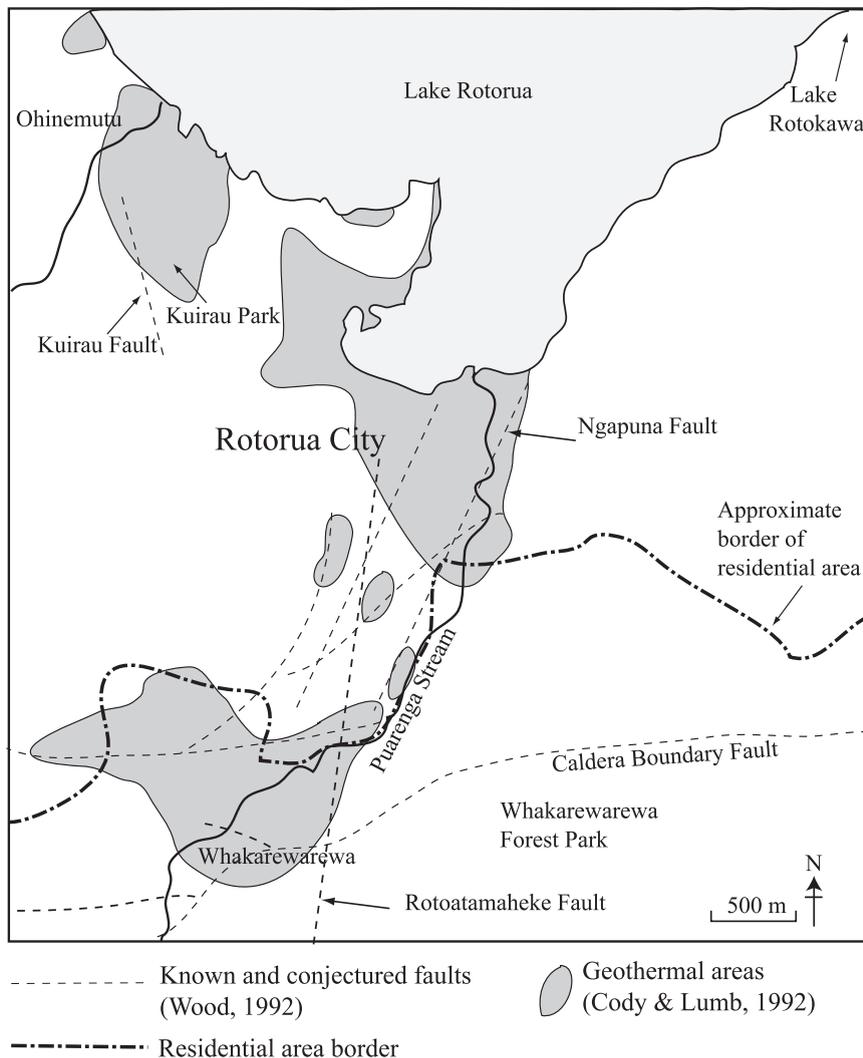


Fig. 2. Map of Rotorua city showing geothermal areas and conjectured faults.

Low sulphidation systems are frequently linked to cooling of magma bodies at depths of approximately 5 km. Magmatic acidic gases from the congealing body ascend through brittle fractures in the surrounding rock envelope and become mixed in supergene convection cells of meteoric waters. The gas species are predominantly HCl, SO₂, CO₂, H₂S, and when dissolved in the geothermal waters they begin to react with surrounding rock. This gives rise to a primary neutralisation process because the feldspar and glass, which are the dominant rock forming components, are converted to kaolinite or illite, releasing Na which combines with the Cl (from dissociation of HCl at pH<1 and 300–400 °C to form NaCl, Giggenschbach, 1981). SO₂ is also reduced to H₂S (at ~300 °C) by disproportionating on contact with water ($4\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + 3\text{H}_2\text{SO}_4$, Giggenschbach, 1997).

At around 1 km depth and a temperature of 280–300 °C, the boiling point-depth curve is intercepted, leading to boiling of the geothermal fluids. This causes the volatile species (mainly CO₂ and H₂S) to vaporise and ascend to the surface. In the vadose zone, some H₂S will be oxidised to sulphate but most gas reaches the surface and discharges through the soil or fumaroles. Where there is low relief, where the ground surface intersects the water table, or where there is a perched water table, vapour-heated acid sulphate waters occur. Here, a third to a half of the H₂S oxidises according to the reaction $\text{H}_2\text{S} + 2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$ (at <150 °C and pH>2.8; Hedenquist, personal communication). The remaining H₂S is emitted as gas—the characteristic ‘rotten eggs’ smell. These acid surface waters, plus the bacteria living in the thermal springs, promote advanced argillic alteration leading to formation of minerals such as kaolinite, alunite, dickite, cristobalite, native sulphur, pyrite and hematite (Hedenquist, 1986). At depth, following vaporisation of H₂S and CO₂, the geothermal fluids are chloride rich and these rise to the surface to discharge as hot springs and geysers. These fluids are mildly acidic (pH 5.5–6.5) and are associated with alteration assemblages of quartz, albite, adularia, illite, chlorite and pyrite (Hedenquist, 1986).

Thus, in the Rotorua geothermal field a continuum of systems between alkali chloride type and acid sulphate type are apparent with some systems appearing to alternate from alkaline to acidic depend-

ing on the local water table characteristics (Bradford et al., 1987).

2. Methods

Hydrogen sulphide is often monitored using expensive pump-based samplers which only measure H₂S concentrations in one location at a time. In attempting to map H₂S distribution across a city, it is preferable to monitor simultaneously many locations to eliminate changes in external factors such as barometric pressure, humidity and seasonal variation over time. To achieve widespread routine use, a method for determining H₂S should be simple, specific, portable, capable of unattended operation, and also inexpensive (Natusch et al., 1974). Passive samplers are most likely to fulfil these criteria as they employ natural diffusion instead of a pumping system. Several designs of passive samplers are available (e.g. Shooter et al., 1995) and have been used in Rotorua in the past (e.g. Siegel and Siegel, 1984). However, they were comparatively expensive and only a few samplers were deployed around the city at any one time.

Here, we have developed a passive sampler device whose operating principle is based on the absorption of H₂S onto treated black and white photographic paper (Ilford Multigrade IV RC deluxe MGD.1M, which contains silver chloride) housed in plastic film canisters. Both the paper and the canisters are inexpensive and available worldwide, thereby allowing easy mass manufacture for simultaneous measurements across a geothermal area. The photographic paper undergoes a colour change on exposure to H₂S, from white through yellow to dark brown. The paper strips were ‘fixed’ using proprietary photographic reagent immediately after sample collection to prevent further colour development during storage. The colour change was calibrated in experiments where samplers were exposed to different H₂S concentrations over varying time intervals. Full details of sampler development and design, manufacturing methods, and calibration and quantification procedures are published in Horwell et al. (2004).

In the presence of H₂S, silver tarnishes with formation of black silver sulphide (Pope et al., 1968), the rate of reaction being dependent on levels

of oxygen and relative humidity. Metallic silver can also react with oxidizing species such as nitrogen dioxide in oxygen, producing mixtures of silver nitrate (AgNO_3) and silver oxide (Ag_2O , which also causes blackening) (Kim, 2003). Similarly, silver halides respond with a colour change reaction when exposed to reduced sulphur compounds. In the atmosphere reduced sulphur exists in the form of compounds including H_2S , dimethyl sulphide ($(\text{CH}_3)_2\text{S}$), carbon disulphide (CS_2), carbonyl sulphide (COS), methyl mercaptan (CH_3SH) and dimethyl disulphide ($(\text{CH}_3)_2\text{S}_2$). Of these compounds, hydrogen sulphide and dimethyl sulphide dominate the reduced sulphur gas emissions budget due, respectively, to their volcanogenic and oceanic sources (Berresheim et al., 1995). Silver oxide may be formed in the presence of oxidizing species such as NO_2 or H_2O_2 , however, in the volcanic regions where H_2S is likely to be of concern, concentrations of such oxidants tend to be low, so that in the absence of light, any darkening of a silver halide substrate is due overwhelmingly to the presence of sulphide. Since dimethyl sulphide is not emitted during volcanic activity, H_2S measurement in volcanic regions, using the technique described here, is virtually interference-free.

2.1. Sampling procedures

Using a street map of the city (Rotorua 'Handimap'), samplers were deployed on 13 June 1997 (winter, Southern Hemisphere), two per chosen location in each grid square encompassing either residential or commercial premises. Samplers were placed, on their side, mainly in free-standing letter boxes which are close enough to dwellings to give similar concentrations of H_2S as may be found indoors, but could be distributed and collected with minimal disruption to the residents. Letter boxes also provide a sheltered, dark environment, where air can easily enter and circulate. Where letter boxes were unavailable, samplers were placed with their opening facing downwards on the outside of drainpipes or other discrete sites. Samplers were distributed, in duplicate, across the entire city of Rotorua at approximately 70 locations over a few hours, and one from each grid square collected after 7 days and the second after 28 days, to test the response times of

the samplers. During the month, temperature varied between 1.0 and 13.7 °C and humidity between 72% and 100% (Rotorua Airport Automatic Weather Station (RAAWS), Agent no. 1770, Network no. B86133, 7 km from city centre). A continuous pump-based H_2S analyser (TLD-1, MDA Scientific) was co-located at one site in the west of the city by the National Institute of Water and Atmospheric Research (NIWA, New Zealand). The results of this test were used for comparison following quantification of the samplers (see Horwell et al., 2004).

The experiment was repeated the following summer (distributed in duplicate on 1 December 1997 and collected after 7 and 28 days) using the same locations for deployment wherever possible. During this month, temperature varied between 12.0 and 20.8 °C and humidity was 60–92% (RAAWS).

3. Results

After collection and applying the fixing process, the photographic paper samplers were used to compile a map, according to their grid square locations. For the winter experiment, the samplers exposed for 1 week show a clear 'corridor' of high H_2S concentration running north–south where the samplers turned brown/black (Fig. 3a). Although there was colour variation to the west of the central corridor, it appears that the west side of the city was not exposed to high concentrations of H_2S during the test week. The east of the city shows a slightly darker colour change than the west. The map of samplers exposed for 1 month shows an enhanced version of the trends that developed in the first week (Fig. 3b). A distinct 'plume' is visible across the east of the city which appears to have been blown from the central corridor.

Similar results were obtained during the summer experiment for both week-long and month-long sampling periods, except that the 'plume' was less pronounced, and samplers from the west of the city were slightly darker in summer (Fig. 4). Wind speed and direction data were obtained from the NIWA Climate Database for RAAWS for the duration of the two experiments. The data show that during the winter month, the wind blew mainly from the south/south-west, therefore spreading H_2S emissions towards the

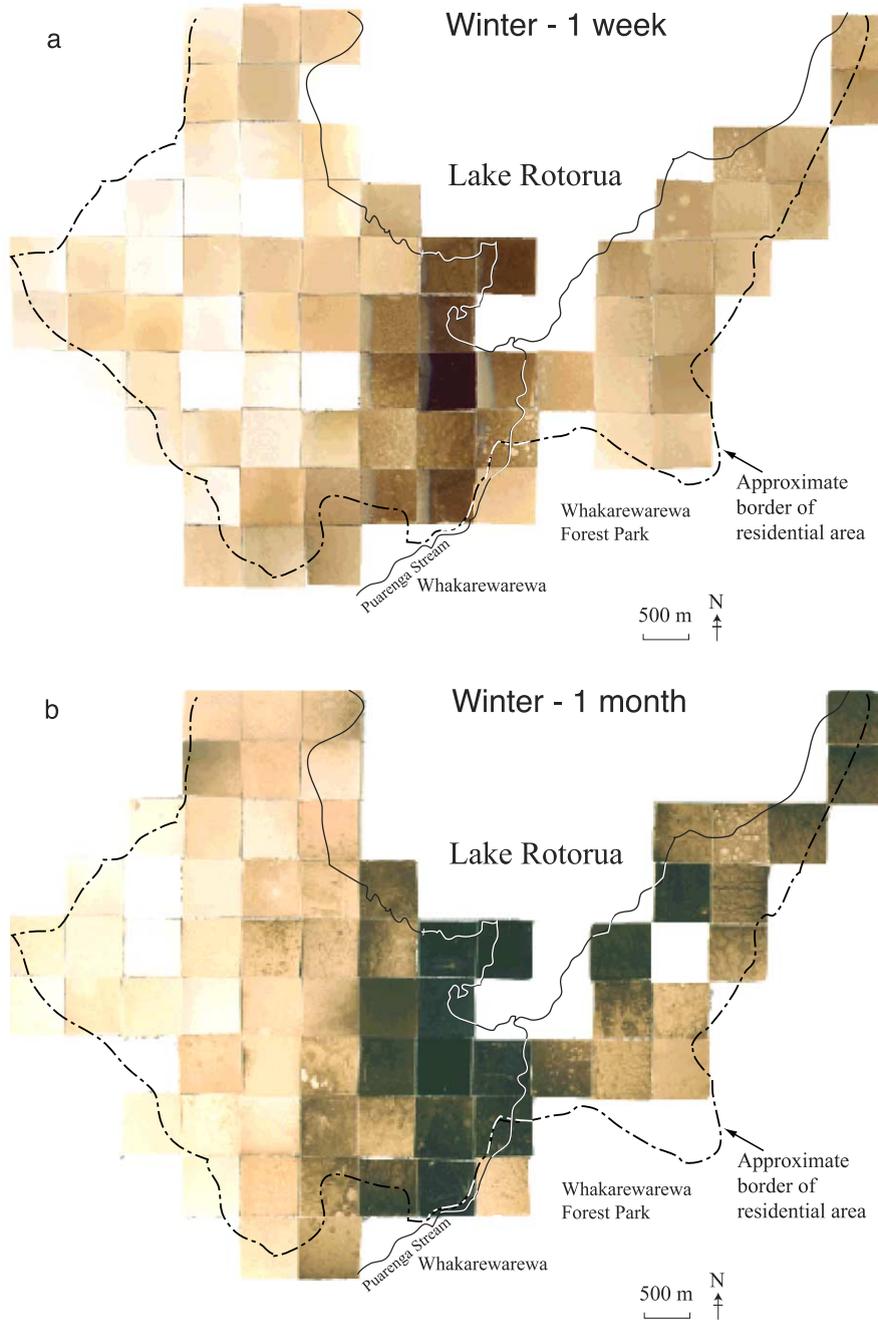


Fig. 3. Rotorua maps showing photographic sampler results by grid location for winter conditions (a) over 1 week; (b) over 1 month. Coloured version available in online version, JVGR website.

north/north-east. The data for the summer month show that the wind blew mainly from the westerly to north-easterly sectors, explaining why the plume was

less pronounced, as H₂S emissions would have been advected into the Whakarewarewa forest park and adjacent regions (Fig. 5).

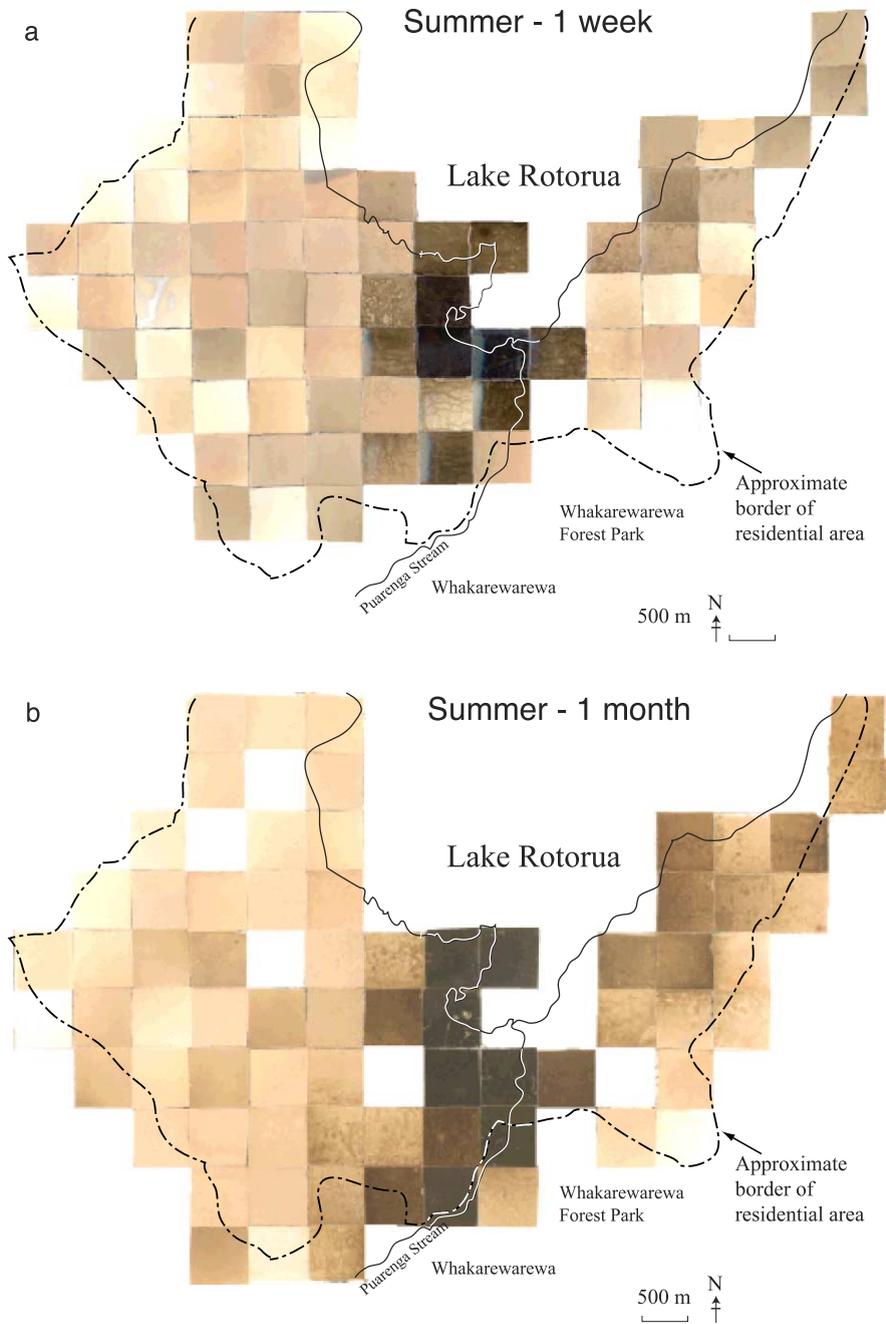


Fig. 4. Rotorua maps showing photographic sampler results by grid location for summer conditions (a) over 1 week; (b) over 1 month. Coloured version available in online version, JVGR website.

Other meteorological factors, such as temperature, humidity, rainfall and pressure, may also affect the atmospheric concentrations of H₂S. When

comparing the difference in colour change of the samplers between winter and summer, no certain relationship could be determined with meteorolog-

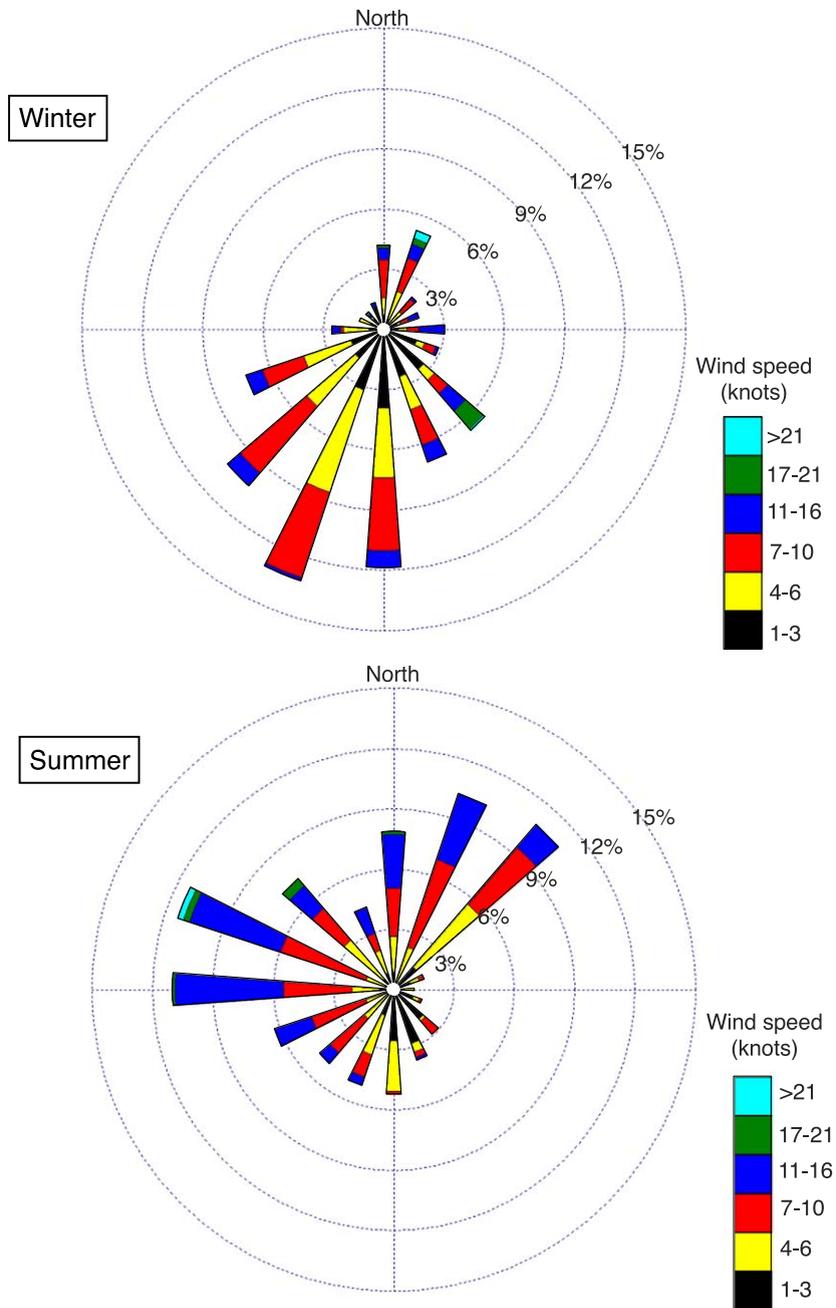


Fig. 5. Wind rose diagrams for Rotorua city for 1 month during (a) winter and (b) summer experiments. Coloured version available in online version, JVGR website.

ical data collected at RAAWS during the experiments. With the difference in colour between the two experiments being fairly indistinct, the results

are most-easily explained by the differences in wind direction during the two periods. Low pressure together with low cloud cover can cause inversions,

trapping H₂S at ground level, and high humidity is known to cause silver to tarnish more rapidly (Pope et al., 1968), but these factors could not be attributed with certainty to these results. Other factors which might affect H₂S concentrations are increased degassing caused by increased soil permeability in dry conditions, and changes in atmospheric pressure which could cause fluids to boil more vigorously at shallow depths.

A further experiment where samplers were placed in greater concentration in the central ‘corridor’ showed that the sources of high emissions of H₂S are very localised, and sites relatively close by may hardly be affected if, for example, the wind is blowing in another direction.

Following calibration and quantification of the samplers in the laboratory, the sulphide from six Rotorua samplers, ranging in colour from almost white to dark brown was extracted (see Horwell et al., 2004, for details and full methodologies). Of these, five had $<10 \mu\text{g cm}^{-2} \text{S}^{2-}$, with H₂S concentrations ranging from 0 to 803 ppb over a 7-day period. The lowest of these (0, 30 and 40 ppb) were representative of H₂S concentrations experienced in the west of the city (i.e. little or no H₂S). These results were in good agreement with the values (0–30 ppb) obtained from the co-located continuous H₂S analyser operated during the winter experiment. The Rotorua samplers giving highest concentrations (320 and 800 ppb) were representative of the samplers located near the centre of the city, in and adjacent to the central ‘corridor’, and were dark brown in colour. The sixth sampler, located in an emissions hotspot, was almost black, and contained $25 \mu\text{g cm}^{-2} \text{S}^{2-}$ (and was, therefore, out of the range of linear response, see Horwell et al., 2004), giving an estimated H₂S concentration of 2.5 ppm. These results indicate that the west of the city is rarely exposed to significant H₂S concentrations whilst the central ‘corridor’ will often have ambient H₂S concentrations of around 1 ppm. The east of the city experiences raised concentrations, perhaps of around 500 ppb when the wind blows in this direction.

Based on the results obtained from this network of samplers, within the city boundaries, Rotorua can be divided into three zones of H₂S concentration—a high central ‘corridor’, a low concentration area in the west

of the city which is rarely affected by more than background levels of H₂S, and a medium concentration area in the east of the city which is variably affected by the central ‘corridor’ depending on wind direction.

4. Geological implications of results

The central ‘corridor’ identified here gives a surface expression of the main upflow zone and the direction of the conjectured faulting below. While the faults actively release vapour and fluid at depth, the shallow aquifers close to the surface must act to store and diffuse the vapour over a wider surface area. The results add weight to a hypothesis proposed by Giggenbach and Glover (1992), that the main upflow zone is situated beneath the eastern part of the field, along the Puarenga Stream, with a closely associated secondary plume feeding Whakarewarewa to the south. The Puarenga Stream upflow zone coincides with the conjectured NE–SW-trending faults beneath Rotorua as confirmed by our results. A separate plume of more altered, high bicarbonate waters, probably centred beneath Kuirau Park, supplies the northern areas. These two areas of upflow are separated by a distinct area of downflow which coincides with the ‘saddle’ between the two Rotorua city rhyolite domes. It is not known if this area of downflow is natural or induced by the extensive exploitation of the field. This hypothesis is also supported by Bibby et al. (1992) whose resistivity data show that, at depth, a large plume of geothermal fluids extends beneath the postulated source regions, so that the passage of the fluids to the surface will depend on permeability. Bibby et al. also make the point that fluids may travel great distances horizontally away from the original plume, but that gases are unlikely to have travelled horizontally. Therefore, they should represent the surface expression of a plume at depth.

This hypothesis overrides an earlier hypothesis that the main upflow zone for the entire Rotorua geothermal field was beneath Whakarewarewa, with a smaller upflow zone near Ohinemutu/Kuirau Park (e.g. Glover, 1974). Houghton (1982) hypothesised that a large body of superheated water rose rapidly to

the surface below Whakarewarewa, where one third of the volume was discharged. The remainder was diverted northwards towards Lake Rotorua as a tongue of hot water trapped within the buried sediments. Whakarewarewa was assumed to be the main upflow zone because of the vigorous discharge here, caused by the proximity of the ignimbrite to the surface.

Had the main source of geothermal fluids been below Whakarewarewa and Kuirau Park, as originally hypothesised, more H₂S would be discharged in these areas, and our map of H₂S concentrations would have shown separate centres of high H₂S concentrations, rather than one ‘corridor’ of high emissions.

5. Conclusions

The passive sampler developed for this study is specific to H₂S, simple to mass manufacture, deploy and analyse, portable, capable of unattended operation and inexpensive (~US\$10 per 100 samplers plus labour). H₂S was measured using a network of passive sampling devices at many locations simultaneously in Rotorua, producing a semi-quantitative map of H₂S concentrations across the city. Eastbay Health have used the map to assess the risks of living and working in the different zones of the city. The results of this study give new insight into the subsurface routes of degassing in the Rotorua geothermal field, by showing the surface expression of the main upflow zone and the direction of the conjectured faulting below.

Acknowledgements

CJH acknowledges a Leverhulme Trust Research Interchange Grant. The calibration was carried out with Tamsin Mather (University of Cambridge, UK) through a collaboration founded by the International Volcanic Health Hazard Network. Dr. Phil Weinstein (University of Western Australia) and Dr. Phil Shoemack (Pacific Health, NZ) were closely involved with the design and application of the project. The authors are grateful to Ross Price (Toi Te Ora Public Health) for useful advice and help with sample collection and distribution, and to Dr. Roy Lawrence

(University of Birmingham) for assistance with the chemistry.

References

- Berresheim, H., Wine, P.H., Davis, D.D., 1995. Sulfur in the atmosphere. In: Singh, H.B. (Ed.), *Composition, Chemistry and Climate of the Atmosphere*. Van Nostrand Reinhold, New York, pp. 251–307.
- Bibby, H.M., Dawson, G.B., Rayner, H.H., Bennie, S.L., Bromley, C.J., 1992. Electrical resistivity and magnetic investigations of the geothermal systems in the Rotorua Area, New Zealand. *Geothermics, Special Issue-Rotorua Geothermal Field, New Zealand* vol. 21 (1/2), pp. 43–64.
- Bibby, H.M., Caldwell, T.G., Davey, F.J., Webb, T.H., 1995. Geophysical evidence on the structure of the Taupo Volcanic Zone and its hydrothermal circulation. *Journal of Volcanology and Geothermal Research* 68, 29–58.
- Bradford, E., Cody, A.D., Glover, R.B., 1987. Rotorua hot spring data, 1982–1987. DSIR Geothermal Report No. 118.
- Giggenbach, W.F., 1981. Geothermal mineral equilibria. *Geochimica et Cosmochimica Acta* 45, 393–410.
- Giggenbach, W.F., 1995. Variations in the chemical and isotopic composition of fluids discharged from the Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research* 68, 89–116.
- Giggenbach, W.F., 1997. The origin and evolution of fluids in magmatic-hydrothermal systems. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*, 3rd ed. Wiley Interscience, pp. 737–796.
- Giggenbach, W.F., Glover, R.B., 1992. Tectonic regime and major processes governing the chemistry of water and gas discharges from the Rotorua geothermal field, New Zealand. *Geothermics, Special Issue-Rotorua Geothermal Field, New Zealand* vol. 21(1/2), pp. 121–140.
- Glover, R.B., 1974. *Geochemistry of the Rotorua Geothermal District*. Geothermal Resources Survey, Rotorua Geothermal District, DSIR Geothermal Report No. 6.
- Hedenquist, J.W., 1986. Geothermal systems in the Taupo Volcanic Zone: their characteristics and relation to volcanism and mineralisation. *Royal Society of New Zealand Bulletin* 23, 134–168.
- Horwell, C.J., Allen, A.G., Mather, T.A., Patterson, J.E., 2004. Evaluation of a novel passive sampling technique for monitoring volcanogenic hydrogen sulphide. *Journal of Environmental Monitoring* 6, 630–635.
- Houghton, B.F., 1982. *Geysersland: a guide to the volcanoes and geothermal areas of Rotorua*. Geological Society of New Zealand Guidebook 4, 48 pp.
- Houghton, B.F., Wilson, C.J.N., McWilliams, M., Lanphere, M.A., Weaver, S.D., Briggs, R.M., Pringle, M.S., 1995. Chronology and dynamics of a large silicic magma system: central Taupo Volcanic Zone, New Zealand. *Geology* 23, 13–16.
- Kim, H., 2003. Corrosion process of silver in environments containing 0.1 ppm H₂S and 1.2 ppm NO₂. *Materials and Corrosion* 54, 243–250.

- Milner, D.M., Cole, J.W., Wood, C.P., 2003. Mamaku Ignimbrite: a caldera-forming ignimbrite erupted from a compositionally zoned magma chamber in Taupo Volcanic Zone, New Zealand. *Journal of Volcanology and Geothermal Research* 122, 243–264.
- Natusch, D.F.S., Sewell, J.R., Tanner, R.L., 1974. Determination of hydrogen sulfide in air—an assessment of impregnated paper tape methods. *Analytical Chemistry* 46, 410–415.
- Pope, D., Gibbens, H.R., Moss, R.L., 1968. The tarnishing of Ag at naturally-occurring H₂S and SO₂ levels. *Corrosion Science* 8, 883–887.
- Shooter, D., Watts, S.F., Hayes, A.J., 1995. A passive sampler for hydrogen sulfide. *Environmental Monitoring and Assessment* 38, 11–23.
- Siegel, S.M., Siegel, B.Z., 1984. Geothermal Hydrogen Sulfide and Health in Rotorua, New Zealand. Prepared for the Hawaii Natural Energy Institute's Environmental Quality Study.
- Wilson, C.J.N., Houghton, B.F., McWilliams, B.F., Lanphere, M.A., Weaver, S.D., Briggs, R.M., 1995. Volcanic and structural evolution of Taupo Volcanic Zone, New Zealand: a review. *Journal of Volcanology and Geothermal Research* 68, 1–28.
- Wood, C.P., 1992. Geology of the Rotorua geothermal system. *Geothermics, Special Issue-Rotorua Geothermal Field, New Zealand* 21(1/2), pp. 25–41.