Investigation of air quality arising
from flaring of fracturing fluids -
emissions and ambient air quality

Technical Report 2012– 03

Executive summary

The Taranaki Regional Council has previously investigated the nature of air emissions and downwind effects arising from the flaring of hydrocarbons (both natural gas and condensate) at exploration sites. This information has proven valuable in the development of robust and defensible technical requirements for incorporation into the Council's regional air quality plans[1], and for assessing applications for discharges to air from flaring at exploration and production sites. The combustible flows to flare pits giving rise to flaring activities will initially include entrained materials used in drilling activities, such as drilling mud residues.

However, more recently speculation has focused on the nature of potential effects arising from the use of hydraulic fracturing (HF) fluids within production enhancement activities, as these fluids include compounds additional to those used in drilling. These compounds will include biocides, gelling and gel-breaking agents, inert proppants such as sand or microscopic ceramic beads, and 'slicking' agents.

Normal exploration practice is to separate the recovered fluids from the entrained hydrocarbon gas.   However, under emergency circumstances, safety and equipment protection requirements may necessitate the discharge of the fluids to a flare pit without separation so that the entrained hydrocarbon gas can be combusted for reasons of safety. In this situation, some of the fluids will be combusted/evaporated with the gas, with the majority remaining within the pit for recovery from the pit at some point after the emergency event is under control. While used at extremely low concentrations within the hydraulic fluids (which comprise approximately 98% water and proppants), the presence of hydraulic fracture compounds within the mixture entering a flare raises the possibility of additional environmental effects.

The Council therefore undertook a study of the nature of flare characteristics and downwind consequences, at a wellsite in North Taranaki in February 2012. While the region's exploration and production companies endorsed the project, it should be noted that its design and implementation were completely independent of any influence or direction from the companies. The design was subject to peer review. It reflected and developed the original flaring investigations conduced by the Council in 1998.

The HF fluids used within this study had additives at a somewhat higher concentration that is typical.

The investigation covered combustion zone emissions of particulate matter (PM), dioxins and furans (PCDD/PCDF), polyaromatic hydrocarbons (PAHs), aldehydes (formaldehyde, acetaldehyde, and propionaldehyde), volatile organic compounds (VOC), methanol, and the more conventional products of combustion (oxygen, carbon dioxide, carbon monoxide, nitrogen oxides, and sulphur dioxide).

Emissions from the fluid surface were collected to determine emissions (evaporation) of PAHs, aldehydes, VOCs, and methanol.

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[1] Most recently the *Regional Air Quality Plan for Taranaki*, Taranaki Regional Council, July 2011

Ambient (downwind) measurements covered particulate (of particle sizes PM1.0, 2.5, and 10), carbon monoxide and dioxide, formaldehyde, and volatile organic compounds.

Estimations were made of ambient concentrations of dioxins, PAHs, and methanol, using emission and receiving environment data for other parameters. It should be noted that because of differences in timing around sample collection for various parameters, these estimations should be used with caution and regarded as approximations only. Nevertheless they serve a useful purpose if regarded as indicative rather than absolute.

It should be noted that all results relate to a field study carried out under specific source, topographic, and meteorological conditions. Therefore they cannot and must not be applied universally. To gain greater value and more regional application from this study, modelling of dispersion under varying meteorological conditions is being undertaken, utilising the emission data generated herein. As a provisional finding, it can be noted that the results of this study are consistent with and uphold those of the studies (field monitoring and modelling studies) conducted in 1998, which established that a separation distance of 300 metres between a flare and residential properties gave a substantial health and safety buffer for the protection of local populations.

Particulate matter (PM2.5, PM10): the PM2.5 data showed no correlation of distance downwind of the flare with concentration (the closest sampling point was about 120 metres downwind), indicating that at the most by 120 metres from the flare and site there was no effect upon ambient PM2.5. The two sites closest to the flare and wellsite had the lowest PM2.5 results.

The PM2.5 concentrations in the vicinity of the flare were similar to or slightly below those found elsewhere in the region as background (ambient) concentrations, and are far below international guidelines.

The PM10 data showed no correlation of distance downwind of the flare with concentration (the closest sampling point was about 120 metres downwind), indicating that at the most by 120 metres from the flare and wellsite there was no effect upon ambient PM10. The two sites closest to the flare and wellsite had the lowest PM10 results, while the second highest result was recorded at the site that was furthest away.

The PM10 concentrations in the vicinity of a flare are somewhat below those found elsewhere in the region, and are far below (less than 10% of) the national environmental standards for air quality (AQNES) (50 µg/m³). The air downwind of the flare would be rated according to MfE criteria as 'excellent' in respect of the PM10 concentration.

Dioxins/furans: emissions of dioxins and furans expressed as toxic equivalents could not be distinguished from zero (i.e there was no meaningful difference between the combustion zone result and the laboratory blank result, at the limits of detection of mass quantities used within the study). This is consistent with the very low levels of particulate matter emitted from the combustion zone.

Polyaromatic hydrocarbons (including BaP): PAHs were detected within the combustion zone and at much lower concentrations within the evaporation zone. The two samples had quite different compositions. BaP, the PAH of most significance, comprised 63% of the USEPA BaP toxicity equivalent concentration in the PAHs found in the combustion zone sample, but was not detected in the evaporation zone sample.

The estimation of downwind (ambient) PAH concentration suggested an elevation in downwind concentration of all PAHs at a distance of 70 metres, of between 12 and 38 ng/m^3 (total BaP equivalent), and in actual BaP of between 7.5 and 24 ng/m^3. As noted above, these figures should be regarded as estimates only; and further, that they are specific to this particular study.

Within the evaporation zone, levels of BaP equivalents were lower than is found in ambient air within central city locations in New Zealand, and that only minimal further dilution (dispersion) would be required to reduce PAH/BaP concentrations to levels similar to or lower than is typically encountered in urban areas.

Aldehydes (including formaldehyde): the formaldehyde concentrations in the vicinity of the flare, including those sites closest to the flare, are similar to those found elsewhere in the region, and are well below (less than 20% of) the MfE guideline.

The air downwind of the flare beyond the closest ambient monitoring location would be rated as 'excellent' according to MfE criteria in respect of the formaldehyde concentrations, and even at the site 70 metres downwind would be rated as 'good'.

Volatile organic compounds (including BTEX): results for BTEX compounds are discussed both without and with application of a correction to take into account any detection of these compounds within blank samples in laboratory analysis. A number of laboratory results for field deployed samples were indistinguishable from the results from laboratory analysis of blanks- that is, there was no detectable concentration of these compounds at some sites.

Benzene results show that within a distance of 300 metres from the flare, benzene levels had reduced to a steady (background) level. All results further than 140 metres from the flare were below the limit of quantifiable detection. All results, including those closest to the flare, were below the MfE guideline criterion, and at 140 metres downwind were half or less of the MfE guideline value.

Air beyond 140 metres downwind of the flare would be rated as at least being 'good' according to MfE criteria in respect of the benzene concentrations, and further away (beyond 300 metres) would be rated as 'excellent' in respect of benzene concentrations.

Toluene and xylene were found 70 metres downwind of the flare, at 10% and 3% respectively of the MfE ambient guidelines (unadjusted results). The air at all points sampled downwind of the flare would be rated as 'excellent' according to MfE criteria in respect of the toluene and xylene concentrations.

The study has identified that benzene is the parameter of most interest in terms of most closely approaching guideline values; whereas toluene is the BTEX of highest concentration.

Methanol: even within the combustion zone and the evaporation zone as sampled, the levels of methanol were far below limits that might be derived for population health protection.

Carbon monoxide and carbon dioxide: no carbon monoxide was detected downwind at the limit of detection of the meter used. This means that the air at all points sampled downwind

of the flare would be rated as 'good' or better according to MfE criteria in respect of the carbon monoxide concentration.

This report includes recommendations in Section 5, as follows:-

1. THAT it be noted that the findings of this study are that there were minimal effects upon ambient air quality in the vicinity of a flare at which the incidental combustion of hydraulic fracturing fluids was undertaken, in the context of prevailing air quality within the region and nationwide;

2. THAT it be noted that all results relate to a field study carried out under specific source, topographic, and meteorological conditions, but as a provisional finding, it can be noted that the results of this study are consistent with and uphold those of the air quality studies of flaring (field monitoring and modelling studies) conducted in 1998;

3. THAT this report be referenced by the Taranaki Regional Council in the assessment of any applications for air discharge permits for contingency flaring, and in any review of the *Regional Air Quality Plan for Taranaki* (2011)

4. THAT this report be distributed to hydrocarbon exploration companies and their consultants, for reference in the preparation of Assessments of Environmental Effects in support of applications for air discharge permits, and to other interested parties upon request

5. THAT the emission data contained herein be incorporated into modelling of dispersion from flares in which hydraulic fracturing fluids are combusted, to apply the findings and results of this study more widely across the variety of meteorology and landscapes that could be encountered within Taranaki.

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1. Introduction

1.1 Air discharges and the Resource Management Act 1991

1.1.1 Introduction

The appropriate management of regional air quality resources is the responsibility of the Taranaki Regional Council, under the *Resource Management Act 1991* ('the RMA'). Specifically, section 30(1) (f) requires the regional council to control discharges of contaminants into the air, including, if appropriate, the establishment of rules in a regional plan to allocate the capacity of air to assimilate a discharge of a contaminant.

This report sets out the undertaking and findings of a study into the nature of emissions and downwind effects from the flaring of fracturing fluids as used within the hydrocarbon exploration industry to enhance the recovery of hydrocarbons (gas and liquid hydrocarbons) from wells.

1.1.2 Structure of this report

Section 1 of this report is a background section. It sets out general information about the Council's obligations under the Resource Management Act to acquire the knowledge it needs to undertake good and well-informed resource management in the region. It includes a description of the general nature of air emissions potentially arising from hydraulic fracturing activities and operations as conducted in Taranaki

Section 2 references the manner in which monitoring and investigations were conducted in the study.

Section 3 discusses the results and their interpretation, while Section 4 summarises their significance for the environment.

Section 5 presents recommendations relating to the assessment of future applications for the flaring of fracturing fluids, including the nature of possible consent conditions, and to any review of the Council's *Regional Air Quality Plan for Taranaki* (2011).

A glossary of common abbreviations and scientific terms, and a bibliography, are presented at the end of the report.

The appendices cover the rules contained within the 'Regional Air Quality Plan for Taranaki' (Taranaki Regional Council, July 2011) that govern flaring at wellsites (Rules 9 and 10), a typical air discharge consent for emissions from a wellsite, and the full reports on emissions monitoring (Appendix III) and ambient monitoring (Appendix IV)

1.1.3 The Resource Management Act (1991) and discharges to air from flaring at exploration sites

The Resource Management Act primarily addresses environmental `effects' which are defined as positive or adverse, temporary or permanent, past, present or future, or cumulative. Effects may arise in relation to:

(a) the neighbourhood or the wider community around a discharger, and may include cultural and socio-economic effects;
(b) physical effects on the locality, including landscape, amenity and visual effects;
(c) ecosystems, including effects on plants, animals, or habitats, whether aquatic or terrestrial;
(d) natural and physical resources having special significance (eg, recreational, cultural, or aesthetic);
(e) risks to the neighbourhood or environment.

Section 15 (1) (c) stipulates that
No person may discharge any..contaminant from any industrial or trade premises into air... unless the discharge is expressly allowed by a national environmental standard or other regulations, a rule in a regional plan as well as a rule in a proposed regional plan for the same region (if there is one), or a resource consent.

The Council has sought to provide clarity and certainty around the potential effects arising from exploration activities within Taranaki, by providing rules within the Regional Air Quality Plan (RAQP) making flaring at exploration and production sites a controlled or discretionary activity, and by setting out within the RAQP and consents conditions regulating such activities. Rules 9 and 10, the rules within the RAQP providing for flaring at exploration wells or at production wells undergoing redevelopment or enhancement, are attached to this report in Appendix 1.

The *Resource Management (National Environmental Standards for Air Quality) Regulations 2004* ('the AQNES') stipulate in Regulation 10, that
(1) the burning of oil in the open air is prohibited
(2) Subclause (1) does not apply if...
    (d) the burning is-
        (i) done by means of a flare; and
        (ii) for the purpose of undertaking health and safety procedures in the petroleum exploration and production industry or the petrochemical industry; and
        (iii) expressly allowed by a resource consent.

Thus, flaring is allowed under the AQNES if provided for by way of a resource consent.

1.1.4 Evaluation of environmental performance

In accordance with section 35(1) of the Resource Management Act 1991, the Council undertakes or commissions investigations and research studies, for the purpose of gathering information that enables it to carry out effectively its functions under the RMA. This in turn enables the Council to have a clear understanding of the possible local and regional effects of the exercise of consents; to implement effective and appropriate setting of conditions and monitoring for consents and rules in regional plans; and to maintain an overview of performance of resource users against regional plans and consents. These investigations and studies also enable the Council to continuously assess its own performance in resource management as well as that of resource users, particularly consent holders, and ultimately, through the refinement of methods, and considered responsible resource utilisation, to move closer to achieving sustainable development of the region's resources.

1.2 Process description

Drilling
During the drilling of a hydrocarbon exploration well, drilling muds are used to cool and lubricate the drill shaft and to pressurise the well against the risk of a blowout of pressurised gas or condensate. Once the target depth has been reached, casing is run and cemented. After this the well is secure and the drilling rig is moved off location.

Completion-conventional wells
The completion or well testing phase of a conventional well begins with 'cleaning up' the well (removal of drill cuttings and debris and/or drilling fluids from the well, and then perforating the casing in the deepest potentially productive zone and allowing it to flow. A properly designed separator and clean burning flare system are utilised to eliminate the return of solids and liquids to the flare system, thus avoiding the potential for black smoke from the flare because of incomplete combustion of heavier hydrocarbons, during clean up and/or testing operations.

After separation of liquid hydrocarbons, gas, and water has been achieved, initial zone testing will normally continue over a period of up to 15 days but usually for a shorter period. Liquid hydrocarbons produced during initial testing are usually directed to storage tanks prior to removal from the wellsite by road tanker or, once sufficient pressure is established, can be directed to a production pipeline where one exists.

Completion-hydraulic fracturing
In cases where the flow of hydrocarbons is low following initial flow testing, hydraulic fracturing may be undertaken to create fractures within the hydrocarbon bearing formation and allow easier flow. Fracturing involves the injection of a fracturing fluid, typically water and a proppant such as sand or inert ceramic beads (the proppant remains within the fracture once created so as to prevent it re-closing under pressure), together with a small percentage of other chemicals intended to enhance and maintain the fracture (eg gels to carry the proppant, 'wetting' agents to enhance flow, additives to avoid clay swelling, and biocides to prevent bacterial growths). Once the fracturing has occurred (this usually takes several hours), a proportion of the fracturing fluid is recovered.

Inital recovery will be entirely fracture fluid and some solids (proppant) which can be sent directly to tanks for recycling or disposal offsite. As well cleanup continues hydrocarbon gas entrained in the fluid will start to flow back. The flowback stream, still mainly water will be directed to the separator / flare system. The liquids will be separated out, to the greatest extent practicable, and again sent to tanks. The hydrocarbon gas will be sent to the flare system. This process continues until the well is essentially cleaned up of flowback fluids and is flowing primarily gas. The well is now ready to be production tested as described above.

Certain contingency scenarios exist in which solids may begin to plug up the surface equipment, risking overpressure, and the well would need to be directed to a lined flare pit without passing through the separator. In the event of such an emergency potentially dangerous levels of hydrocarbons could build up in the pit, and so the gas would be proactively ignited to prevent an explosion. After the emergency situation has been addressed the well will no longer be flowed to the pit, the flare

will extinguish, and the fluid in the pit will be sucked out and disposed of appropriately.

The intention of lighting the gas in the emergency flare pit is to burn off hydrocarbon gas to prevent explosive risk. The intention is not to burn off the liquids, although some will evaporate in the process. The emergency system can be configured in a number of ways, some of which include burner heads on the end of the pipe entering the pit, and potential injection of pilot gas to ensure the flare stays lit.

Therefore there can at times be an operational requirement to discharge the return flow to a flare pit, without complete recovery and containment within tanks.

Operators therefore seek consent to allow the material entrained in the well stream, namely the gas and other fluids (fracture fluid, sand, and potentially reservoir fluid), to be ignited in the flare pit if needs be.

1.3 Resource consents

1.3.1 Air discharge permit

Section 15(1)(c) of the Resource Management Act stipulates that no person may discharge any contaminant from any industrial or trade premises into air, unless the activity is expressly allowed for by a resource consent, a rule in a regional plan, or by national regulations.

A typical consent providing for discharges to air from an exploration wellsite is attached in Appendix II. It should be noted that one of the purposes of this present study is to provide clarity and certainty around the degree of environmental protection and good exploration practice that is appropriate. The attached consent represents an interim regime while the results of the study are evaluated for future reference.

1.4 Scope of investigations

1.4.1 Introduction

Section 35 of the Resource Management Act sets out obligations upon the Taranaki Regional Council to gather information, monitor, and conduct research on the exercise of resource consents, and the effects arising, within the Taranaki region and report upon these.

The Taranaki Regional Council may therefore make and record measurements of physical and chemical parameters, take samples for analysis, carry out surveys and inspections, conduct investigations, and seek information from consent holders.

1.4.2 Previous studies

The Taranaki Regional Council has previously undertake field studies at two wells (one gas, the other producing oil and heavier condensates), together with dispersion modelling at a third site.[2]

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[2] Reported in *Fletcher Challenge Energy Taranaki Ltd Tariki-2C wellsite Monitoring programme report 1997-98*, Taranaki Regional Council November 1998;

The previous studies are referenced in the bibliography of this report. In brief, measurements of carbon monoxide, carbon dioxide, and methane found concentrations to be safe at all points downwind, including within 50 metres of the flarepit. Measurements of suspended particulate matter found concentrations typical of background levels, and measurements of PM10 found compliance with national standards even in close proximity to the flare. Beyond 120 metres from the flarepit, concentrations of PAHs approached background levels, as did levels of dioxins beyond 250 metres from the flare.

In summary, the studies established that under combustion conditions of high-volume flaring of gases with some light entrained liquids etc, atmospheric concentrations of all contaminants had reduced by a distance of 250 metres downwind to become essentially typical of or less than elsewhere in the Taranaki environment e.g. in urban areas. These levels are far below any concentrations at which there is any basis for concern over potential health effects.

However, the introduction of additional substances into a fracturing fluid mixture meant that the universal relevance of these studies to the present situations could not be taken for granted. While internal and external review of the likely effects of combusting fracturing fluids concluded that they should be no different from those of the earlier studies, it was considered, given the value of demonstrable certainty for public reassurance, that a further study of emission and ambient air quality characterisation should be undertaken.

1.4.3 Study of the flaring of fracturing fluids

The investigation programme for the flaring of fracturing fluids at the wellsite consisted of three primary components. From the flare pit, samples were collected from both the zone of the flame, to identify products of combustion including products of incomplete combustion, and from the surface of the liquids and fluids within the flare pit, to capture volatilisation emissions. Simultaneously, sampling was being conducted at various locations downwind and in the vicinity, in order to directly measure ambient concentrations of some of the contaminants of interest.

The data gathered will also be used to undertake modelling of dispersion under various meteorological conditions, to estimate the variability in ambient concentrations and hence the degree of potential environmental effects.

1.4.3.1 Chemical sampling-emissions

The scope of the monitoring was as follows:-

Combustion zone sampling
Total suspended particulate matter
Dioxins and furans
Polyaromatic hydrocarbons
Aldehydes (formaldehyde, acetaldehyde, propionaldehyde)
Volatile organic compounds (including benzene, toluene, xylene and ethyl benzene)

Fletcher Challenge Energy Taranaki Ltd Mangahewa 2 gas well Monitoring programme report 1997-98, Taranaki Regional Council August 1998, and
Report to the Taranaki Regional Council Atmospheric dispersion modelling of emissions from the Pohokura A well, ESR Environmental August 1998

Methanol
Combustion process parameters- oxygen, carbon dioxide, carbon monoxide, nitrogen oxides, and sulphur dioxide

Evaporation zone sampling
Polyaromatic hydrocarbons
Aldehydes
Volatile organic compounds
Methanol

1.4.3.2 Chemical sampling- downwind (ambient)

The scope of the downwind sampling was as follows:-

Particulate matter (PM1.0. 2.5, and 10) by meter (instantaneous readings)
Carbon monoxide and carbon dioxide by meter (instantaneous readings)
Formaldehyde (absorption tubes)
Volatile organic compounds (including benzene, toluene, xylene and ethyl benzene) (absorption tubes)

1.4.4 Contaminants of interest

1.4.4.1 Composition of fracturing fluid

A sample of the HF fluid was collected for analysis for components of particular interest. Samples were taken from the tank feed to the flare pit at the start and again at the end of testing on the first day of the survey, and composited for analysis. The HF fluid is water-based.

The analytical results are shown in Table 1, together with analytical data from other HF samples taken at different wellsites. The results show that except for total petroleum hydrocarbons (TPH), the HF fluid used in the study had constituents that tended to be higher in concentrations than found in other HF fluids used in the region.

Table 1   Key components of HF fluid

Component	Unit	Concentration	Other HF analyses
Methanol	g/m^3	10	11- 18
Benzene	g/m^3	8.9	0.020- 4.6
Toluene	g/m^3	22	0.037- 7.5
Ethyl benzene	g/m^3	3.3	0.016- 0.66
m- & p- xylene	g/m^3	24	0.12- 4.4
o-xylene	g/m^3	8.1	0.060- 1.68
Formaldehyde	g/m^3	1.05	<0.03[2]
C7-C9 [1]	g/m^3	460	9- 24
C10-C14 [1]	g/m^3	1,190	87- 4,700
C15-C36 [1]	g/m^3	1,490	132- 12,600
TPH (C7-C36) [1]	g/m^3	3,100	240- 17,200
Benzo-a-pyrene	g/m^3		<0.004

[1]Total petroleum hydrocarbons and fractions as indicated
[2] Gluteraldehyde

It is noted that while the data in Table 1 represents the HF fluid as discharged into the flare pit, the composition of the latter (and of the vaporised gases) would be changing during the evaporative process. Components of lower boiling temperature and higher vapour pressure would tend to be vaporised first, while components of higher boiling temperature and lower vapour pressure would tend therefore to become somewhat relatively more concentrated within both the liquid and ultimately within the vapour zone during the day.

1.4.4.2 Emitted components of interest[3]

Methanol[4]
Methanol (also known as methyl alcohol or wood alcohol) is not normally an air contaminant of interest, due to its low toxicity, but its common use within fracturing fluid mixtures meant its inclusion in the sampling programme.

Methanol is a substance in common use. It occurs naturally in wood, as a product of the decay of organic matter, and in volcanic gases. It is heavily used within industrial processes as a basis for the production of other substances, and as an ingredient in formulations such as paint strippers, aerosols, paints, car care products, and as a fuel additive. It degrades quickly within the environment. In the presence of other volatile organic substances in air, it can contribute to the formation of photochemical smog.

In very high doses (intentional consumption) methanol can be fatal, with other toxic effects at lesser levels of exposure. These effects are not likely at levels normally found in the environment. High workplace exposure has caused symptoms such as headaches, sleep disorders, and stomach upsets.

Benzene, toluene, ethyl benzene and xylenes (collectively BTEX)
Motor vehicles are the predominant sources of volatile organic compounds in urban areas. Benzene, toluene, and xylene, are all largely associated with petrol vehicle emissions, resulting from the benzene and aromatics contents of petrol. Evaporative emissions, as well as exhaust emissions, can be significant, especially for benzene. Of the volatile organic compounds, the most important in the New Zealand context is benzene. The benzene content of petrol is high, 1% by volume[5] (or about 1,000 times higher than the concentration in HF fluid). Tobacco smoke and household solvents and cleaning products are other sources of exposure. Benzene is a known human carcinogen and toxicological agent.

Toluene is extensively used in paints and adhesives and cosmetics. Primary exposure comes through petrol fumes and tobacco smoke. Vegetation is also a source. Toluene has toxicological effects upon the central nervous system. It is not considered carcinogenic.

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3 Summarised from *Air Quality Guidelines for Europe, European series 23*, World Health Organization 1987; or *Health effects due to motor vehicle air pollution in New Zealand: Report to the Ministry of Transport* GW Fisher et al January 2002, unless otherwise specified.

4 Based on *Chemicals in the environment: methanol EPA 749-F-94-013*, Office of Pollution Prevention and Toxics, United States Environmental Protection Agency 1994

5 Appendix 3, *Good practice guide for assessing discharges to air from Land Transport,* Ministry for the Environment June 2008,

BTEX components are present in crude oils and condensates. They are found in low concentrations in returned HF fluids. The potential exists for BTEX to be emitted by both combustion (flaring) and by vaporisation from HF storage.

Dioxins and furans[6]

Polychlorinated dibenzo-*p*-dioxins (PCDDs, or dioxins) and polychlorinated dibenzofurans (PCDFs, or furans) can be found throughout the world in air, soil, sediment and water. Once in the environment, they accumulate in the fatty tissues of animals such as birds, fish, shellfish, marine mammals and domestic animals, and in people. They break down very slowly and can remain in the environment and in people's bodies for a very long time.

Dioxins and furans have never been produced intentionally, other than for research, but are formed as unintentional by-products in various chemical production processes and in most thermal processes, including combustion. In particular, incomplete combustion (evidenced by smoke) is considered a significant source of dioxins and furans. This was the reason for including them in this study.

The major sources of dioxins and furans in New Zealand are residential rubbish fires (backyard incinerators), vegetation fires (forest, crop, scrub), and landfill fires, and then to a lesser extent, industrial and domestic wood-burning home heating and boilers, coal combustion, and structural fires.

Dioxins and furans can have up to eight chlorine atoms attached to their basic skeleton. Each individual compound resulting from this arrangement is referred to as a congener, and specific congeners are distinguished by the number and position of chlorine atoms around the core structure. In total there are 75 possible PCDD congeners and 135 possible PCDF congeners. Congeners containing one, two or three chlorine atoms are thought to be of no toxicological significance. However, the 17 congeners with chlorine atoms substituted in the 2,3,7,8 positions are thought to pose a risk to human and environmental health. Of these, the most toxic and widely studied congener is 2,3,7,8-TCDD. Further increasing substitution from four to eight chlorine atoms generally results in a marked decrease in potency.

In environmental media the dioxins and furans occur as complex mixtures of congeners, which results in complex, multivariate data sets. A system of toxic equivalents (TEQs) has been developed in response to this, so that the data from any mixture can be reduced to a single toxicity value. The toxic equivalents method is based on the available toxicological and *in vitro* biological data, and knowledge of structural similarities among the dioxins and furans. This information has been used to produce a set of weighting factors, each of which expresses the toxicity of each dioxin and furan congener in terms of an equivalent amount of 2,3,7,8-TCDD. Multiplication of the concentration of a dioxin or furan congener by the toxic equivalence factor (TEF) gives a corresponding 2,3,7,8-TCDD TEQ concentration. The toxicity of any mixture of dioxins and furans, expressed as 2,3,7,8-TCDD, is derived by summing the individual TEQ concentrations. This is reported as the 'total TEQ' for a mixture. A number of toxic equivalents schemes have been developed, one being the World Health organisation Toxic Equivalents Factor (WHO-TEF) scheme.

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[6] *New Zealand Inventory of Dioxin Emissions to Air, Land and Water, and Reservoir Sources :2011* Ministry for the Environment 2011

Animal studies show that some dioxins and dioxin-like compounds are extremely toxic. Although less is known about their impact on human health, it is widely assumed that dioxins have the potential to cause neurobehavioural, developmental, reproductive and immunotoxic effects at low doses. Significantly, 2,3,7,8-TCDD was evaluated by the International Agency for Research on Cancer in 1997 and was classified as a "known human carcinogen" (class I).

Particulate matter (PM1.0, PM2.5, and PM10)[7]
Particles in the air can exist across a range of different sizes and chemical compositions. It is recognised that the greatest health hazard from particles comes from the smallest ones, of less than 10 microns (10µm or 10 micrometres) across, because these are most easily inhaled into our lungs. These particles are referred to as PM10 (referring to their size) or as inhalable particulate (referring to their potential effect). In terms of comparative size, a human hair is approximately 50 microns across, while the finest beach sand is approximately 100 microns across.

The majority of the particle health effects studies both in New Zealand and overseas have been based on measurements of PM_{10}. The PM_{10} size fraction includes particles referred to as coarse and fine particles. These classifications were originally intended to separate particles based on the nature of their source, with coarse particles representing those formed through abrasive type mechanisms and fine particles those formed through combustion processes (such as flaring of gas) and chemical reactions. However, the terms are more commonly used now to represent particles in the size ranges less than 2.5 microns (fine) and between 2.5 and 10 microns (coarse).

Fine-mode particles are formed through processes of nucleation, and subsequent coagulation and condensation of other gases on the particle nuclei. Fine and ultrafine particulates can be derived from many sources, including motor vehicles (particularly diesels), solids and oil-burning processes, incineration, and photochemical processes, especially as products of incomplete combustion. Coarse particles arise from many natural sources such as pollens, spores, dusts formed by abrasion, and sea spray.

Emerging research is focusing more and more on the smaller fractions of the particles under PM_{10}- $PM_{2.5}$ (fine particles) or $PM_{1.0}$ (ultrafine particles)- as it is increasingly recognised that these smaller fractions have the greatest health effect.

The focus of much of the particle monitoring carried out in New Zealand has been the PM_{10} size fraction. More recently, some monitoring of particles less than 2.5 microns ($PM_{2.5}$) has been carried out in some locations.

It was because of their possible formation during any incomplete combustion of flared hydrocarbons, that they were included in this study.

From a health perspective, the size of the particles is important as it affects their ability to penetrate into the lungs and cause adverse health effects. The larger particles (e.g. those greater than 10 microns) tend to settle in the nose and mouth and are unlikely to pose a health risk. Finer particles can penetrate further into the lung and alveoli and therefore may be associated with more severe health impacts.

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[7] Taken from *Health Effects of PM10 in New Zealand*, Ministry for the Environment 2003

The mechanisms of formation (e.g. nucleation, coagulation and condensation for the finer fraction or the more abrasive formation systems of the coarser fraction) may also have implications for respiratory related health effects.

The significance of PM for human health is shown by studies indicating, for example, a 4.3-10% increase in mortality per 10 μgm^{-3} increase in annual average PM_{10} and a mortality increase of 6.9- 8.3% per 10 μgm^{-3} increase for $PM_{2.5}$. WHO (2002) recommends the use of a factor of a 10% increase in mortality per 10 μgm^{-3} increase in PM_{10} for determining/modelling the impacts of long-term exposure.

Polyaromatic hydrocarbons (PAHs)
PAHs are a large group of compounds comprising two or more benzene rings within their core structure. They vary considerably in environmental significance. The most significant is benzo[a]pyrene, or BaP. Mixtures of PAHs are often expressed in terms of BaP equivalents, derived using a similar procedure to that for dioxin toxic equivalents.

They arise from the incomplete combustion of fuels, including diesel and oils in vehicles and from open coal fires, and tend to be associated with smoke. Cigarette smoke is a major route of exposure. The potential therefore exists for PAHs to be formed during poorly controlled flaring of liquid hydrocarbons.

BaP is considered a human carcinogen.

Aldehydes (formaldehyde, acetaldehyde, propionaldehyde)
Formaldehyde occurs naturally. Anthropogenic emissions result from incomplete combustion of hydrocarbons and other organic materials. The major emissions sources arise from the use of formaldehyde, especially in the indoor environment-resins and glues used in textiles and furniture manufactured from chipboards and plywood, and using glues as jointing and bonding materials. Other sources are cooking, cigarette smoking, vehicle exhausts, the incineration of wastes, and the burning of fuels (natural gas, fuel oil and coal).

Motor vehicles are major sources of formaldehyde and acetaldehyde. These carbonyls are very reactive and are important in atmospheric reactions, being products of most photochemical reactions (which are secondary reactions following the combustion of hydrocarbons).

Formaldehyde is known to cause irritation of the eyes, skin and mucous membranes of the upper respiratory tract. In areas of heavy traffic density it has been found to be a major promoter in the formation of photochemical smog. It has been found to be carcinogenic to some species. Evidence about its carcinogenicity in humans is not considered conclusive either way[8].

Formaldehyde and glutaldehyde are present within additives used to formulate some HF fluid blends. The potential exists for formaldehyde and other aldehydes to be emitted both from combustion (flaring) and from HF holding tanks.

Combustion process parameters (oxygen, carbon dioxide, carbon monoxide, nitrogen oxides, and sulphur dioxide)

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[8] *Air Quality Guidelines for Europe*, World Health Organization European Series 23, 1987

Carbon monoxide is formed due to incomplete combustion of fuels in sources such as vehicles, incinerators, and open fires. WHO advises that it is the most common air pollutant by volume. Most cities have peak carbon monoxide concentrations that reflect traffic flows and densities. Carbon monoxide is not present in HF fluids, but may be generated during poorly controlled flaring of liquid or gaseous hydrocarbons.

Its effects (primarily cardio-vascular) tend to be short-term.

Nitrogen dioxide is a product of efficient (high temperature) combustion in terms of human activities. Natural generation (lightning, volcanic action, bacterial action) far out-weighs the total human generation, although background concentrations are well distributed and therefore very small. Gas-fired appliances (heating, especially unflued gas or kerosene heaters, and cooking) and tobacco smoke are significant indoor sources. Well-controlled flaring of liquid or gaseous hydrocarbons will generate nitrogen dioxide.

Its effects (pulmonary function) tend to be short-term. Some, but not all, long-term studies of exposure have found evidence of a link to a slightly elevated rate of respiratory illnesses in younger children.

Sulphur dioxide is generated when compounds containing sulphur are oxidized (combusted). This applies especially to coal, and various industrial processes. Natural gas and condensate in New Zealand fields are extremely low in sulphur when compared with overseas sources[9]. However, the sulphur content in diesel sold domestically has been relatively high by international standards (although reducing).

Sulphur dioxide is not expected to be significant in terms of a potential pollutant arising from the flaring of gas. HF fluids may contain some additives with sulphur content, but the overall concentrations would be extremely low.

Sulphur dioxide has both acute (aggravation of asthma, bronchial and pulmonary irritation), and long-term effects (bronchitis).

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[9] Pg 25, *New Zealand Sulphur Dioxide Industrial Emissions Inventory*, 2007 Environet

2. Sampling

2.1 Methodology

Emissions sampling took place on 7-8 February. On the first day, the sampling train was configured to capture emissions from the zone of the flame, while on the second day a collection hood was used to recover emissions (vaporisation) from the surface of the fluids within the pit.

Ambient sampling was conducted on 7 February in conjunction with the flare emissions sampling.

Full details of the emissions sampling methodologies for each parameter, notes on the conduct of the sampling including difficulties, quality assurance/quality control measures, and the results of analysis of the combustion zone and the evaporation zone for each parameter, are attached in Appendix III.

Full details of the ambient sampling methodologies for each parameter, notes on the conduct of the sampling, and the results of analysis of the ambient parameters, are presented in Appendix IV.

Table 2 presents the sampling and analytical methods used for emissions monitoring, which are further detailed below.

Table 2   Emissions sampling methods

Contaminant	STNZ Standard Test Methods	IANZ Accreditation for STNZ Test Method?
Gas Molecular Mass Determination (Products of Combustion)	Method 3 "Gas Analysis for Carbon Dioxide, Oxygen, Excess Air and Dry Molecular Weight"	Yes
Determination of Moisture Content	Method 4 "Determination of Moisture Content in Stack Gases"	Yes
Determination of Total Particulate Matter	Method 5 "Determination of Particulate Emissions From Stationary Sources'	Yes
Determination of Sulphuric acid mist (including SO_3) and sulphur dioxide (SO_2)	Method 8 "Determination of sulphuric acid mist (including SO_3) and sulphur dioxide (SO_2) from stationary sources"	Yes
Determination of Aldehyde Compounds	Method 0011 "Sampling for Selective Aldehyde and Ketone Emissions From Stationary Sources"	Yes
Determination of Volatile Organic Compounds	Method 18 'Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"	Yes
Determination of PCDD/PCDF Compounds	Method 23 "Determination of PCDD/PCDF from Municipal Waste Combustors"	Yes
Determination of PAH Compounds	Method 23 "Determination of PCDD/PCDF from Municipal Waste Combustors"	Yes
Determination of Methanol	USEPA Method 308 "Procedure for the Determination of Methanol Emissions from Stationary Sources"	No
Determination of Nitrogen Oxides and Sulphur Dioxide	Testo 350XL Combustion Gas Analyser	No
Determination of Combustion Gases (oxygen, carbon dioxide, carbon monoxide)	Testo 350XL Combustion Gas Analyser	No

Gaseous products of combustion

Gaseous products of combustion were measured using a Testo 350 XL combustion gas analyser. It was configured to monitor oxygen (O_2 %), carbon monoxide (CO ppmv), nitric oxide (NO ppmv), nitrogen dioxide (NO_2 ppmv) and sulphur dioxide (SO2) using electro-chemical cells. The carbon dioxide (CO_2 %) concentration was measured using an infrared cell. Further details are provided in Section 2.4.3 of Appendix III.

Particulate matter

Particulate matter was withdrawn directly from the sampling manifold at a rate of approximately 20 L/min and collected on a glass fibre filter maintained at a temperature of 120 °C ± 14 °C. The particulate mass was determined gravimetrically, after the removal of un-combined water. This approach conforms to USEPA Method 5 "Determination of Particulate Matter from Stationary Sources". Particulate analysis was performed by STNZ.

Oxides of sulphur discharges

Oxides of sulphur discharges were collected in accordance with USEPA Method 8 "*Determination of Sulphuric Acid Mist and Sulphur Dioxide Emissions From Stationary Sources*". A sample of gas was withdrawn from the sampling manifold via an 8 mm Teflon sampling line at a rate of approximately 20 L/min. Sulphur trioxide and sulphuric acid were collected in a solution of 80 % isopropanol and on a glass fibre filter, with sulphur dioxide being collected in a solution of 3 % hydrogen peroxide. On completion of the sampling, the isopropanol was purged with ambient air to ensure any SO2 captured in the isopropanol was transferred to the hydrogen peroxide. Each solution was analysed using a barium-thorin titration method by STNZ staff in their Wellington laboratory.

Aldehyde discharges

Aldehyde discharges were collected in accordance with USEPA Method 0011 "*Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources*". Gaseous and particulate pollutants were withdrawn from the sampling manifold via a heated Teflon sampling line at a rate of approximately 20 L/min and collected in aqueous solution acidified 2,4-dinitrophylhydrazine (DNPH) (aldehydes react with DNPH to form stable compounds). These compounds were then extracted, solvent-exchanged, concentrated and then analysed by high performance liquid chromatography (HPLC). Analysis was performed by AsureQuality Ltd, Auckland who is an IANZ accredited laboratory for this analysis. AsureQuality Ltd, Auckland also provided the DNPH solution.

Volatile organic compounds

Volatile organic compounds were measured in accordance with USEPA Method 18 – "*Measurement of Gaseous Organic Compounds Emissions by Gas Chromatography*". Gases were extracted from the sampling manifold and subsequently passed through a charcoal sorbent tube to collect VOC's at a rate of approximately 1.0 L/min. This sampling was conducted in duplicate using spiked and un-spiked sorbent tubes. The samples were then forwarded to Hill Laboratories Ltd, Hamilton where carbon disulphide was used to desorb the collected VOC's. The extract was subsequently analysed by gas chromatography- mass spectrometry (GC-MS). Hill Laboratories Ltd is IANZ accredited for VOC analysis.

The total organic carbon content was then determined by summation of the individual compounds detected and expressed as carbon.

Dioxin/Furans (PCDD/PCDF) & Poly Aromatic Hydrocarbons (PAHs)

Dioxins/Furans and PAHs were collected in accordance with USEPA Method 23 – "*Determination of PCDD/PCDF from Municipal Waste Combustors*". This sampling method also allows for the determination of PAH compounds. A gas sample was extracted from the sampling manifold via a heated Teflon sampling line at a rate of approximately 20 L/min. The gas stream was then passed through a glass fibre filter maintained at 120 °C ± 14 °C connected to a combined condenser and XAD-2 resin trap. The condenser was continuously cooled (to below 20 °C) by circulating chilled water via a submersible pump.

Upon completion of the sampling, the system was leak checked, the trap and filter were recovered and sealed. The condensate was collected and the whole sampling system rinsed with acetone and dichloromethane. All three components (filter, resin trap, and condensate/rinse were combined at the laboratory to form a single sample for analysis.

The PCDD/PCDF and PAHs were extracted from the sample, separated by high resolution gas chromatography (HRGC), and measured by high resolution mass spectrometry (HRMS). Sampling reagents and the analysis were provided by AsureQuality Ltd, Gracefield, who are IANZ accredited for this work.

Methanol

Methanol emissions were measured in accordance with USEPA Method 308 – "*Procedure for the Determination of Methanol Emissions from Stationary Sources*". A gas sample was extracted from the sampling manifold via a ¼ inch Teflon sampling line at a rate of approximately 1 L/min. Methanol was collected in distilled water contained in a midget impinger and adsorbed onto a silica gel sorbent tube. The liquid portion of the sample was recovered using distilled water. The liquid sample and sorbent tube were forwarded to Hill Laboratories Ltd, Hamilton for analysis. The methanol in the water fraction was separated from other organic compounds using gas chromatography (GC) with subsequent measurement by a flame ionization detector (FID). The fraction adsorbed on the silica gel tube was extracted with an aqueous solution of n-propanol with analysis by GC/FID.

Photograph 1 Flare, HF fluid, and sampling probe
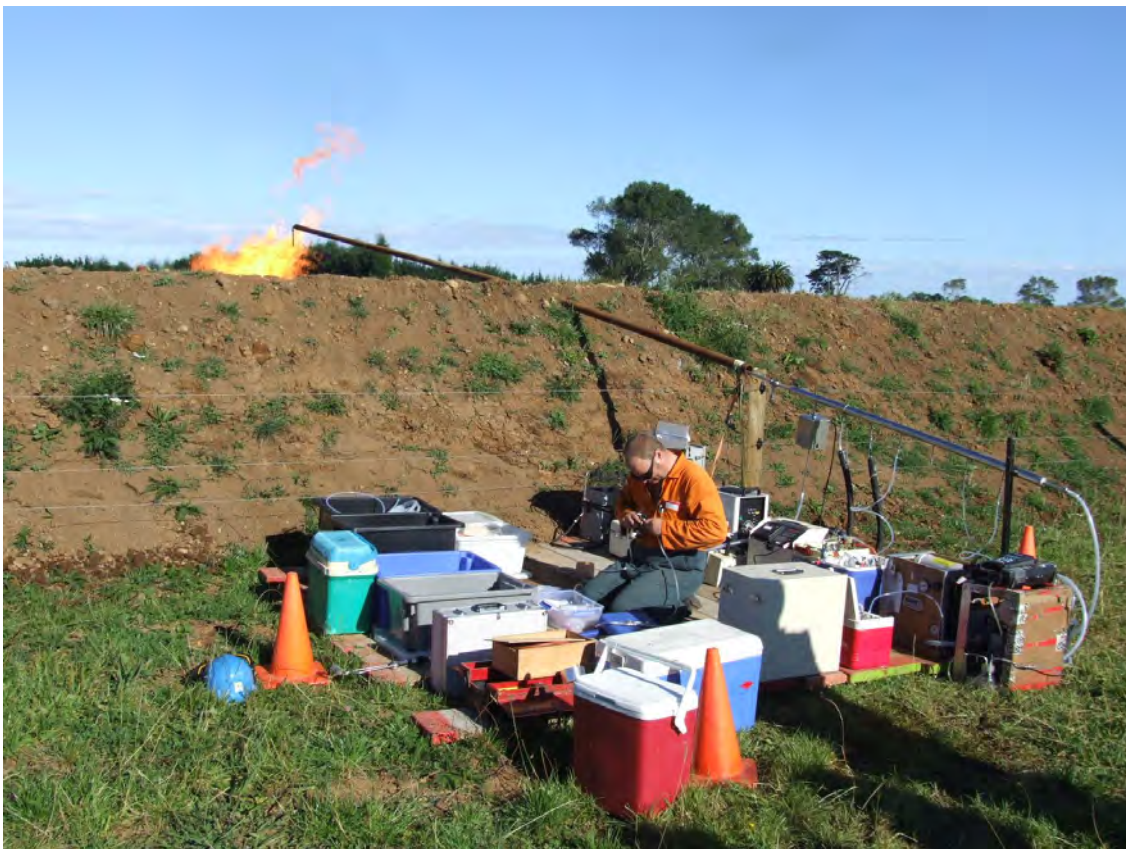
Photograph 2 Combustion zone testing set-up

3. Results

3.1 Flare zone emissions

Three sampling runs were conducted between the hours of 1300 and 1700 on 7 February, to collect triplicate samples of emissions from the flare. It was noted during sampling that a wind shift later in the day reduced capture by flare emissions, due to the particular location of the sampling probe. This shows in the changes in concentrations recorded against each sampling run.

The average concentration of carbon dioxide in each run was respectively, 0.3%, 0.2%, and <0.1%, confirming the visual observation of limited capture of flare emissions during the final run.

Results (concentrations) are given in Tables 3-6. Full details of each sampling run and of mass recoveries are presented in Appendix III. Concentration results are adjusted to 0° C, one atmosphere pressure and dry gas basis.

Particulate, sulphur oxides, aldehydes, VOCs, and methanol
As shown in Table 6, captured concentration of particulate was much lower on the third sampling run, indicating that the flare emissions were the source of the particulate that was being captured on the first two runs.

No sulphur oxides were detected on any run (either SO_2 or as acid mist- $SO_2 + SO_3$), confirming the note that natural gas and condensate from the field is very low in sulphur.

The analyses of aldehyde species shows that aldehydes were present almost exclusively solely as formaldehyde, either released from the fracturing fluid or formed *de novo* within the flame.

Of 44 VOC species tested for, only BTEX were found at concentrations above respective limits of detection (ie less than 0.02 ppm, for each species).

Methanol was detected only during the second run.

Comparing relative concentrations within the fracturing fluid (Table 1) with concentrations found within the combustion zone (Table 6), the ratio of formaldehyde to methanol appears similar in both. However, while benzene, toluene, and m-,p-xylene are of similar concentrations to methanol within the fracturing fluid, they are present within the combustion zone only at concentrations orders of magnitude lower than that of methanol (on the one occasion that methanol was detected).

Dioxins and furans
A single sample was collected for analysis for dioxins/furans, to ensure meaningfully low limits of detection were achieved. Results are shown in Table 3.

As discussed in Section 1.4.4.2,, the concentration of dioxins/furans is expressed in terms of toxic equivalence factors. Lower, medium and upper-bound results are presented. Lower-bound results treat the contribution of non-detected congeners as

zero. For medium bound results non-detected congeners contribute an amount equivalent to half the respective limit of detection and in upper bound results the contribution is equivalent to the full limit of detection.

Because of the extreme sensitivity of analytical methods to detect dioxins and furans, it is customary to run field blanks to detect interference from sources other than the intended sample. Concentration results are adjusted to 0°C, one atmosphere pressure and dry gas basis. As indicated by the lower bound results, no dioxin toxic equivalents were detected in the sample. No dioxin toxic equivalents were detected in the field blank sample also. Therefore the results reflect solely the use of lower, medium, and upper-bound factors, rather than any detection of dioxins/furans. No blank correction has been applied to the sample results.

Table 3   Combustion zone: dioxin concentration

Calculation of result	Sample concentration ng/m^3
WHO-TEQ Lower bound	0.0000
WHO-TEQ Medium bound	0.0017
WHO-TEQ Upper bound	0.0035

There is no meaningful difference between the sample results and the laboratory blank results.

A presumptive low level of dioxins within the combustion zone is consistent with visual observations of the lack of visible smoke, and the lack of particulate matter within the flare (Table 6) noted during the study.

Polyaromatic hydrocarbons (PAHs)
A single sample was collected for analysis for PAH analysis. The full suite of PAHs analysed for is given in Appendix C ('raw analytical results') of the report in Appendix III of this report. In summary, napthalene and acenaphthylene were the individual species present in the highest concentrations, followed by phenanthrene, fluoranthene, and pyrene. The PAH of primary environmental and health concern, benzo(a)pyrene, had virtually the lowest concentration of any PAH- around 1% of the concentration of the PAHs present at highest concentration- in the combustion zone sample.

All PAH species analysed were detected within the combustion zone at concentrations above the LOD, and so there is no difference between lower bound, medium bound, and upper bound results for the combustion zone sample. **There has been no adjustment of combustion zone results for the blank measurements.** Concentration results are adjusted to 0° C, one atmosphere pressure and dry gas basis.

Table 4   Combustion zone: PAH concentration

Calculation of result	Sample concentration ng/m^3
USEPA Lower bound	208
USEPA Medium bound	208
USEPA Upper bound	208

These results indicate that a low level of PAH emissions was occurring from the combustion zone.

Products of combustion
Results of sampling for products of combustion during each of the 3 sampling runs are shown in Table 5. As with the particulate results, concentrations are much lower on Run 3, indicating less capture of flare emissions and more ambient air. Concentration results are adjusted to 0° C, one atmosphere pressure and dry gas basis.

Table 5   Combustion zone: products of combustion

Run		Oxygen %	Carbon dioxide %	Carbon monoxide ppmv	Nitrous oxide ppmv	Nitrogen dioxide ppmv	Total nitrogen oxides ppmv	Sulphur dioxide ppmv
Run 1	Average	20.8	0.3	11	2	0.5	2	1
	Minimum	19.7	0.2	<1	<1	<0.1	<1	<1
	Maximum	20.9	1.0	99	6	1.1	6	5
Run 2	Average	20.8	0.2	8	1	0.2	1	1
	Minimum	20.4	0.2	<1	<1	<0.1	<1	<1
	Maximum	20.8	0.5	89	5	0.5	6	5
Run 3	Average	21.0	<0.1	1	<1	0.1	<1	<1
	Minimum	21.0	<0.1	1	<1	0.0	<1	1
	Maximum	21.0	<0.1	<1	<1	0.2	<1	1

Note: ppmv parts per million per volume, dry gas basis

Table 6 Combustion zone: summary of results for particulate, sulphur oxides, aldehydes, BTEX, and methanol

Sampling run	Particulate mg/m³	SOx (acid mist) mg/m³	Total aldehydes[1] mg/m³	Form-A[2] mg/m³	Acet-A[3] mg/m³	Propion-A[4] mg/m³	Acrolein mg/m³	Total VOC[5] ppm	Benzene ppm	Toluene ppm	Ethyl benzene ppm	m-,p- Xylene ppm	o-Xylene ppm	Methanol mg/m³
1	1.6	<0.03	0.25	0.23	<0.01	<0.01	<0.01	0.171	0.100	0.052	0.003	0.009	0.005	<1.22
2	0.8	<0.03	0.18	0.16	<0.01	<0.01	<0.01	0.020	0.005	0.012	<LOD	0.003	0.001	2.66
3	<0.3	<0.04	0.05	0.04	<0.01	<0.01	<0.01	<LOD[6]	<LOD	<LOD	<LOD	<LOD	<LOD	<1.49

[1] expressed as formaldehyde
[2] formaldehyde
[3] acetaldehyde
[4] propionaldehyde
[5] volatile organic compounds. 44 compounds were analysed for. Only BTEX were detected.
[6] limit of detection

3.2 Evaporation zone emissions

Three sampling runs were conducted between the hours of 1000 and 1400 on 8 February, to collect triplicate samples of evaporative emissions from the fluid surface. The sampling hood was located as close to the surface of the fluid as practicable, and downwind of and lower than the flare to isolate emissions capture from flare discharges.

Results (concentrations) are given in Tables 7 and 8. Full details of each sampling run and of mass recoveries are presented in Appendix III. Concentration results are adjusted to 0° C, one atmosphere pressure and dry gas basis.

Aldehydes, VOCs, and methanol
The results for measurements of aldehydes, VOCs, and methanol are presented in Table 7.

Of the aldehyde species investigated only formaldehyde was present at concentrations above limits of detection with a range of 0.03 – 0.04 mg/m^3. To put the formaldehyde concentrations found within the evaporative emissions in context, it can be noted the Ministry for the Environment has a guideline (not an AQNES) for formaldehyde in ambient air, of 100 µg/m^3 (0.10 mg/m^3) measured over any 30 minute period. The concentrations of formaldehyde measured within the evaporative zone were less than half of the guideline value for ambient air.

Of 44 VOC species tested for, only the BTEX species were found at concentrations above limits of detection (ie less than 0.02 ppm, for each species). In Run 1, only toluene could be detected(at 0.003 ppm); in Run 2, no VOCs at all (including any of the BTEX) were detected; and in Run 3 benzene was measured at 0.012 ppm, toluene at 0.03 ppm, no ethyl benzene, m- and p- xylene at 0.004 ppm, and o-xylene at 0.003 ppm. Thus, while Run 3 had the highest concentrations of BTEX, all results are extremely low- barely at the limit of detection.

To put the BTEX concentrations found within the evaporative emissions in context, it can be noted the Ministry for the Environment has guideline values (not an AQNES) for benzene, toluene and xylene of, respectively, 22, 500, and 1,000 µg/m^3 (0.002 ppm, 0.13 ppm, and 0.23 ppm, respectively) measured over any 1 hour period. Thus, the concentrations of BTEX found within the evaporative zone were either close to although above (for benzene) or were well under (for toluene and xylene) of the respectively guideline values for ambient air.

BTEX concentrations in both the combustion zone and the evaporation zone were so low as to make any comparison between the two zones, meaningless.

Methanol was detected in only one of the evaporation zone samples at a concentration above the limit of detection. The Ministry for the Environment does not have an ambient guideline or standard for methanol. The short-term workplace exposure limit[10] for methanol is 328 mg/m^3. It is commonplace to apply various factors to a workplace limit, in order to derive a population limit.

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[10] *Workplace exposure standards and biological exposure indices*, Department of Labour 2010

These factors range from 1/30th to 1/100th, depending upon the degree of safety margin desired. Even applying the most conservative of these factors, it is apparent that the concentrations of methanol found within the evaporative zone were at or well within guideline values that might be derived for methanol in ambient air.

Polyaromatic hydrocarbons (PAHs)
A single sample was collected for analysis for PAH analysis. The full suite of PAHs analysed for is given in Appendix C ('raw analytical results') of the report contained in Appendix III of this report. In summary, napthalene and 2-methyl naphthalene were the individual species present in the highest concentrations, followed by (at much lower concentrations) phenanthrene, fluorene, and fluoranthene. The PAH of primary environmental and health concern, benzo(a)pyrene, could not be detected in the evaporation zone sample.

The result is presented in Table 7. **There has been no adjustment of evaporation zone results for the blank measurements.** Concentration results are adjusted to 0° C, one atmosphere pressure and dry gas basis. Because a number of PAHs could not be detected, the calculation of toxicity equivalents varies depending on the way in which non-detection results are taken into account.

Table 7   Evaporation zone: PAH concentration

Calculation of result	Sample concentration ng/m^3
USEPA Lower bound	3.98
USEPA Medium bound	4.98
USEPA Upper bound	5.98

These results indicate that only an extremely low level of PAH emissions could be detected within the evaporation zone.

To put these results into perspective, reference can be made to studies elsewhere in New Zealand[11]. Sampling in Auckland found that 12 out of 148 samples recorded BaP concentrations above the detection limit of around 0.8 ng/m^3. The maximum BaP concentration measured was 4.4 ng/m^3. The analytical results were specific for BaP. In Christchurch, winter evening monitoring found a maximum concentration of 79 ng/m^3. This result appears to be for the average over a 4 hour period. An annual average exposure calculated from all the data in the survey estimated an annual exposure concentration in central Christchurch of 4 ng/m^3.

These results indicate that the emissions within the evaporation zone contained less BaP than is found in ambient central city locations in New Zealand, and that emissions within the combustion zone would require only minimal dilution to be reduced to concentrations similar to or below ambient BaP concentrations in urban areas in New Zealand.

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[11] *Monitoring of CO, NO2, SO2, ozone, benzene and benzo(a)pyrene in New Zealand* Ministry for the Environment 2003

Table 8   Evaporative zone: summary of results for aldehydes, BTEX, and methanol

Sampling run	Total aldehydes[1] mg/m^3	Form-A[2] mg/m^3	Acet-A[3] mg/m^3	Propion-A[4] mg/m^3	Acrolein mg/m^3	Total VOC[5] ppm	Benzene ppm	Toluene ppm	Ethyl benzene ppm	m-,p- Xylene ppm	o-Xylene ppm	Methanol mg/m^3
1	0.05	0.04	<0.01	<0.01	<0.01	0.003	<LOD	0.003	<LOD	<LOD	<LOD	<2.32
2	0.04	0.03	<0.01	<0.01	<0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	5.25
3	0.05	0.04	<0.01	<0.01	<0.01	0.047	0.012	0.03	<LOD	0.004	0.003	<2.01

[1] expressed as formaldehyde
[2] formaldehyde
[3] acetaldehyde
[4] propionaldehyde
[5] volatile organic compounds. 44 compounds were analysed for. Only BTEX were detected.
[6] limit of detection (0.02 ppm)

3.3   Results of receiving environment monitoring

3.3.1 Introduction

The methodology and results of the ambient monitoring undertaken are reported in full in Appendix IV.

The sampling was undertaken on 7 February 2012. The prevailing wind direction at the time was from the south to south east.

Particulate monitoring was undertaken using a portable dust monitoring device capable of measuring ambient concentrations of several particle sizes simultaneously. The instrument was deployed at six sites sequentially, at varying distances downwind from the flare pit and in a pattern that included points directly downwind and also at a slight angle from the direct downwind direction. Sites are shown in Figure 1 below.

Ambient carbon monoxide and carbon dioxide were sampled by portable meter at the same sites as for the particulate monitoring.
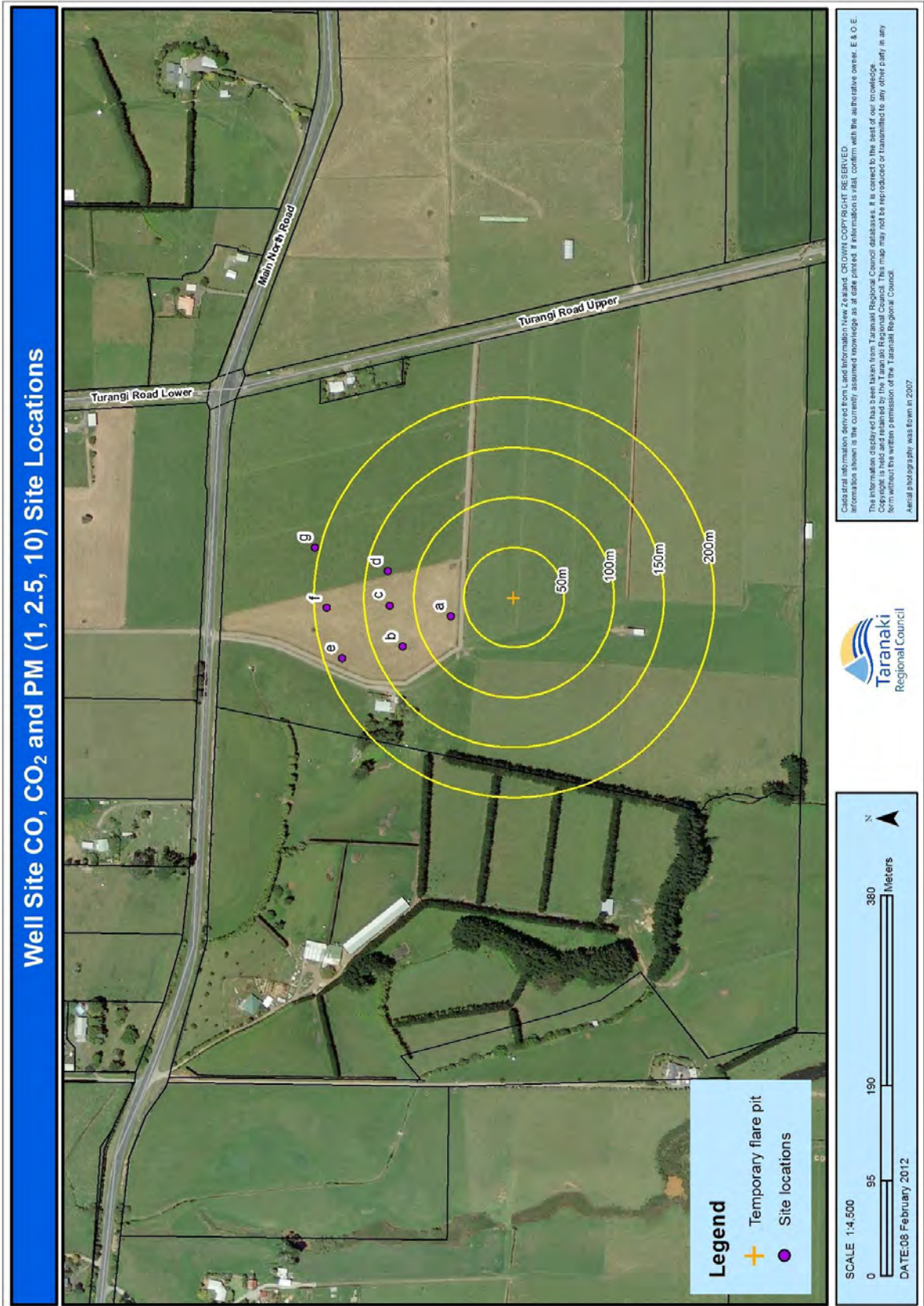
Figure 1   CO, CO2, and PM10, PM 2.5, and PM 1.0 sampling locations

Formaldehyde was measured by deploying passive samplers left in situ at 5 sites for a duration of approximately 8 hours, during the flaring. The pattern of deployment is shown in Figure 2. Because there is detectable formaldehyde across the countryside (eg from vehicle exhausts), both upwind and downwind sites were used, as was one on the nearby state highway and one at a nearby residence.

Volatile organic compounds (VOCs) were also measured by means of passive absorption samplers, at the same sites used for formaldehyde monitoring.

Figure 2   Formaldehyde and volatile organic compound (BTEX) sampling locations

3.3.2 Particulate matter

Results

The duration of sampling for PM varied at each site, from 11 minutes up to 70 minutes. The concentration of ambient particulate was measured at 1 minute intervals. The results are shown in Table 9. The lowest, highest, and average of the data readings is given for each site.

Conversion of exposure results to a standardised exposure time period

The results in Table 9 represent the average ambient concentration when taken over the entire period of exposure. It is recognised that in fact the ambient concentration will have been varying on a short-term basis throughout this period. In particular, it is noted that the period of measurement was shorter than the comparable guideline, and 24-hour average if measurements had continued for that long during the study would generally be lower than that shown in Table 9 for the actual period of exposure (up to 570 minutes).

The issue is therefore that of estimating an indicative equivalent exposure concentration over alternative time periods of interest (eg as referenced in guidelines or other criteria). For comparison with the Ministry for the Environment guideline for PM10 and WHO guideline for PM2.5, from the average concentration measured, it is desirable to calculate an indicative theoretical 24 hour concentration that represents the concentration that may have been found should the emissions and monitoring have continued for a full 24 hours. There are mathematical equations used by air quality scientists to predict equivalent concentrations over varying time periods. These are somewhat empirical, in that they take little account of local topography, micro-climates, variations in activity processes, diurnal variation, etc. Nevertheless, they are conservative (they tend to over-estimate) and have some recognition of validity as a screening tool. One formula in general use[12] is of the form:

$$C(t_2) = C(t_1) \times \left(\frac{t_1}{t_2}\right)^P$$

where $C(t)$ = the average concentration during the time interval t, and p = a factor lying between 0.17 and 0.20. When converting from shorter time periods to longer time periods, using $p = 0.17$ gives the most conservative estimate (i.e. the highest calculated result for time period $t2$ given a measured concentration for time period $t1$).

Using the 'worst case' factor of $p = 0.17$, the monitoring data reported herein have also been converted to equivalent 'maximum' 24 hour exposure levels (Table 9).

The same calculations have been used further within this report to provide a basis for comparison of measured data with other time-specific criteria (formaldehyde, BTEX). Where actual data has been related to criteria that apply over shorter periods, the 'p' factor in the above equation has been taken as $p = 0.20$ to give a conservative estimate for comparison.

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[12] *Workbook of atmospheric dispersion estimates*, United States Environmental Protection Agency, 1970, author B Turner

Table 9   Sites, sampling periods, and results for ambient carbon monoxide, carbon dioxide, and particulate measurements

Site ID		GPS	Start Stop (NZST)	Time sample. (min)	CO (ppm)	CO2 (ppm)	PM1 µg/m³	PM2.5 µg/m³	PM10 µg/m³	PM2.5 µg/m³ 24 hour equiv	PM10 µg/m³ 24 hour equiv
a	Min Max Mean	1713592 5682646	11:50 13:00	70	Nil	296 371 312	No Data	No Data	No Data	No Data	No Data
b	Min Max Mean	1713562 5682694	13:10 13:57	47	Nil	333 382 349	0.00 1.00 0.04	0.00 2.00 0.84	2.00 12.00 2.72	0.47	1.52
c	Min Max Mean	1713603 5682707	14:02 14:29	27	Nil	347 370 358	0.00 13.34 0.55	0.00 14.30 0.80	2.00 19.00 5.05	0.41	2.57
d	Min Max Mean	1713637 5682709	14:47 14:58	11	Nil	342 354 348	0.00 2.00 0.87	2.00 4.00 2.26	5.00 38.00 12.71	0.99	5.55
e	Min Max Mean	1713550 5682755	15:07 15:39	32	Nil	336 350 344	0.00 10.41 0.22	1.00 12.26 1.35	4.00 14.41 5.87	0.71	3.07
f	Min Max Mean	1713601 5682770	15:44 16:03	19	Nil	339 361 344	0.00 0.00 0.00	1.00 2.00 1.17	3.09 11.00 5.97	0.56	2.86
g	Min Max Mean	1713661 5682782	16:09 16:45	36	Nil	336 361 346	0.00 0.00 0.00	1.00 2.00 1.02	6.00 18.00 9.7	0.54	5.18

The PM2.5 data showed no correlation of distance downwind of the flare with concentration (the closest sampling point was about 120 metres downwind), indicating that at the most by 120 metres from the flare and site there was no effect upon ambient PM2.5. The two sites closest to the flare and wellsite had the lowest PM2.5 results.

The highest single result was 14.3 µg/m³, and the highest mean result at any site was 2.26 µg/m³.

Considering the estimated equivalent concentrations for PM 2.5, the two lowest concentrations were again found at two of the sites closest to the flare. The highest and second-highest concentrations lay in different directions. There was no clear pattern of distribution according to distance from the flare site (see graph in report in Appendix 4).

The PM10 data showed no correlation of distance downwind of the flare with concentration (the closest sampling point was about 120 metres downwind), indicating

that at the most by 120 metres from the flare and wellsite there was no effect upon ambient PM10. The two sites closest to the flare and wellsite had the lowest PM10 results, while the second highest result was recorded at the site that was furthest away.

The highest single result was 38.0 µg/m³, and the highest mean result at any site was 12.7 µg/m³.

Considering the estimated equivalent concentrations for PM10, there was again no clear pattern of distribution according to distance from the flare. While the two highest concentrations both lay on the same axis from the flarepit, it should be noted that this axis was slightly east of north, which is off the prevailing wind direction during the trial, and while the two results were very similar, one was approximately 50% further away. If the flare was a significant source, a decrease in PM10 with increasing distance from the source would be expected. Along other axes, downwind concentrations increased with distance from the flare.

Perspective
The Ministry for the Environment's *Resource Management (National Environmental Standards Relating to Certain Air Pollutants, Dioxin, and Other Toxics) Regulations 2004* (the AQNES) set a national standard for PM10 particulate (particulate matter that is less than 10 microns- µm- in aerodynamic diameter) of an average concentration of no more than 50 microgrammes per cubic metre (50 µg/m³) when measured over a 24 hour period. The AQNES allows one exceedance of this standard at any measuring site per year.

Internationally there is a move away from a standard based on PM10, to standards based on PM2.5 or even PM1.0. This is because it is recognised that the primary cause of adverse health effects associated with particulate is the concentration of the finer particle sizes. The Ministry for the Environment does not yet have proposed criteria for these sizes of particles.

The World Health Organisation has promulgated a guideline for PM2.5, of 25 µg/m³ when measured over a 24 hour period[13].

The mean results of **PM2.5** measurements at the seven sites lie in the range 0.80-2.26 µg/m³. When converted to an equivalent 24 hour exposure concentration, the average results lie in the range 0.47-0.99 µg/m³.

For comparison, it can be noted the Council has previously undertaken PM2.5 monitoring surveys at a number of locations around Taranaki[14]. These results were as follows: New Plymouth (city) 4.3 µg/m³ (range 0.5-12.4 µg/m³); Stratford (urban) 2.9 µg/m³ (range 1.0-6.4 µg/m³); coastal rural 3.4 µg/m³ (0.5-8.8 µg/m³), and pristine (National Park) 0.8 µg/m³ (0.1-1.6 µg/m³).

Thus, the PM2.5 concentrations in the vicinity of a flare are similar to or slightly below those found elsewhere in the region, and are far below international guidelines.

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[13] *WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide, Global update 2005 Summary of risk assessment,* World Health Organisation 2005
[14] Reported in *Taranaki-our place, our future report on the state of the environment of the Taranaki region 2003* Taranaki Regional Council February 2003

The mean results of **PM10** measurements at the seven sites lay in the range 2.72-12.71µg/m³. When converted to an equivalent 24 hour exposure concentration, the average results lie in the range 1.52-5.55 µg/m³.

For comparison, it can be noted the Council has previously undertaken PM10 monitoring surveys at a number of locations around Taranaki[15]. These results were as follows: New Plymouth (city) 9.6 µg/m³ (range 0.7-26 µg/m³); Stratford (urban) 9.2 µg/m³ (range 1.7-24.1 µg/m³); coastal rural 7.2 µg/m³ (1.0-16.5 µg/m³), and pristine (National Park) 1.6 µg/m³ (0.2-3.6 µg/m³).

Thus, the PM10 concentrations in the vicinity of a flare are somewhat below those found elsewhere in the region, and are far below (less than 10% of) the AQNES (50 µg/m³).

The NES sets an acceptable daily (24 hour) level for PM10, and requires continuous monitoring throughout the year in areas of New Zealand where PM10 is likely to breach the standard. The MfE has reported[16] that forty airsheds were monitored in New Zealand in 2007. Of these, 17 airsheds (42 per cent) complied with the PM10 standard. 13 of the 40 monitored airsheds (32 per cent) had a peak daily level below the standard of 50 µg/m³. Each airshed is allowed to exceed the standard once a year, which is why four airsheds with peak daily levels greater than 50 µg/m³ still complied with the standard. In 2007, on average, South Island peak daily levels were higher than North Island levels. Eight of the 10 airsheds that recorded the highest daily PM10 levels in New Zealand are located in the South Island. Levels ranged from 104 to 168 µg/ m³, with the three highest levels recorded in airsheds in Otago, Auckland and Reefton.

The MfE gives a rating to air quality based on the level of any parameter when compared with a guideline or standard[17]. On this basis, air downwind of the flare even at the closest site sampled (approximately 120 metres downwind) would be rated as 'excellent' in respect of PM10.

3.3.3 Carbon monoxide and carbon dioxide

Results

The duration of sampling for carbon monoxide and carbon dioxide varied at each site as for the sampling for PM. The results are show in Table 9. The lowest, highest, and average of the data readings is given for each site.

No carbon monoxide was detected at any time.

The manufacturer of the meter specifies that the limit of detection for the meter is 3 ppm CO (see appendix of report contained in Appendix IV for further details). Under ambient conditions, 1 ppm CO is equivalent to 1.14 mg/m³. This suggests the concentration of any carbon monoxide was less than 3 ppm (3.5 mg/m³).

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[15] Reported in *Taranaki-our place, our future report on the state of the environment of the Taranaki region 2003* Taranaki Regional Council February 2003

[16] *Environmental Report Card INFO 363* Ministry for the Environment February 2009

[17] *Ambient Air Quality Guidelines*, Ministry for Environment May 2002

The average carbon dioxide concentration found downwind of the flare was 343 ppm, and the highest average at any site was 358 ppm. The highest single reading was 382 ppm. Readings at all sites were consistent (means lay within 1.5% of each other), except at site A, which was both the site closest to the flare (70 metres away) and also the site with the lowest readings (by about 12%). Given that emissions from a combustion source raise carbon dioxide levels, this indicates that the flare was having no measured effect on concentrations in the vicinity.
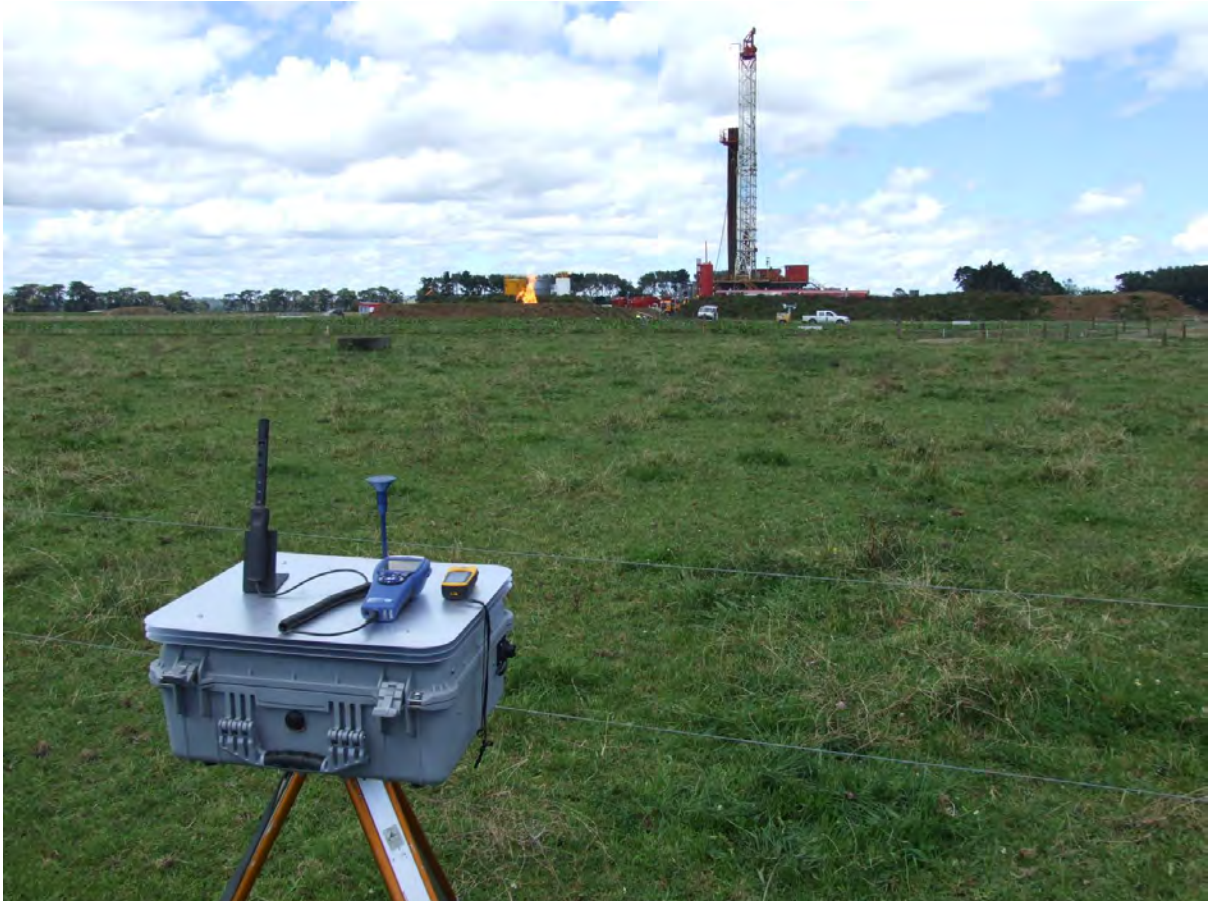
Photograph 3 Carbon dioxide, carbon monoxide, and particulate sampling meters

Perspective
The AQNES sets a national standard for carbon monoxide of 10 milligrammes per cubic metre (10 mg/m³) when measured at any one measuring site over any 8 hour period. The AQNES allows one exceedance of this standard at any measuring site per year.

The level of carbon monoxide downwind of the flare remained below the limit of detection (3.5 mg/m³) at all times.

For comparison, it can be noted the Council has previously undertaken carbon monoxide monitoring surveys at a number of locations around Taranaki[18]. These results were as follows: New Plymouth (city) 1.6 mg/m³ (range 0.1-9.2 mg/m³); and Stratford (urban) <1.0 mg/m³ (range <1.0-3 mg/m³).

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[18] Reported in *Taranaki-our place, our future report on the state of the environment of the Taranaki region 2003* Taranaki Regional Council February 2003

Thus, the carbon monoxide concentrations in the vicinity of a flare are similar to those found elsewhere in the region, and are at the least less than one-third of the AQNES (10 mg/m^3).

The Ministry for the Environment has collated the results of monitoring around New Zealand for carbon monoxide[19]. In larger cities, a number of results have been found to be more than 66% of the AQNES, and even to exceed it. In provincial centres, results were more typically similar to or slightly above those in Taranaki. On this basis, the air quality downwind of the flare was similar to or better than that experienced by a sizeable part of the population of New Zealand.

The MfE gives a rating to air quality based on the level of any parameter when compared with a guideline or standard. On this basis, air downwind of the flare even at the closest site sampled (approximately 120 metres downwind) would be rated as 'good' (10%-33% of AQNES) or better, in respect of carbon monoxide.

From these results it is concluded that the flare and wellsite emissions had at most a negligible effect upon carbon monoxide concentrations downwind of the site (if at all).

There is no AQNES for carbon dioxide. The short-term exposure limit (15 minutes) in workplaces for New Zealand is 30,000 ppm (54,000 mg/m^3), and the 8-hour exposure limit in workplaces is 5,000 ppm (9,000 mg/m^3).[20]

The average background atmospheric concentration is 392 ppm (706 mg/m^3). Carbon dioxide concentrations vary naturally, especially in a rural environment, because of the effects of pasture-driven photosynthesis (reducing carbon dioxide levels) during the day and pasture respiration (increasing carbon dioxide levels) during the night.

Readings from downwind were all below the average background (pristine) concentrations. This is consistent with the site being set within a rural environment.

From these results it is concluded that the flare and wellsite emissions had at most a negligible effect upon carbon dioxide concentrations beyond 70 metres from the site (if at all).

3.3.4 Formaldehyde

Results

The duration of sampling for formaldehyde varied between 484 minutes (8 hours 4 minutes) and 570 minutes (9 hours 30 minutes). The absorption tube method provides an average concentration over the period of exposure. It does not provide a range (eg maximum or minimum concentrations). Locations of deployment are shown in Figure 2. The results are given in Table 10. Figure 3 presents the results correlated against distance from the flare.

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[19] *Monitoring of CO, NO2, SO2, ozone, benzene and benzo(a)pyrene in New Zealand*, Ministry for the Environment October 2003

[20] *Workplace Exposure Standards and Biological Exposure Indices*, Department of Labour September 2010

Table 10   Results of ambient formaldehyde monitoring

Site	Where	Time: start stop	Time total Min.	Formaldehyde Lab. Results ($\mu g/m^3$)	Formaldehyde 30 min Calc. ($\mu g/m^3$)
1	70 m. downwind	08:18 16:37	499	11.4	20.0
2	Cnr. SH3 and side road, 300m away, approx cross-wind	07:40 17:10	570	3.1	5.59
3	House 400 m. NW (veering west of downwind)	07:55 17:15	560	3.2	5.75
4	90m. directly upwind	08:06 17:00	534	6.7	11.9
5	140 m. downwind	08:38 16:42	484	2.9	5.06
MfE guidelines 2002 (30 min average)					100

Results ranged from 5.06 to 20.0 $\mu g/m^3$ (when adjusted to 30-minute equivalent exposures). The mean of all 5 results was 9.6 $\mu g/m^3$.

The Ministry for the Environment has a guideline (not an AQNES) for formaldehyde, of an average concentration of 100 $\mu g/m^3$ measured over any 30 minute period. Whenever exposure is measured over a time interval other than that referenced in a guideline or standard, it is possible to calculate a theoretical highest likely exposure for the time interval desired. This calculation is described more fully in Section 3.3.2, and has been applied to the measured formaldehyde concentrations to more closely evaluate the degree of comformity to the guideline value. These calculated results are also shown in Table 10. It can be noted that when converting from a longer period to a shorter period, the modelled concentration will be increased.

Perspective
Formaldehyde is present at low concentrations (g/m^3 range) within hydraulic fracturing fluids used within the exploration industry.

The MfE guideline for formaldehyde sets a criterion of 100 microgrammes per cubic metre (100 $\mu g/m^3$) when measured at any one measuring site over any 30 minute period. It should be noted that the air inside buildings can be much higher than this, (because of the multiple sources of formaldehyde in textiles, furniture, furnishings, consumer products, and cigarette smoking) and a primary driver of the ambient air guideline is to ensure fresh air is available to dilute and flush indoor air, which typically contains formaldehyde at concentrations well above the MfE guideline (e.g. up to 5,000 $\mu g/m^3$, but more usually up to 200 $\mu g/m^3$).

The highest average ambient concentration of formaldehyde measured in this study was 11.4 $\mu g/m^3$, or 11 % of the MfE guideline for formaldehyde.

When converted to a theoretical equivalent maximum 30 minute exposure concentration, this result gives rise to a concentration of 20.0 $\mu g/m^3$. This is 20% of the MfE ambient guideline.

As noted above, the mean of all 5 results (adjusted to theoretical equivalent maximum 30 minute exposure concentrations) was 9.96 µg/m^3.
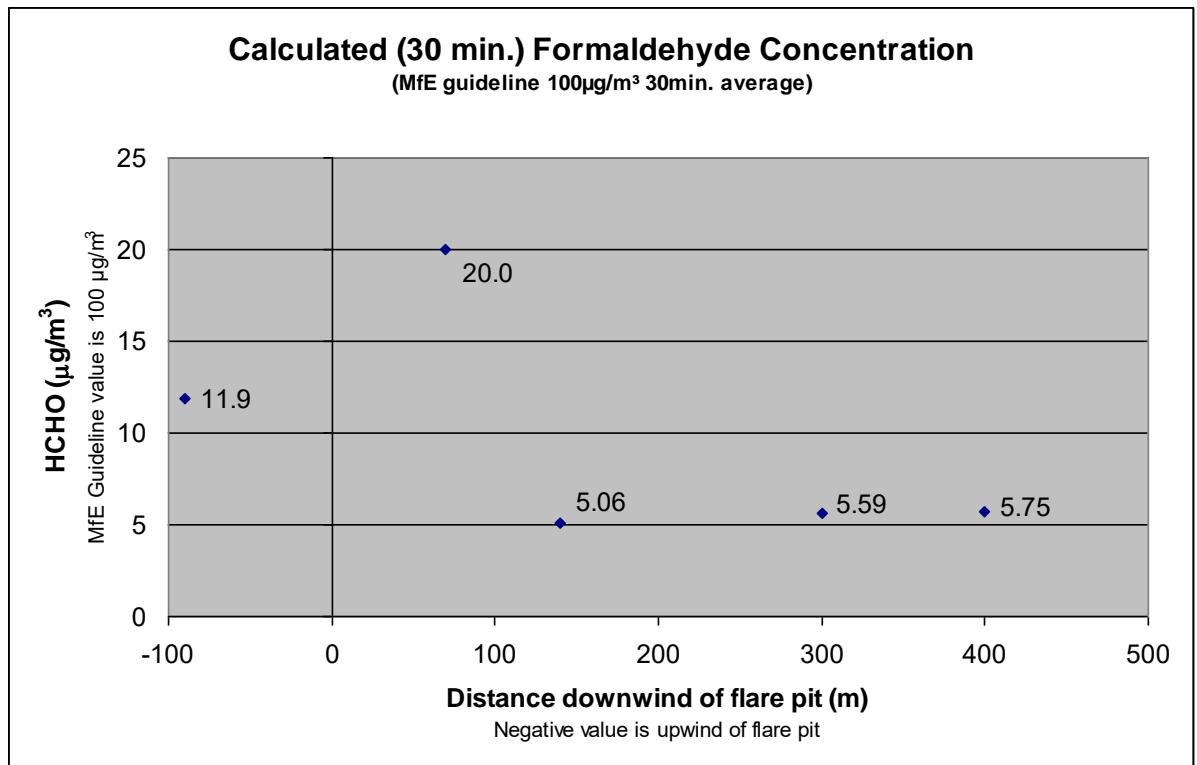

Figure 3   Formaldehyde concentrations in relation to the distance from the flare pit

Figure 3 shows the formaldehyde results (calculated to equivalent 30 minute concentrations) against distance from the flare. Theses results show that within a distance of less than 100 metres from the flare, formaldehyde levels had reduced to a steady (background) level. Road traffic was probably the source of a slight elevation upwind of the site.

For comparison, it can be noted the Council has previously undertaken formaldehyde monitoring surveys at a number of locations around Taranaki[21]. These results were as follows: New Plymouth (city) – two surveys, giving 3.8 and 6.0 µg/m^3 (range 1.3-7.2 µg/m^3); Stratford (urban) 2.9 µg/m^3 (range 1.0-4.5 µg/m^3), and Bell Block (industrial) 50-90 µg/m^3. Thus, the formaldehyde concentrations in the vicinity of a flare, including those sites closest to the flare, are similar to those found elsewhere in the region, but are still well below (less than 20% of) the AQNES (100 µg/m^3).

The MfE gives a rating to air quality based on the level of any parameter when compared with a guideline or standard. On this basis, air at monitoring sites downwind of the flare beyond the closest location would be rated as 'excellent' in respect of the formaldehyde concentrations, and even at the site 70 metres downwind would be rated as 'good (ie equivalent to the range 10%-33% of AQNES).

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[21] Reported in *Taranaki-our place, our future report on the state of the environment of the Taranaki region 2003* Taranaki Regional Council February 2003

3.3.5 Volatile organic compounds

Results

Volatile organic compounds (VOCs) include species such as benzene, ethyl benzene, toluene, and the various isomers (variant structural forms) of xylene. The duration of sampling for VOCs varied between 484 minutes (8 hours 4 minutes) and 570 minutes (9 hours 30 minutes). The absorption tube method provides an average concentration over the period of exposure. It does not provide a range (eg maximum or minimum concentrations). Locations of deployment are shown in Figure 2. The results are given in Table 11. Figures 4-6 presents the results correlated against distance from the flare.

The laboratory analysis of the passive absorption tubes includes a step of measuring the quantity of BTEX compounds collected on the samplers, and converting this to an equivalent ambient concentration. When analysis of the field blank shows the presence of BTEX compounds, it is appropriate to consider subtracting this blank result from the quantities detected on the remaining samples, before calculating causal ambient concentrations. Unadjusted results give the maximum concentration that could have been present; results adjusted for blank corrections will give a result closer to the more likely 'actual' result. In Table 11 below, the adjusted results are shown alongside the uncorrected results. A conservative approach will be to consider the 'actual' concentration lies between the two figures. (Text added in January 2019)

The Ministry for the Environment has a guideline (not an AQNES) for benzene, of an average annual concentration of 3.6 µg/m^3. [22]

Whenever exposure is measured over a time interval other than that referenced in a guideline or standard, it is possible to calculate a theoretical highest likely exposure for the time interval desired. This calculation is described more fully in Appendix IV of this report, and has been applied to the measured benzene, toluene, ethyl benzene and xylene concentrations to more closely evaluate the degree of comformity to the respective guideline values. These calculated results are also shown in Table 11. It can be noted that when converting from a longer period to a shorter period, the modelled concentration will be increased.

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[22] *Ambient Air Quality Guidelines*, Ministry for the Environment May 2002

Table 11   Results of ambient BTEX monitoring around well site: actual, calculated 1-hour equivalent, and calculated 1-hour equivalent with blank correction applied

Site	Where	Time: start stop	Time total Min.	Benzene			Toluene			Ethyl Benzene			o,m,p – Xylene Total		
				Lab. Results	1 hr. Calc[1].	1 hr. Calc[2].	Lab. Results	1 hr. Calc[1].	1 hr. Calc[2].	Lab. Results	1 hr. Calc[1].	1 hr. Calc[2].	Lab. Results	1 hr. Calc[1].	1 hr. Calc[2].
1	70 m. downwind	08:18 16:37	499	12.2	18.6	11.1-18.6	32.5	49.7	41.1-49.7	3.06	4.7	1.0-4.7	16.6	25.4	14.7-25.4
2	Cnr. SH3 and side road, approx 300m crosswind	07:40 17:10	570	<4.08	<6.4	<6.4	8.4	13.2	5.0-13.2	<2.01	3.1	<3.7	<6.00	9.4	<10.7
3	House 400 m. NW	07:55 17:15	560	<4.15	<6.5	<6.5	4.5	7.03	<8.1	<2.04	3.1	<3.7	<6.02	9.4	<10.7
4	90m. upwind	08:06 17:00	534	<4.36	<6.75	<6.8	11.9	18.4	10.2-18.4	<2.14	3.3	<3.7	<6.32	9.8	<10.7
5	140 m. downwind	08:38 16:42	484	8.43	12.8	5.3-12.8	12.5	19.0	10.8-19.0	<2.37	3.6	<3.7	<7.04	10.7	<10.7
Blank				<4.8	<7.5	-	<5.3	<8.2		<2.4	<3.7		<7.0	<10.7	
MfE recommended guidelines (2000), one -hour average.				-	22		-	500		-	None		-	1000	

* All results in µg/m³

Calc[1] 1-hour average ambient concentration, no blank correction
Calc[2] 1-hour average ambient concentration adjusted for blank recovery (*This data added in January 2019*)

Perspective

The MfE guideline for **benzene** sets a criterion of 22 microgrammes per cubic metre
(22 µg/m³) when measured at any one measuring site for 60 minutes.

The highest average ambient concentration of benzene actually measured was 12.2
µg/m³, or 55 % of the MfE guideline for formaldehyde, and is the average ambient
concentration when taken over the entire period of exposure. This was at the site
closest to the flare (approximately 70 metres downwind).

When converted to a theoretical equivalent maximum 60 minute exposure
concentration, this result gives rise to a concentration of 18.6 µg/m³. This is 85% of
the MfE ambient guideline.

Figure 4 shows the benzene results (calculated to equivalent 60 minute
concentrations) against distance from the flare. These results show that within a
distance of 300 metres from the flare, benzene levels had reduced to a steady
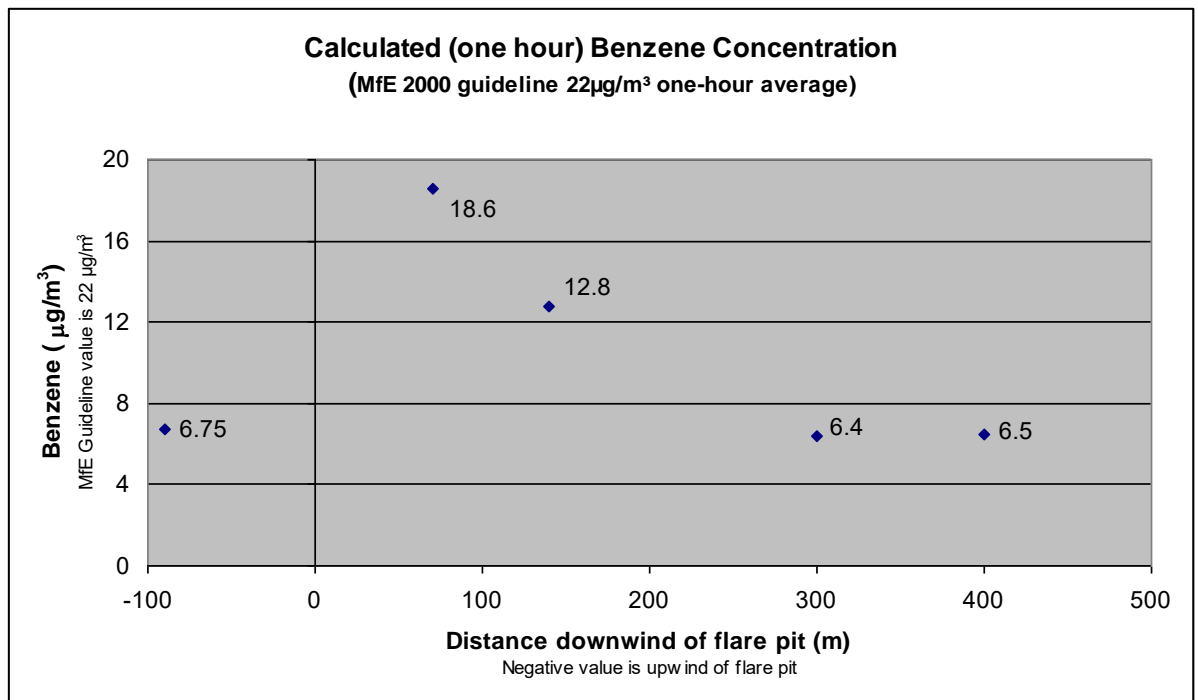(background) level.

Figure 4   Benzene concentrations in relation to the distance from the flare pit (nb numerical data not
corrected for detection of benzene in blank. See Table 11)

All results, including those closest to the flare, were below the MfE guideline
criterion, and at 140 metres downwind were half or less of the MfE guideline value.
The MfE gives a rating to air quality based on the level of any parameter when
compared with a guideline or standard. On this basis, air at monitoring sites
downwind of the flare beyond 140 metres downwind would be rated as 'good' in
respect of benzene concentrations.

The Ministry for the Environment has collated the results of monitoring around New Zealand for benzene[23]. This collation showed that central sites in larger cities exceeded the then-current annual benzene guideline of 10 µg/m^3. Such sites would have one-hour averages well in excess of the corresponding MfE guideline.

The draft MfE guidelines for **toluene and xylene**[24] set criteria of 500 and 1,000 microgrammes per cubic metre (500 and 1,000 µg/m^3), respectively, when measured at any one measuring site for 60 minutes.

The highest average ambient concentration of toluene actually measured was 32.5 µg/m^3, or 6 % of the MfE draft guideline for toluene. This was at the site closest to the flare (approximately 70 metres downwind).

When converted to a theoretical equivalent maximum 60 minute exposure concentration, this result gives rise to a concentration of 49.7 µg/m^3. This is 10% of the MfE ambient guideline.

The highest average ambient concentration of xylene actually measured was 16.6 µg/m^3, or 3 % of the MfE draft guideline for xylene. This was at the site closest to the flare (approximately 70 metres downwind).

When converted to a theoretical equivalent maximum 60 minute exposure concentration, this result gives rise to a concentration of 25.4 µg/m^3. This is 3% of the MfE ambient guideline.

Figures 5, 6, and 7 show the toluene, xylene and ethyl benzene results (calculated to equivalent 60 minute concentrations) against distance from the flare. Theses results show that within a distance of 140 metres from the flare, levels of xylene and ethyl benzene had reduced to a steady (background) level.

All results for toluene and xylene including those closest to the flare, were far below the MfE draft guideline criteria. The MfE gives a rating to air quality based on the level of any parameter when compared with a guideline or standard. On this basis, air at monitoring sites downwind of the flare would be rated as 'excellent' in respect of toluene and xylene concentrations.

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[23] *Monitoring of CO, NO2, SO2, ozone, benzene and benzo(a)pyrene in New Zealand,* Ministry for the Environment October 2003
[24] *Health Effects of Eleven Hazardous Air Contaminants and Recommended Evaluation Criteria*, Ministry for the Environment October 2000.
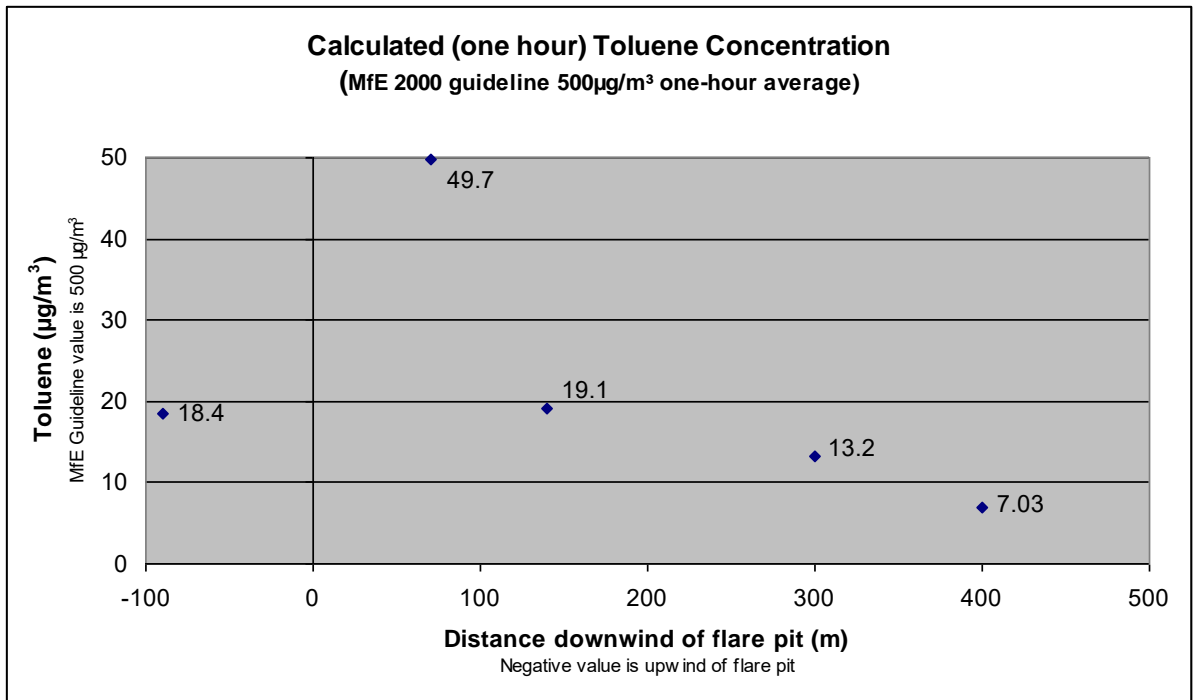
Figure 5   Toluene concentrations in relation to the distance from the flare pit (nb numerical data not corrected for detection of toluene in blank. See Table 11)
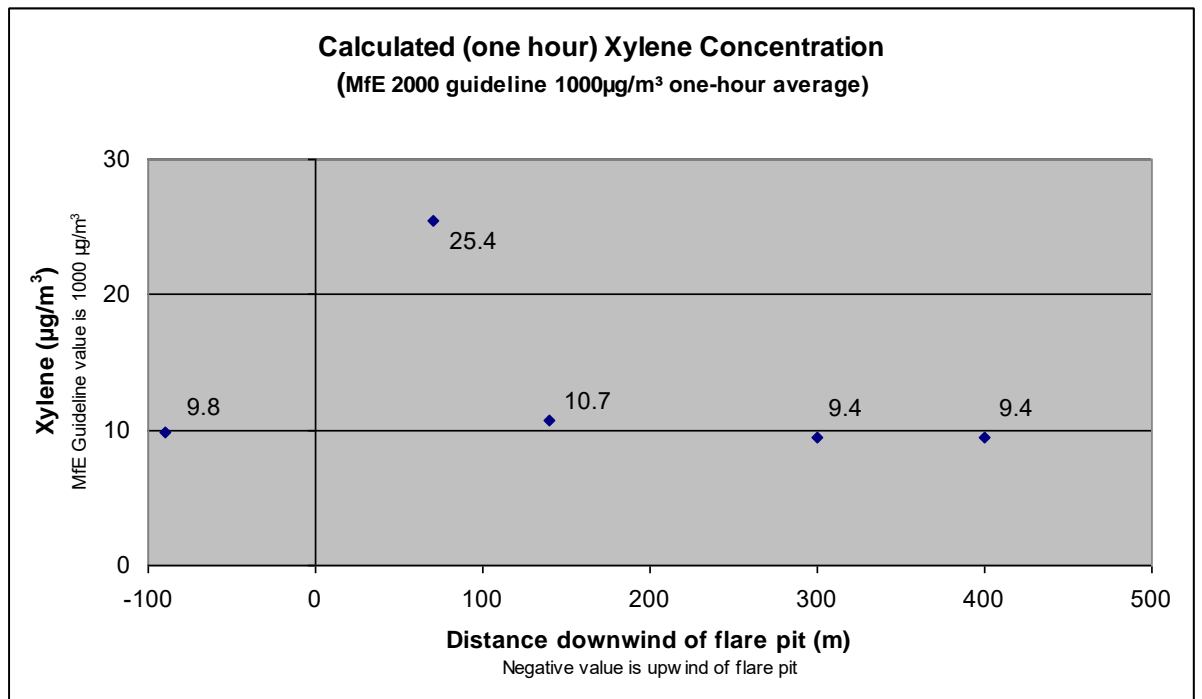

Figure 6   Xylene (total) concentrations in relation to the distance from the flare pit (nb numerical data not corrected for detection of xylene in blank. See Table 11)
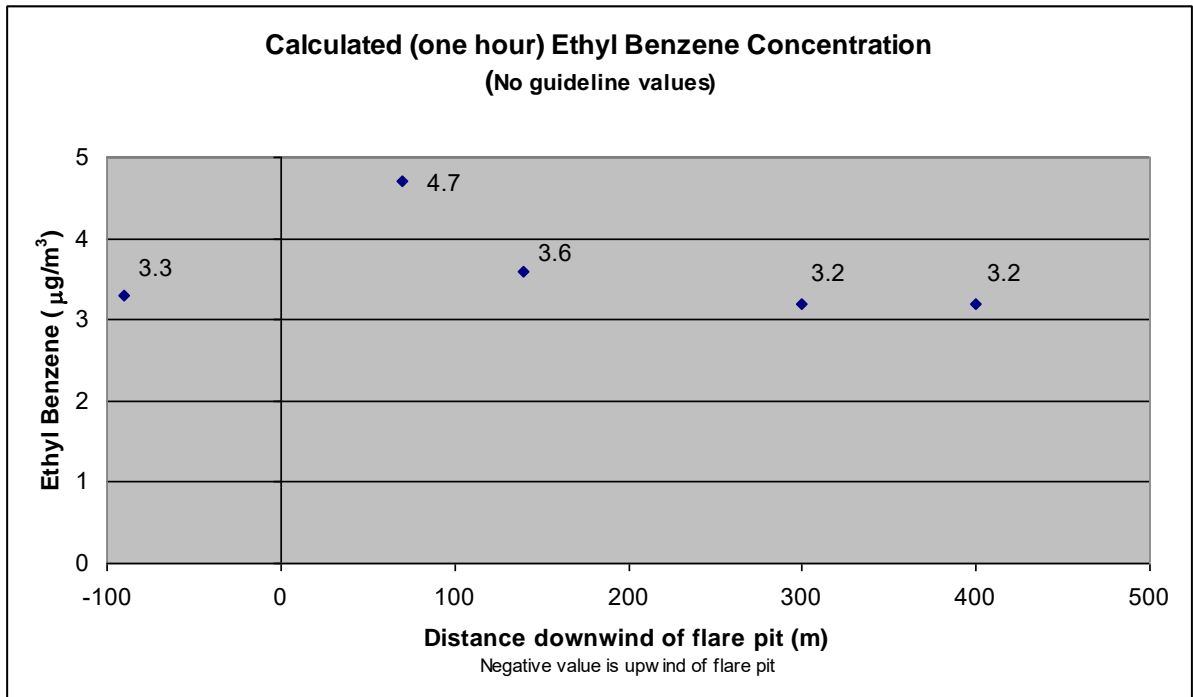
Calculated (one hour) Ethyl Benzene Concentration
(No guideline values)

Figure 7   Ethyl benzene concentrations in relation to the distance from the flare pit (nb numerical data not corrected for detection of ethyl benzene in blank. See Table 11)

Conclusion

Results (exposure averaged over the duration of the survey) from the BTEX survey ranged from <4.08-12.2 µg/m³ for benzene, <4.5-32.5 µg/m³ for toluene, <2.01-3.06 µg/m³ for ethyl benzene, and <6.00-16.6 µg/m³ for xylenes. For all individual species, the highest concentrations were detected at the location closest to and downwind of the flare pit (70 metres), and the second highest concentrations were detected at the location 140 metres downwind, indicating that the flare was a major source.

The variations in measured concentrations between ambient sampling sites were considerable. In the case of benzene, the highest concentration was 3 times higher than the lowest; for toluene more than 7 times; for ethyl benzene less than 1.5 times higher; and for xylenes 2.8 times higher. This implies that the flare pit was a significant source of toluene emissions, less so for benzene and xylene, and only a minor source at most for ethyl benzene. For benzene and toluene, the results at the location 140 metres downwind were still significantly higher than the background levels; whereas for ethyl benzene and xylene, concentrations 140 metres downwind were approaching or the same as background concentrations.

The calculated 'equivalent' 60-minute exposure concentrations range from <6.4-18.8 µg/m³ for benzene, <7.03-49.7 µg/m³ for toluene, and <9.4-25.4 µg/m³ for xylenes. These results are below (benzene) or well below (toluene, xylene) the respective MfE 60-minute guideline values of 22 µg/m³ for benzene (85%), 500 µg/m³ for toluene (10%), and 1000 µg/m³ for xylene (2.5%).

Even allowing for the arbitrary basis of the calculated equivalent concentrations, the survey showed that at the closest point of monitoring, a distance of 70 metres, levels of BTEX compounds still remain below guideline values.

The survey showed that in terms of BTEX compounds that approach most closely guideline values, benzene is of most interest; in terms of highest concentrations, toluene is of most interest.

3.4 Estimated ambient concentration for dioxins, PAH and methanol

Ambient measurements were made for PM, some products of combustion, formaldehyde, and BTEX, as outlined above. Formaldehyde and BTEX were also measured within the combustion zone. From the relative changes between concentrations of formaldehyde and BTEX in the combustion zone and as measured in ambient air, a crude estimate can be made of ambient concentrations for other parameters of interest- dioxins, PAHs , and methanol- based on their concentrations as determined within the combustion zone.

Limitations of this approach are acknowledged. For example, the emission concentrations were not necessarily measured at the same time as all the downwind concentrations, and so varying combustion and meteorological conditions would have been at play. The ratios between concentrations within the combustion zone and downwind would have been varying.

It should be noted that a separate project is being undertaken to model dispersion from flaring, under a variety of meteorological conditions, so that the results and finings of this study can be applied more widely and with more accuracy. It should also be noted that calculating concentrations of the parameters as outlined involves some approximations and assumptions. Nevertheless, such an exercise helps to semi-quantify the downwind effects upon air quality, at least for this study.

It is noted that the mass flow through the flare was constant throughout the two days of the study. It is assumed that the greater mass flow of contaminants was from the flare rather than by evaporation from the surface of the fluid.

Where there were repeated samplings of constituents of the combustion zone, the highest concentration found has been taken for purposes of estimation of downwind concentrations. This will give a conservative (worst case) result.

Because each combustion zone sampling was for a period of about 1 hour when there were repeated sampling, the calculated 30 minute or 1 hour average ambient concentrations have been used to compare with the combustion zone results, to derive dilution factors.

In Run 1, formaldehyde was found within the combustion zone at 0.25 mg/m^3 (250 µg/m^3). The calculated 30 minute exposure concentration at the nearest site downwind was 20.0 µg/m^3, and the mean background concentration appears to have been around 5.4 µg/m^3. Thus, the increase in ambient concentration 70 metres from

the flarepit was the difference of (20.0-5.4) µg/m^3 = 14.5 µg/m^3. This indicates an initial dilution factor of about 250/14.5 = 17 times.

In Run 1, toluene was found within the combustion zone at 0.052 ppm, which is equivalent to 200 µg/m^3. The calculated 1 hour exposure concentration at the nearest site downwind was 49.7 µg/m^3, and the mean background concentration appears to have been around 13 µg/m^3 (having regard to cross-wind sites). Thus, the increase in ambient concentration 70 metres from the flarepit was the difference of (49.7-13) µg/m^3 = 37 µg/m^3. This indicates an initial dilution factor of about 200/37 = 5.4 times.

From these two sets of data, the dilution applying between the combustion zone and the first sampling site downwind (at a distance of 70 metres) can be taken as lying in the range 5.4-17 times, for first approximation purposes.

These derived rates of dilution are much lower than would normally be anticipated for the dispersion of pollutants emitted from a point source and then flowing 70 metres in open air. This is probably due to the degree to which the sampling from the combustion zone was at times capturing background air, due to swirling of the flame, thus diluting the source concentration. This does not invalidate the approach being adopted, as ambient concentrations of dioxins, PAHs/BaP, and methanol are being estimated on the basis of relative changes in concentration between two sampling points, and not on the basis of an absolute concentration within an 'undiluted' source.

Dioxin: once blank corrections are taken into account, emissions of dioxins from the flare lie below the limit of detection inherent within the sampling and analytical methodology. There is no purpose in calculating subsequent dilution and any change in downwind concentration.

PAHs (especially BaP): the combustion zone PAH result was a concentration of 208 ng/m^3 (USEPA BaP equivalents). Study of the full laboratory results for PAH analysis shows that within the combustion zone, BaP itself accounted for 63% of this result.

Applying the two calculated dilution rates of 5.4 and 17, this suggests at a distance of 70 metres downwind, an elevation in downwind concentration over background concentrations, of all PAHs of between 12 and 38 ng/m^3 (total BaP equivalent), and in actual BaP of between 7.5 and 24 ng/m^3.

Methanol: the highest concentration measured within the combustion zone was 2.7 mg/m^3 (Run 2).

Applying the two calculated dilution rates of 5.4 and 17, this suggests an elevation in downwind concentration of methanol at a distance of 70 metres, of between 0.15 and 0.5 mg/m^3.

4. Discussion

4.1 Environmental effects of flaring and evaporative disposal of hydraulic fracturing fluids

Particulate matter (PM2.5, PM10)
The PM2.5 data showed no correlation of distance downwind of the flare with concentration (the closest sampling point was about 120 metres downwind), indicating that at the most by 120 metres from the flare and site there was no effect upon ambient PM2.5. The two sites closest to the flare and wellsite had the lowest PM2.5 results.

The PM2.5 concentrations in the vicinity of the flare were similar to or slightly below those found elsewhere in the region as background (ambient) concentrations, and are far below international guidelines.

The PM10 data showed no correlation of distance downwind of the flare with concentration (the closest sampling point was about 120 metres downwind), indicating that at the most by 120 metres from the flare and wellsite there was no effect upon ambient PM10. The two sites closest to the flare and wellsite had the lowest PM10 results, while the second highest result was recorded at the site that was furthest away.

The PM10 concentrations in the vicinity of a flare are somewhat below those found elsewhere in the region, and are far below (less than 10% of) the AQNES (50 µg/m^3). The air downwind of the flare would be rated according to MfE criteria as 'excellent' in respect of the PM10 concentration.

Dioxins/furans
Emissions of dioxins and furans from the flare were below the limits of detection. Given the very low levels of particulate matter emitted from the combustion zone, a low level of dioxins/furans is to be expected.

Polyaromatic hydrocarbons (including BaP)
PAHs were detected within the combustion zone and at much lower concentrations within the evaporation zone. The two samples had quite different compositions. BaP, the PAH of most significance, comprised 63% of the USEPA BaP toxicity equivalent concentration of the PAHs found in the combustion zone sample, but was not detected in the evaporation zone sample.

A crude estimation of downwind (ambient) PAH concentration suggested an elevation in downwind concentration of all PAHs at a distance of 70 metres, of between 12 and 38 ng/m^3 (total BaP equivalent), and in actual BaP of between 7.5 and 24 ng/m^3.

The evaporation zone results showed that levels of BaP were lower than is found in ambient air within central city locations in New Zealand, and that only minimal further dilution (dispersion) would be required to reduce PAH/BaP concentrations to levels similar to or lower than is typically encountered more widely in urban areas.

Aldehydes (including formaldehyde)

Formaldehyde concentrations monitored at the ambient sites in the vicinity of the flare, including those sites closest to the flare, are similar to those found elsewhere in the region, and are well below (less than 20% of) the MfE guideline.

The air downwind of the flare beyond the closest location would be rated as 'excellent' according to MfE criteria in respect of the formaldehyde concentrations, and even at the site 70 metres downwind would be rated as 'good'.

Volatile organic compounds (including BTEX)

Benzene results show that within a distance of 300 metres from the flare, benzene levels had reduced to a background level that was below the level of detection. All results, including those closest to the flare, were below the MfE guideline criterion, and at and beyond 140 metres downwind were half or less of the MfE guideline value.

Air at monitoring sites beyond 140 metres downwind of the flare would be rated as being at least 'good' according to MfE criteria in respect of the benzene concentrations.

Toluene and xylene were found 70 metres downwind of the flare, at 10% and 3% respectively of the MfE ambient guidelines. The air at all points sampled downwind of the flare would be rated as 'excellent' according to MfE criteria in respect of the toluene and xylene concentrations.

The study has identified that benzene is the parameter of most interest in terms of most closely approaching guideline values; toluene is of most interest as the BTEX of highest concentration.

Methanol

Even within the combustion zone and the evaporation zone as sampled, the levels of methanol were far below limits that might be derived for population health protection.

Carbon monoxide and carbon dioxide

No carbon monoxide was detected downwind. This means that the air at all points sampled downwind of the flare would be rated as 'good' or better according to MfE criteria (AQNES) in respect of the carbon monoxide concentration. The concentrations of carbon dioxide were less than background, indicating in all likelihood that the background reduction in carbon dioxide due to photosynthesis by pasture was having a greater effect than any increase in carbon dioxide by flare combustion. (This assumption is based on the findings of previous monitoring of carbon dioxide levels undertaken elsewhere by the Council)

5. Recommendations

1. THAT it be noted that the findings of this study are that there are minimal effects upon ambient air quality in the vicinity of flares being employed for the destruction of emissions from hydraulic fracturing fluids, in the context of prevailing air quality within the region and nationwide

2. THAT it be noted that all results relate to a field study carried out under specific source, topographic, and meteorological conditions, but as a provisional finding, it can be noted that the results of this study are consistent with and uphold those of the air quality studies of flaring (field monitoring and modelling studies) conducted in 1998

3. THAT this report be referenced by the Taranaki Regional Council in the assessment of any applications for air discharge permits for contingency flaring, and in any review of the *Regional Air Quality Plan for Taranaki* (2011)

4. THAT this report be distributed to hydrocarbon exploration companies and their consultants, for reference in the preparation of Assessments of Environmental Effects in support of applications for air discharge permits, and to other interested parties upon request

5. THAT the emission data contained herein be incorporated into modelling of dispersion from flares in which hydraulic fracturing fluids are combusted, to apply the findings and results of this study more widely across the variety of meteorology and landscapes that could be encountered within Taranaki.

Glossary of common terms and abbreviations

The following abbreviations and terms are used within this report:

AQNES	The *Resource Management (National Environmental Standards for Air Quality) Regulations 2004,* (and all subsequent amendments), Ministry for the Environment
BaP	benzo[a]pyrene
BTEX	collectively refers to benzene, toluene, ethyl benzene, and xylene, which in turn collectively refers to the m-, p-, and o- forms of xylene
CO	Carbon monoxide
CO_2	Carbon dioxide
g/m^3	grams per cubic metre, and equivalent to milligrams per litre (mg/L). In water, this is also equivalent to parts per million (ppm), but the same does not apply to gaseous mixtures
MfE	Ministry for the Environment, New Zealand
mg/m^3	milligrammes per cubic metre
$\mu g/m^3$	microgrammes per cubic metre. One microgramme is one-millionth of a gramme (one million times smaller than a gramme)
ng/m^3	nanogrammes per cubic metre. One nanogramme is one-thousandth of a millionth of a gramme (one thousand times one million times smaller than a gramme)
NO	Nitric oxide
NO_2	Nitrogen dioxide
PAH	Polyaromatic hydrocarbons
$PM_{1.0}$ $PM_{2.5}$ PM_{10}	relatively fine airborne particles, of less than 1, 2.5, and 10 micrometre diameter respectively. Now increasingly referred to as 'coarse' (PM_{10}), fine ($PM_{2.5}$) and ultrafine ($PM_{1.0}$) particles
RAQP	*Regional Air Quality Plan for Taranaki*, Taranaki Regional Council July 2011
resource consent	refer Section 87 of the RMA. Resource consents include land use consents (refer Sections 9 and 13 of the RMA), coastal permits (Sections 12, 14 and 15), water permits (Section 14) and discharge permits (Section 15). The latter include air discharge permits.
RMA	Resource Management Act 1991 and including all subsequent amendments
Temp	temperature, measured in °C (degrees Celsius)
TEQ	Toxic equivalent factors, used to adjust a suite of results (eg for all dioxins/furans, or all PAHs) to a single toxicity value based on an equivalent amount of a particular chemical (eg 2,3,7,8-TCDD for dioxins, or BaP for PAHs)
TPH	Total petroleum hydrocarbons
USEPA	United States Environmental Protection Agency
VOC	Volatile organic compounds. The most well-known and environmentally significant are BTEX
WHO	World Health Organisation

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