Ministry for the
Environment
Manatū Mō Te Taiao

Vehicle Emissions and

Air Quality

Ambient Air Quality and Pollution Levels in New Zealand; Targets for Vehicle Emissions Control

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Disclaimer

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1.0 Introduction

An essential part of developing ways to manage discharges into the air from any source is understanding the nature of the contaminants in the discharge and their effects on the environment. This technical document, prepared as part of the Ministry of Transport's Vehicle Fleet Emission Control Strategy (VFECS), summarises the current information on the effects vehicle emissions on air quality in New Zealand. It also describes the approach used to relate emissions from vehicles to their effects on air quality, to indicate where reductions may be required in vehicle emissions to maintain local air quality targets.

To assess the effects of vehicle emissions on air quality, it is necessary to understand the relationship between emissions of pollutants and their presence in the air we breathe. This relationship is complex due to influences of meteorology on both local and regional atmospheric dispersion processes and chemical reactions that occur in the air. One of the main complications is attributing a particular effect to any one source or group of sources, in any precise, quantifiable manner.

Equally important is the need to observe appropriate measures of air quality. These will generally be in the form of guidelines or standards for specific key pollutants, often referred to as "indicator" pollutants (their presence typically indicating certain types of emission source) . However, both internationally and in New Zealand, such guidelines or standards are only available for a limited range of indicators, and do not cover the full range of contaminants potentially discharged to the atmosphere from combustion sources. This presents a problem when considering how to address each of the potential air quality impacts from a sector such as motor vehicles. Where New Zealand guidelines are not available, overseas guidelines and/or the latest international research have been referred.

This first section outlines the current status of Government policies and the legislative environment in New Zealand, that specifically relates to air quality. Then addressed is how to identify the effects of vehicle emissions on air quality, as the basis for the procedural approach to achieving clean, healthy air in New Zealand. Also discussed are temporal and spatial issues involved in the assessment of air quality, especially the complexities in relating local impacts to particular sources of emission.

Following this, and comprising the main part of this report, are brief overviews of the situation for each of the main indicator pollutants, associated with combustion. Each section contains a discussion on the pollutant's effect on the environment (particularly human health), the concentrations that have been monitored in New Zealand, and estimates of the extent to which vehicle emissions contribute to the total pollutant load. Where appropriate, the aim has been to derive measures of reduction required in emissions from road transport, to ensure air quality is improved, where necessary, or at least maintained. The ambient air pollutants of principal concern (and for which vehicles are a source of emission) are; carbon monoxide (CO), particles (or particulate matter, PM), nitrogen oxides (NOx), volatile organic compounds (VOC), and photochemical oxidants.

This exercise does not attempt to place a progressive dollar cost on the adverse impacts on health and the environment, caused by a particular contaminant or the overall effects. The basis for managing air quality aims to avoid altogether the adverse effects on health or the wider environment, by adopting the necessary air quality targets.

The focus of this technical document is on ambient air quality. It specifically does not cover the effects of vehicle emissions on global issues such as climate change impacts. These relationships are referred to in the main VFECS report, and are addressed by other government policy developments.

To establish the full context for this review, it is worth reiterating the main principles embodied in the rational approach adopted in the VFECS. These principles are;

Impacts based - the analysis addresses the ultimate problem, in the form of the measured local air quality, then nets back through the effects-to-cause relationships to determine where the improvements required can best be gained.

Sustainable development - which translates to adopting a long range future perspective in examining these relationships, to ensure that the underlying root causes are properly identified; this calls for a wider scope of investigation and analysis, extending beyond just the on-vehicle technologies.

Localisation - a structured "framework" approach to formulating the overall policy mix whereby solutions are targeted and appropriate to the different levels of localisation, corresponding spatially with the area-wide extent of the pollution problems.

Quantified targets: to set clearly understood numerical targets, as objective measures of the degree of control required, based upon scientific consensus and and recognising the adequacy of information available; the analytical approach should also be responsive to the availability of new and improved information.

Regarding this last point, it is important to understand that this VFECS study is the first coherent appraisal of the air quality situation in New Zealand, in understanding the effects of vehicle source emissions on the environment. It represents the first iteration in an on-going process of air quality management, which monitors and reviews the performance of measures introduced against air quality targets and the need for improvements, as they become identified through the future.

It is also important to note that this assessment attempts to distinguish the effects of the vehicle sector as a whole, in comparison with other source groups such as industry and domestic emissions. It does not seek to further apportion contributions from different types of vehicle e.g. diesel versus petrol. This is undertaken within the analysis in the main VFECS report.

1.1   Overview of Environmental Strategies and Legislation in New Zealand

1.1.1   Government Strategies for the Environment

The Government's strategy for New Zealand's environment is outlined in *Environment 2010 Strategy - A Statement of the Government's Strategy on the Environment* (September 1995) (E2010). Although this strategy is not a statutory document, for example as a national policy statement under the RMA, it presents the Government's goals for the environment. Two goals in E2010 which are relevant to the study of vehicle emissions are:

"To maintain air quality in parts of New Zealand that enjoy clean air and improve air quality in places where it has deteriorated" (Chapter 6.3 Maintaining clear, clean, breathable air, page 32)

and

"To manage the provision of transport services in a manner that minimises adverse effects on the natural and physical environment and human health" (Chapter 6.8 Managing the environmental effects of transport, page 42)

These policy goals send a clear message that New Zealand's air environment should be managed to minimise potential adverse environmental effects, and that where air quality is already poor, resulting in adverse effects or potential adverse effects, it should be improved.

Also relevant in E2010 are the principles for integrating environment, society and the economy. These include; the precautionary principle, environmental "bottom lines", internalisation of external environmental costs, sustainable property rights, least cost policy tools and the concepts of social costs and benefits.

1.1.2   The Resource Management Act (RMA).

The framework for assessing and managing air quality in New Zealand is outlined in the RMA 1991. The RMA brought significant changes to the way air pollution was managed under the former Clean Air Act 1972 (CAA). Unlike the discharge control focus of the CAA, the RMA requires an effects-based approach to managing discharges of contaminants into the air. It also transferred the responsibility for managing air pollution from local and central government agencies to the newly formed regional councils.

The RMA requires decisions about air quality management to be based on the effects of discharges including, health effects, social effects and environmental effects (refer to the definition of effects in RMA Section 3 and the Fourth Schedule). It also requires consideration of the cumulative effects of discharges, the development of regional policy goals for the environment, community consultation and monitoring of the state of the environment.

The fundamental purpose of the RMA is to promote sustainable management of natural and physical resources, including air, so that they are maintained for future generations. Sustainable management is defined in the RMA as follows;

"Sustainable management means managing the use, development, and protection of natural and physical resources in a way or at a rate which enables people to provide for their social, economic, and cultural wellbeing and for their health and safety while -

(a) Sustaining the potential of natural and physical resources (excluding minerals) to meet the meet the reasonably foreseeable needs of future generations; and
(b) Safeguarding the life supporting capacity of air, water soil and ecosystems; and
(c) avoiding, remedying or mitigating any adverse effects of activities on the environment."

The RMA provides the framework with which local authorities manage air quality. Their duties include preparing regional policy statements, implementing regional plans, considering applications for permits to discharge contaminants to air, undertaking enforcement action and monitoring the state of the environment.

The Minister for the Environment also has duties and powers under the RMA that are relevant to air quality management. The Minister can recommend national environmental standards and

national policy statements, and also call for information from local government. At this stage, no national environmental standards have been promulgated. On behalf of the Minister, the Ministry for the Environment also plays a role in producing guidelines and guidance on environmental management. With regard to air quality, the Ministry has produced *Ambient Air Quality Guidelines* (1994) and a guide to *Compliance Monitoring and Emission Testing of Discharges to Air* (1998).

1.1.3   Regional Air Quality Plans and Regional Policy Statements

Under the RMA, Regional Councils and Unitary Authorities must prepare a Regional Policy Statement describing environmental issues in the region and the way in which the Council intends to address them. To achieve environmental goals, the council can also devise a regional air quality plan. This outlines in further detail the council's strategy for managing the regions air quality and contains policies and rules to address air quality issues. The major differences between regional policy statements and plans concern the level of detail and that plans, through the setting of rules, are enforceable.

Regional air quality plans are at different stages of development throughout New Zealand. Several are still in a draft stage while others are proposed or operative. Most of these plans consider vehicle emissions to be a significant source of contaminants. However, the majority consider that vehicle emissions need to be addressed from a national perspective. Regional policies relating to vehicles include supporting national initiatives to reduce vehicle emissions through the policies proposed in Stage 1 of the VFECS and providing comment on the final stage of the VFECS.

The general feeling of councils, and the Ministries for the Environment and Transport, is that the RMA is unclear on whether councils can promulgate regional plan rules and policies for managing the environmental effects of vehicle emissions on air quality. Discharges of stormwater from roads, on the other hand, can be managed by councils under section 15(1) of the RMA. In general, most councils do not consider that air quality effects of vehicle emissions can be appropriately managed under current RMA provisions. Proposals to amend the RMA, to ensure councils have the ability to devise and implement regional plans addressing road transport emissions, are currently being considered as part of road reform legislation.

1.1.4   Other Relevant Legislation

Certain types of possible policy options for controlling vehicle emissions, such as economic incentives, petrol specifications etc. fall outside the scope of the RMA. Where these options are discussed and supported, the appropriate legislative mechanisms involved with their implementation will be discussed in the main body of the VFECS. At present the only existing control is through section 28 of the Traffic Act, which provides for the arraignment of excessively smoky vehicles where they present a visibility hazard to other road users. This was introduced as part of road safety legislation, rather than through environmental concerns.

1.2   Approach to Managing Air Quality

1.2.1   Introduction

Vehicle emissions are just one source of the air pollutants of concern in local airsheds. For some pollutants they are the predominant source, for others they are a contributor but not the dominant source. In approaching air quality management a set of consistently applied procedures must be observed, to understand the sector-wise balance of management strategies required. These procedures are outlined below and form the basis of the approach used in the VFECS.

To gauge the state of air quality, and its potential impacts, concentration levels of a particular contaminant in the air are compared with the air quality guidelines or standards applying for that contaminant. Guidelines or standards provide a measure of the extent of degradation of air quality compared with "pristine" natural background levels, towards levels that pose a significant danger to human health or the environment.

It is impossible to measure all contaminants in the air. The first stage in setting guidelines is to select key or priority pollutants that provide a representative picture of air quality. These pollutants are commonly referred to as "indicators". In the case of air quality, the most commonly used indicators are pollutants can arise from the combustion of fuels, such as carbon monoxide, particulate matter and nitrogen oxides.

The second stage is to select the criteria upon which the guideline or standards will be based. Criteria are developed from reviews of existing information on selected indicators. They may be based on human health effects, effects on ecosystems or human values such as preservation of amenity (e.g. dust nuisance, odour nuisance or visible smoke, pollution haze). Once established, the guidelines set the minimum requirements for air quality.

However, because a degree of adverse impact may occur at exposure levels below the guideline value, air quality management policies should aim to achieve ongoing improvement, beyond ensuring that guidelines are not exceeded. The ultimate objective is to control pollution tendencies such that concentrations remain comfortably below the guideline, including the occasional incidence of high peak levels. Management policies also need to maintain air quality where it is already good, and prevent further deterioration. Therefore a third step is required, to aim for continuous improvement in air quality, through the use of air quality "targets". For the purposes of the VFECS, targets have been based on categories of air quality defined by a percentage range of the guideline limit. This approach has been developed under the Ministry for the Environment's, Environmental Performance Indicators programme, and is discussed in more detail in section 1.2.4.

Fourthly, it is necessary to monitor the concentrations of the indicator pollutants in areas where people or the environment may be exposed. This requires equipment to be installed at monitoring sites where concentrations of the indicators are measured over time. The monitoring data collected can then be compared with the guideline to determine where action is needed to improve air quality.

Fifthly, and before any management strategies are devised, the source of the pollution measured in the air and factors that influence air quality, such as containment and meteorology, must be understood. Typically, sources of pollution around a monitoring site are identified using emissions inventories. An emissions inventory estimates the proportion of contaminant emissions from different sources e.g. vehicles versus industry versus domestic fires. Care is

needed in using these inventories as they tend to provide estimates rather than absolute values, and the proportion of contaminants from each source measured in the air may not be equal to their emission rate. This is further complicated by the complex interactions between airborne contaminants following their discharge into the atmosphere. The assumptions involved in identifying the proportion of vehicle emissions contributing to ambient pollution levels, at different monitoring sites, are discussed in each pollutant chapter.

Finally, once the vehicle sector contribution is derived, appropriate reductions in emission rates to achieve a given air quality can be estimated. However, to then develop the best management options, more detail about the relative contributions from different vehicle types and how they may change over time, is required. This is the primary objective of the VFECS.

1.2.2   Selecting the Key Contaminants or Indicators of Vehicle Emissions

There are potentially hundreds of different contaminant chemicals released during combustion and not all their environmental effects can be assessed. Some may not be relevant to ambient air quality (e.g. CO_2) while others are released only in trace quantities (e.g. some hydrocarbons) or are unlikely to cause adverse health effects (e.g. water vapour). The VFECS considers the key contaminants released from vehicles that have the potential to cause adverse effects on urban air quality. These are; carbon monoxide, particulate matter (smoke), nitrogen oxides (in particular, nitrogen dioxide), volatile organic hydrocarbons (in particular benzene and polycyclic aromatic hydrocarbons), and photochemical oxidants (formed in the atmosphere by other contaminants, some of which are released by vehicles).

1.2.3   Ambient Air Quality Guidelines

In 1994, the Ministry for the Environment released the Ambient Air Quality Guidelines (AAQG) for New Zealand. These are primarily focused on protecting human health and well-being. The guideline values were largely based on World Health Organisation (WHO) *Air Quality Guidelines for Europe,* although the guidelines and standards of other agencies were reviewed. Not all of the contaminants in the guidelines, such as fluorides and hydrogen sulphide, are relevant to vehicle emissions.

Because guidelines are based on a global pool of knowledge about the effects of a contaminant, they provide the best means of assessing the potential effects of air pollution levels, without having to measure the "actual" effects. Actual effects are often extremely difficult to measure, in meaningful quantitative terms, examples being the increased use of asthma treatments, hospital admissions, premature deaths and plant damage.

The AAQG were designed to provide guidance for policy development at central, regional and local levels. As such they are not enforceable under the RMA. However, many councils are adopting these guidelines, or stricter guidelines, as the basis of policies and rules in regional plans. This effectively gives guidelines the status of *de facto* environmental standards. However, the adoption of these guidelines in regional air quality plans has not been consistent through out New Zealand.

Since 1994, there have been numerous additional studies to determine the impacts of air pollution. In some cases effects have been found at levels lower than those previously considered "safe". More recently the WHO has recommended more stringent guidelines than the MfE AAQG, particularly for NO_2 and particles; these have already been adopted by some countries. Based on these new overseas guidelines/standards and recent studies, several regional councils

have applied stricter guidelines to assessing monitoring data and are proposing to use them as targets/guidelines in their regional plans.

The Ministry for the Environment has commenced a review of the AAQG and how they are used in air quality management in New Zealand. This review will bring the guidelines in to line with the current global knowledge. A draft revised document is expected to be available by mid-1999. Each pollutant chapter discusses where regional guidelines and current international guidelines differ from those in the existing AAQG.

It is important to note that overseas guidelines and subsequent government policies have often been developed for areas with significantly degraded air quality, where improvement is urgently required to attain acceptable levels, rather than just to maintain it at good levels. In general, New Zealand has relatively good air quality due to its isolation and maritime climate, and relatively low population density. We are therefore in the enviable position of being able to focus on developing guidelines and targets to avoid significant degradation of air quality in the first place.

AAQG should be regarded as upper limits not to be exceeded, rather than limits that can safely be polluted up to. They usually represent the level at which adverse effects are sufficient to require urgent action. Significant and often obvious effects, however, may have already occurred before guidelines are exceeded. There are three main reasons for this.

- The current AAQG are primarily based on human health effects and do not consider effects on ecosystems (plants may be far more sensitive to some air pollutants than humans) or effects on amenity values, such as degraded visibility. For example, particulates can degrade the clarity of the atmosphere in concentrations far lower than the guideline set to protect human health.

- Although guideline development attempts to take this into account, there will be some very sensitive individuals who are adversely affected by pollution levels below the guideline value.

- Because the guidelines tend to be based on effects of one pollutant at a time (with the exception of particles and sulphur dioxide), they may not reflect possible effects of exposure to pollutant mixtures. Determining the effects of inhaling multiple pollutants is a challenging task.

Notwithstanding these issues, AAQG represent the best place to start as a method of determining current air quality and effects of air pollution.

Another important consideration is the difficulty in determining the cause and effect relationships between air pollutants and receptors. Guidelines and standards are based on the best available epidemiological and experimental information at the time of promulgation, but it is recognised that they may need to be amended as these relationships are better understood.

Each air pollutant affects the environment in different ways, in varying concentrations and over different exposure periods. There is an array of complex factors influencing whether or not an air pollutant inhaled by an organism, or coming into contact with a surface, will cause an adverse or undesirable reaction. Investigating environmental effects of air pollutants, particularly long term exposures to low concentrations, can be extremely difficult and may take a number of years.

Information on which to base guideline values comes from epidemiological and experimental studies. Epidemiology involves examining the incidence of disease in the population in relation to air pollution levels and exposures, particularly exposures in the work place (as opposed to general ambient exposure). Experimental studies may involve the exposure of sensitive human beings (where suitable) or laboratory animals to air pollutants. A degree of expert judgement is also often applied to determining some guideline values, as rarely is the basis of evidence absolute .

Identifying statistical relationships from epidemiological studies and extrapolating effects from animals studies can involve uncertainty. Discussing the different types of information upon which guidelines are based enables decision makers to be aware of the advantages and disadvantages of using guidelines in air quality management.

Where is there a clear "no observable adverse effects level";

For some contaminants there is significant evidence to show the presence of a threshold in the exposure required to cause an adverse effect. Provided a person or sensitive environment is exposed to levels below the threshold concentration and exposure period (otherwise known as a "no observable adverse effects level -NOAEL"), no adverse effects will occur. This should apply also to those individuals who are most sensitive to the pollutant. These guidelines may be based on experiments on sensitive members of the population (e.g. asthmatics) exposed to the pollutant. Guidelines that fall into this group include carbon monoxide (CO), for which there are relatively clear relationships between period of exposure, concentration of CO in the air, amount of CO in the blood and potential adverse health effects.

This level of certainty tends to be the exception rather than the rule; even with this information the definition of a threshold is not completely absolute.

Where studies have been unable to identify a "NOAEL;

Where there is a lack of scientific information, or where the information cannot determine a robust NOAEL for a concentration and exposure period to a particular contaminant, a guideline may be based on epidemiological studies supplemented with expert judgement to determine appropriate safety factors. These studies are usually carried out in countries with large metropolitan zones, with high populations in a given locality. Safety factors are used to protect the more sensitive members of the population who may not have been included in the studies. This approach applies to contaminants that are not thought to be highly toxic or carcinogenic.

For example, the WHO guideline values for sulphur dioxide, as are used by the MfE , have an uncertainty factor of 2 (the NOAEL is divided by 2). This allows for the possibility that the most sensitive people may not have been part of the experimental tests that established the NOAEL.

Where studies point strongly towards the absence of a NOAEL:

For most contaminants, studies have been unable to determine a NOAEL. These often include contaminants that are known or suspected human carcinogens, that may be referred to as "hazardous air pollutants". The WHO has determined "risk factors" for some of these. By using risk factors or other methods, a number of countries have developed guidelines or acceptable risk levels. Risk factors provide a tool for countries to debate the level of risk that is deemed to be "acceptable" (e.g. a risk of one additional case of leukaemia in one in 100,000 may be considered to be an acceptable risk). The fact that a NOAEL cannot be determined, does not mean that there isn't a level below which exposure will not cause significant adverse effects. It may simply mean that the science has yet to determine the value. A precautionary approach should be considered in such circumstances. Determining environmental and health effects of potentially toxic substances is a subject of world-wide research and debate.

The Ministry's AAQG have been largely based on the first two approaches. This is because they provide guidelines for the common criteria air pollutants and do not include guidelines for hazardous air pollutants that tend to fall into the third group. The Ministry for the Environment currently recommends a precautionary approach to managing hazardous air pollutants (specified in the list in appendix of the guidelines) by minimising their discharge into the air. This is an approach also taken by a number of other countries for some air toxics.

Although some of the MfE guideline values need to be reviewed (specifically nitrogen dioxide and particulates) - it is beyond the scope of, and inappropriate for, the VFECS to promulgate "new" ambient air quality guidelines for New Zealand (nevertheless, the analytical approach being used in VFECS will be responsive to future revisions in the guidelines, as they arise). It is important, however, to consider overseas guidelines and proposed regional guidelines. Where appropriate, these have been discussed in the specific pollutant chapters and have played a role in determining required reductions in vehicle emissions.

There are currently no ambient air quality guidelines for the more subjective impacts of air pollution such as odour nuisance, visibility and the dirtying effects of particle deposition. Such effects are often considered on a case by case basis on whether they are "noxious", "offensive" or "objectionable" to the ordinary person. Where offensive or objectionable effects of vehicle emissions occur, such as a visible black smoke plume, this has been discussed in the main VFECS report.

1.2.4   Using Guidelines and Air Quality Categories for Setting Targets

So far, the discussion has focused on the need to avoid exceedances of guidelines values. However, as stated earlier, this does not necessarily mean that the resulting air quality can be regarded as "good". Environmental policy in New Zealand requires that, beyond ensuring that the guideline limits are adhered to, the quality of the environment should at least be maintained and preferably enhanced.

To provide guidance on these matters, the Ministry for the Environment has developed a set of environmental performance indicators for air quality as part of the Environmental Performance Indicators (EPI) Programme. The purpose of the EPI programme is to develop indicators to measure and report on the health of our environment. Indicators of air quality can provide key information with which to determine:

- the current state of New Zealand's air quality in comparison to guidelines and air quality categories,

- changes in air quality over time,

- whether policy goals and expected environmental outcomes are being achieved,

- the deviation of air quality from natural background air quality.

The indicators for air quality are divided into Stage 1 indicators, those that can be implemented now, and Stage 2, those that require further development. Stage 1 indicators relevant to the VFECS are provided in Table1.1. MfE is currently working with regional councils and other agencies to develop monitoring frameworks and information management systems to collate and present indicator information. The data for the air indicators will primarily come from regional councils, Ministry of Health and Crown Research Institutes carrying out air quality monitoring programmes.

The Ministry's discussion document *Environmental Performance Indicators - Proposals for Air, Fresh Water and Land* (1997) outlines how categories of air quality, based on guidelines as upper reference points, can used to describe air quality monitoring results and develop targets for managing air quality. The categories are given in Table 1.2.

Air quality categories provide an easily understood means for setting targets to achieve ongoing improvements in air quality. They can also be used to establish targets for maintaining air quality where it is already good. Comparing trends in indicator monitoring over time with these categories can also provide a guide to whether action may be needed in the near or distant future.

Table 1.1 - Stage 1 Indicator Pollutants & Guidelines

Issue	Indicator Description	Ambient Air Quality Guideline Value	
		MfE Guideline	Proposed Regional Council Guidelines (where different from MfE value)
Adverse health effects caused by primary and secondary PM	PM less than 10 microns in diameter	120 μg/m3 (24 hour average)	50 μg/m3 (24 hour average) [ARC,EW,ORC and CRC]
Adverse effects on human health	Carbon monoxide	10 mg/m3 (8 hour average) 30 mg/m3 (one hour average)	
Adverse effects on human health and formation secondary particles	Nitrogen dioxide	300 μg/m3 (one hour average) 100 μg/m3 (24 hour average)	200 μg/m3 (one hour average) [ARC]
Adverse effects on human health and on vegetation	Ground level ozone (photochemical oxidant)	150 μg/m3 (one hour average) 100 μg/m3 (24 hour average)	

Table 1.2 - Air Quality Categories

Category	Maximum measured value	Comment
Action	Exceeds the guideline	Completely unacceptable, by national and international standards
Alert	Between 66% and 100% of the guideline	A warning level, which can lead to exceedances if trends are not curbed.
Acceptable	Between 33% and 66% of the guideline	A broad category, where maximum values might be of concern in some sensitive locations but generally at a level which does not warrant dramatic action.
Good	Between 10% and 33% of the guideline	Peak measurements in this range are unlikely to impact air quality.
Excellent	Less than 10% of the guideline	Of little concern, if maximum values are less than a tenth of the guideline, average values are likely to be much less.
Not Assessed		Insufficient monitoring data to assess the category.

Immediate action should taken to improve air quality in areas where a guideline is already being exceeded.

Where air quality is currently acceptable but vulnerable to increasing pressure from pollution sources, it should be monitored periodically to observe any changes. If pollution levels are found to be increasing, entering the "alert" category, the emissions sources in the vicinity should be examined. This may involve predicting how emissions will change over time and whether they are set to continue increasing. Factors affecting the peak results, such as meteorology, should also be investigated. Where possible, reduction strategies should be devised and implemented before the guideline is exceeded. This is particularly important because many of the measures available to reduce emissions are likely to take a number of years to become effective.

Although there are no defined time periods for achieving the guideline and progressive air quality targets, the following indicative timeframes have been proposed for achieving results;

Alert - Immediate term = 0-2 years
Acceptable - Short to medium term = 2-5 years
Good - Long term = 5-10 years

It is stressed that these timeframes are indicative rather than absolutes, and are not stringent guidelines. The timeframes for improvement will depend on the severity of the air quality problem, the measures to be implemented and the period required to give the community due warning and acceptance of new regulations and requirements. Timing is particularly important if some form of capital expenditure is required. Occasionally there will be a mixture of measures that need to be phased in over time to bring about the best results.

The VFECS utilises this air quality indicator approach to analyse the implications, in terms of emissions reduction, of achieving progressively the 'alert', 'acceptable' and 'good' air quality categories.

1.3 Collecting Monitoring Information to Determine Effects and Contribution of Vehicle Emissions

To implement *effective* air quality management polices and rules it is vital to quantify the main sources of the contaminants. Because the VFECS deals only with vehicle emissions, it is extremely important to consider the vehicle contribution to the pollution loading compared to other sources. In this way, the degree to which air quality improvements can be achieved by reducing emissions from vehicles, as opposed to other sources, can be assessed.

1.3.1   Air Quality Monitoring in New Zealand

Air pollution levels are monitored at a number of sites in New Zealand, most notably in Auckland and Christchurch. Certain information is needed to understand the results properly, including details about the monitoring site location, measurement methods used, surrounding pollution sources and meteorology. The VFECS process has highlighted that, in the past, the nature and extent of air quality monitoring undertaken in New Zealand has largely been inconsistent both in the analysis procedures used and siting of the monitoring stations. This limits the usefulness of a large proportion of past monitoring results, as they are not directly comparable between sites, and in trends over time. Consistent monitoring siting and methodology is a key to effective air quality management in the future, and MfE is currently addressing these inconsistencies through the EPI programme.

As part of the VFECS work, coordination of air quality monitoring has been undertaken as well as specific monitoring at representative worst case road corridor sites; this is discussed in each air pollutant chapter. However, the following section provides an indication of the issues involved in obtaining useful monitoring data and identifying the relative contributions from different pollution sources.

1.3.2   Site Representativeness

Ambient air monitoring sites measure the cumulative effects on air quality from a range of emission sources in the vicinity, including such as domestic fires, vehicle traffic and industry. The monitoring sites used to determine reduction targets for the VFECS are mainly in urban areas, with heavy traffic congestion, where the highest levels of exposure are likely to occur. With the exception of contaminants such as NO_2 and photochemical oxidants (ozone), sites adjacent to congested roads generally represent worst case air quality situations attributable to emissions from vehicles. As recent survey monitoring and air shed modelling studies have shown, these sites are representative of the worst case conditions likely to be encountered in New Zealand's major cities.

Air pollution levels in some locations, such as Queen Street in Auckland, have probably reached maximum pollution concentrations simply because the traffic in the street has reached capacity. However, the geographic extent of traffic impacts is likely to be growing, and more widespread throughout the urban airshed, as greater areas of the road system approach congestion. For instance, ten years ago Auckland might have had just a few streets with air quality as affected as Queen Street, but now this is likely to extend to many more within and outside the CBD area.

It was considered appropriate to establish reduction targets based on monitoring results from these peak traffic sites or worst case scenarios. This was because we can be relatively certain that if the necessary air quality improvements can be achieved at these sites, they should also be also be able to bring about comparable reductions at other peak sites, and maintain air quality at other less impacted sites. Where this correlation is not so precise e.g. for photochemical oxidants and nitrogen dioxide, the approach taken is discussed in the relevant air pollutant chapter.

1.3.3   Time and Space - the Critical Dimensions of Air Quality

The traffic corridor airshed concept was introduced in Stage 1 of the VFECS to relate CO concentrations measured at roadsides directly to the emission rates resulting from the local traffic flow. Figure 1.1 indicates the different spatial environments over which air pollutants can cause impacts. The extent to which emissions will affect larger areas will be a function of a number of complex factors including; the nature of the contaminant, meteorological conditions, solar radiation, the presence of other contaminants in the atmosphere and their chemical interactions that occur in the air.

For example, once CO emission enters the air from vehicles on a road, its concentration in the air usually decreases relatively rapidly away from the road to well within guidelines levels. Although the rate of decay away from the roadside has a complex relationship with meteorological factors, the highest concentrations of CO only occur at the most congested or severe containment sites within a road corridor.

However, this relationship does not necessarily hold true for all contaminants. For example, nitrogen dioxide (NO_2) is predominantly formed in the atmosphere when the predominant NO emission discharged in to the air is oxidised to NO_2. This reaction is influenced by a number of factors, including the presence of oxidants (e.g. ozone), temperature and sunlight. Therefore, NO_2 concentrations may be higher away from the immediate road side. NO_2 can be both a traffic corridor concern (if the emission rate is sufficient and local conditions promote rapid conversion) and a wider urban air shed issue.

Figure 1.1 - Airshed Development
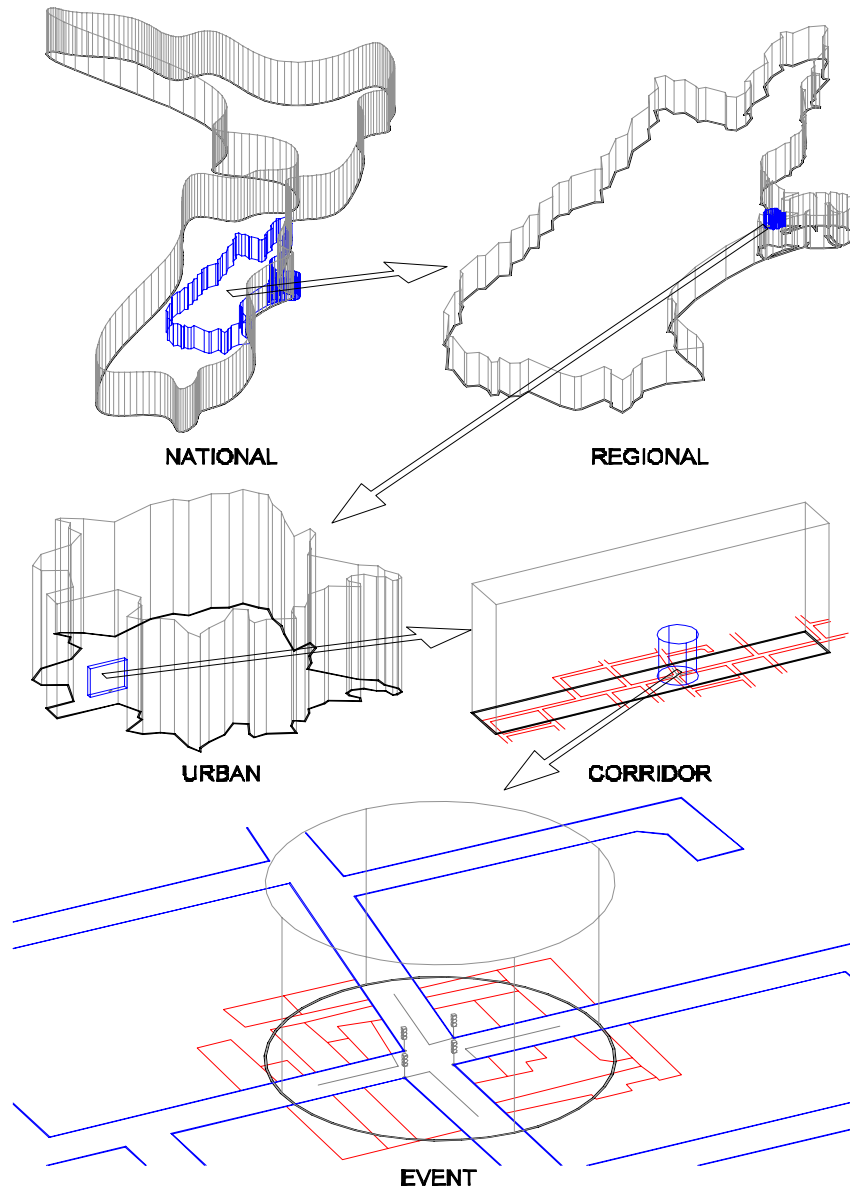
Some pollutants may be relatively stable and are not quickly degraded or easily involved in atmospheric reactions. Under very still weather conditions these pollutants have the potential to accumulate over time. These include contaminants such as benzene that has a half life of 19 days.

Potential effects of contaminants can occur over a few seconds to several hours and even days or years. In most cases, the guideline will provide the time period of interest e.g. for CO there is one guideline for a one hour averaging period and another for eight hours. Other contaminants can cause adverse effects for a number of days e.g. degraded visibility or the build up of nitrogen

dioxide. There are others for which long term exposure, up to a year, to low concentrations represents the greatest risk.

Temporal and spatial aspects of air quality and the effects of air pollutants are explored in further detail in each of the air pollutant chapters. These are important factors to consider when assessing the potential or actual effects of contaminants and the way in which their effects can be mitigated.

Figure 1.2 illustrates this hierarchical concept in its development of the pollution profile. CO is used as an example, and using some order of magnitude relativities to develop this spatial concentration profile; obviously the base is not to any scale.

Figure 1.2 – Spatial Pollution Profile; CO Example
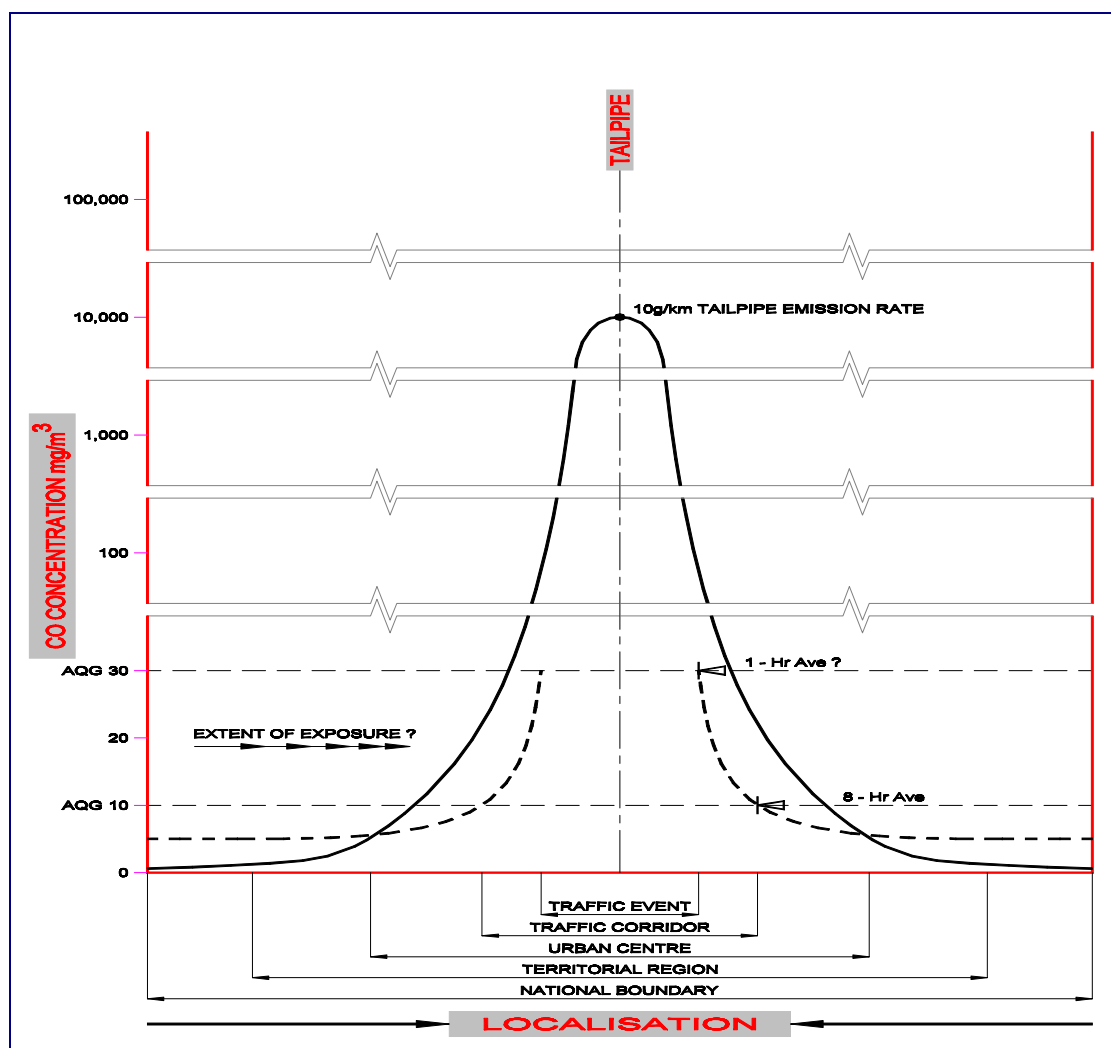
1.3.4   The Influence of Meteorology and Seasonality on Air Pollution

Seasonal changes in weather and temperatures affect air quality in two main ways. Firstly, meteorological conditions, particularly wind speed and atmospheric stability have profound effects on the dispersion of air pollution. In some areas in New Zealand, wind speeds tend to be higher and the atmosphere unstable during summer thereby dispersing contaminants. During winter, wind speeds tend to be very low and the atmosphere very stable. This prevents dispersion

of the contaminant with it accumulating in the air above emission sources, particularly increasing the local effects of air pollution. Air temperatures and the strength of UV radiation, varying seasonally, affects atmospheric reactions and the formation of secondary pollutants such as photochemical oxidants.

Secondly, seasonal changes in weather conditions can alter the quantity of contaminants discharged into the air from different sources. For example, cold temperatures during winter increase home heating needs, which in some areas, involves a significant increase in wood and coal burning on open fires and in wood burners. Also emissions from natural sources will be quite different depending on the seasons. Seasonality is not such a significant factor in the absolute emissions from motor vehicles, as the patterns of vehicle use are typically constant through the year, apart from effects of ambient temperature on cold starting and petrol evaporation rates. However, it is important to account for seasonality when quantifying pollution sources in inventory analysis, as the relative contributions to a pollution incident could vary (especially with domestic fires).

Some areas experience winter time inversion layers which trap air pollutants close to the ground causing pollution to accumulate. This, in conjunction with emissions from domestic fires, is one of the main reasons for Christchurch's winter smog conditions and high particulate concentrations.

1.4   Determining Pollution Sources

Effective air quality management requires a good understanding of the sources of chosen indicators measured in the air. As discussed above this can be a complex task, often based on best estimates and statistical analysis rather than absolutes. The most common method involves compiling an emission inventory. Other methods currently under development include source apportionment techniques.

1.4.1   Emissions Inventories

An emissions inventory is an essential component in urban air quality management. The inventory quantifies the nature and scale of emissions outputs, and also provides a measure of the spatial distribution of their sources. Urban areas are divided into grid squares or specific areas (e.g. 3km by 3km). The total emission rates from various sources in that area or grid are then calculated. Among other processes, emission rates are calculated on the basis of emission factors for particular sources, surveys of fuel usage for combustion sources or production rates, and information on discharges from resource consent applications. Emission rates used in the inventory may include a time factor e.g. for sections in the diurnal cycle, between 6am to 10am, 10am to 4pm etc. Typically, the emission sources are divided into sector groups e.g. domestic, vehicle, and industrial and into different contaminants e.g. particulates, volatile organic compounds, nitrogen oxides etc. There may be greater levels of detail required depending on the main aim of the inventory e.g. domestic emissions can be broken down into those from open fires, wood burners, pot belly stoves etc and from vehicles into those from diesel vehicles, petrol vehicles, and vehicles of different design duties. Also, further detail in the nature of emissions can be included, for example, instead of total volatile organic compounds it is possible to speciate organic components such as toluene, benzene etc.

A number of councils have compiled emissions inventories for their regions and a total emissions inventory for New Zealand has recently been completed by NIWA for MfE. These inventories represent the best knowledge at present. However, they should be treated with a degree of caution on accuracy, in both the aggregate outputs and the different source apportionments, due

to the limited nature of the data they are currently based upon. There is not yet an established, consistent approach used to compile inventories, and the main potential weakness is the extent to which the source groups are characterised in terms of their most significant emission rate influences. Also, emissions inventories need to be responsive to regular updating as better base data is gathered, within a consistent structure, to take account of changes in emissions profiles and particular emphases on local air quality issues.

Emissions inventories should also provide an ability to predict changes in total emissions over time (and hence air quality) and to assess the impact/effectiveness of different policies options or rules. Because many of the policy options have long lead in times between initiation and effect, air quality targets and goals must be based on sound projections of future trends in emissions from any particular sources or sources. The tool for achieving this for the VFECS is the Vehicle Fleet Emissions Model (VFEM), which is a particularly detailed and dynamic inventory, capable of comparative projections through 25 years into the future.

Proportioning emissions by source in inventories does not necessarily reflect the relative contribution to pollution as measured in the local airshed. For example, industrial processes may have high emission rates but they do not necessarily contribute to ground level pollution in comparable proportions, in the immediate vicinity. This is because industrial emissions are often released from a high chimney; under still wind weather conditions the discharge plume may not reach ground level until far from the source at which point, dispersion has reduced the concentration of contaminants in the plume and its overall percentage contribution to pollution concentrations. Sources such as domestic fires released closer to ground level will proportionately have a far greater role in causing local ambient pollution that affects humans and the environment.

A question arising is whether emission rate reductions based on measured ambient air concentrations and emissions inventory apportionment will be commensurate with the need to reduce pollution loading on the wider ambient air shed as a whole. This is especially the case where significant other sources of emissions occur and where meteorological factors play a significant role in air quality.

Details of the contribution of pollutants from different vehicle types e.g. the proportion of particles from petrol vehicles compared to diesel vehicles, are discussed in the main VFECS report.

1.4.2   Source Apportionment

New analytical techniques are being developed to estimate the source of contaminants, from a sample extracted from the air. At this stage primary particulates are the focus of this technique. This is termed "source apportionment" and involves detailed analysis of the chemical makeup of the particulate, comparing the compositions with those characteristic of the various discharge sources. Although results are promising, at this stage the method requires further development and has not been used for this assessment.

1.5 Deriving Vehicle Emissions Reduction Targets from Air Quality Monitoring Data and Emissions Inventory Information

Where appropriate, reduction targets for vehicle emissions have been derived from the monitoring data and emissions inventory data, using the indicators approach to managing air quality. Although this sounds straight-forward there are considerable difficulties in devising quantified reduction targets for all of the chosen indicators. Problems to overcome include;

- the absence of guidelines and a clear understanding of the effects of some of the indicators,
- inconsistencies in emission inventory compilation,
- the use of peak monitoring results or percentile results,
- a lack of monitoring information, and inconsistency in monitoring procedures,
- a lack of understanding about atmospheric chemical reactions.

These issues and how they have been considered in the VFECS are briefly outlined below.

Lack of AAQG

Where an ambient air quality guideline is not available for assessing monitoring results and establishing reduction targets, a judgement on the current state of air quality has been based on overseas guidelines and recent research. This is discussed where appropriate in each chapter, a good example being that of benzene.

Using peak monitoring results versus percentile results to develop management targets

Like all monitoring data sets there are a few extreme results recorded at some of the sites. While these are of concern, it is impracticable to base reduction targets on such data. Therefore, a 99.9 percentile value for 8 hour and one hour averaged data, and 99 percentile for 24 hour averaged data, of total annual hours, has been used to determine improvements required in air quality to meet air quality guidelines and targets (as recommended by New Zealand's air quality expertise).

Lack of monitoring Information

In some cases we simply do not have enough information about a contaminant to know whether or not it is causing environmental effects in New Zealand. Where this is relevant it has been discussed in each chapter. An increasing number of monitoring sites are being established by regional councils throughout New Zealand, however, it will be a number of years before data sets are sufficient to enable useful further analysis. Monitoring of hazardous air contaminants also requires greater attention.

Understanding Complex Atmospheric Reactions

Investigations into the complex chemical reactions occurring between contaminants in the atmosphere are under way. However, it is likely to be a number of years before our understanding of the role of these reactions improves sufficiently to consider them fully in air quality management decisions.

1.6   Summary

This introductory chapter has set the scene and framework for the assessment of the situation for each pollutant, in the following chapters.

It is important to note that the approach outlined above is iterative and there needs to be ongoing re-evaluation of the effectiveness of policy initiatives. As many policy options have long lead times, ongoing air quality monitoring is required to monitor the effectiveness of policy measures in meeting air quality targets. Similarly, emission inventory databases require continuous revision to ensure that they accurately reflect the emissions signature of a particular sector. With the motor vehicle fleet, the factors that effect emissions from the fleet are very complex, requiring considerable detail in the inventory structure to represent properly the significant relationships in the fleet composition and driving conditions, for both the existing and future motor vehicle fleet. The Vehicle Fleet Emissions Model (VFEM) is a tool developed specifically for this purpose.

2.0   CARBON MONOXIDE

2.1   Introduction

Stage 1 of the VFECS used the example of CO emissions to demonstrate the relationships between vehicle emissions and local air quality. This chapter includes that same information for CO, adapted to follow the same format used for review of the other pollutants. Refer to the Stage 1 report for more detailed information.

2.2   Characteristics of Carbon Monoxide

CO is one of the most common and widely distributed air pollutants, being formed during incomplete combustion of any carbonaceous fuel material, such as coal, wood and oil and gas. It also arises from certain industrial and biological processes.

CO is a colourless, odourless gas that is slightly lighter than air. The only important exposure route for CO is via inhalation, as it does not penetrate the skin.

Natural background levels of CO found in New Zealand typically range from between 0.01 and 0.23 mg/m3, as measured from remote monitoring sites.

2.3   Sources of Carbon Monoxide

CO is a trace constituent of the atmosphere, produced by both natural processes (volcanoes, fires, metabolism of organisms) and human activities; for instance, CO is formed either directly or indirectly from natural processes such as the decomposition of chlorophyll and photochemical oxidation of methane in the atmosphere. Global background concentrations of CO fall in the range of 50 to 120 ppb, with higher levels generally occurring in the northern hemisphere. Background levels also fluctuate seasonally, with higher levels in winter than in summer. CO pollution occurs both indoors and out; heating and cooking appliances that use combustion are also sources of CO, as is tobacco smoking. However, the most significant source of CO in the ambient air is vehicle traffic. Places where vehicle emissions accumulate such as roadway congestion, tunnels and car parks are locations where people may be exposed to high CO concentrations, albeit short term. Inhabitants of office buildings and shops located along busy traffic corridors, or above or below car parks, can typically be exposed to elevated CO levels for longer periods.

CO concentrations inside cars may be higher than the concentrations outside in the streets. Air quality data from fixed site monitoring stations can underestimate the very short term peak exposures in traffic environments, but appear to better reflect population exposure for longer averaging times i.e ambient air quality, for such as eight hour exposures.

The Auckland Regional Council's emissions inventory estimates that the vehicle source accounts for approximately 83% of CO emissions during an average winter week day, and increasing to 94% during the summer (as the next most significant sources is domestic fuel combustion, especially for home heating). Other, relatively minor sources include aviation, rail transport, off-road vehicles.

The Canterbury Regional Council inventory indicates that motor vehicle emissions account for between 67% and 70% of the total emissions on a typical winters day, while domestic fires emit 30-33% and industry less than 1%.

2.4 Motor Vehicles as a Source

As with any form of combustion, the sole reason for CO formation the vehicle engine is due to a lack of available oxygen within the combustion zone. This is caused by an over rich mixture, or locally poor fuel volatilisation/mixing with air.

As discussed above, motor vehicles represent the largest source of CO found in ambient air. In a number of particularly local areas, near roadways, vehicles will be responsible for 100% of the CO present in the air e.g. busy intersections and car parks. It is usually only during winter, where domestic fires contribute significantly to overall pollution, that the this other source can also be the reason for locally elevated CO levels, depending on proximity.

2.5 Effects of Carbon Monoxide

In terms of health impacts, the predominant population groups at risk from exposure to CO are:

- non-smoking middle aged and elderly people with documented or latent coronary disease
- foetus's of non-smoking pregnant mothers

CO is readily absorbed from the lungs into the blood stream. Haemoglobin (Hb) molecules in human blood, will attach themselves to CO much more rapidly that oxygen, if both are present in the air. This is because of the affinity of Hb for CO is 240 times its affinity for oxygen. The presence of CO in the blood reduces its oxygen (O_2) carrying capacity. This impairs O_2 release into tissue, potentially affecting sensitive organs such as the brain and heart.

Carboxyhaemoglobin (COHb) levels in the blood can be measured and serves as an indicator of exposure to CO. While the formation of COHb is a reversible process, it takes time for the body to metabolise CO from the blood. In 2 to 6.5 hours after exposure resulting in a given blood concentration, the body eliminates half of it. This is termed the "elimination half time" and explains why prolonged exposure to CO can be hazardous. Cumulative exposure to even low levels of CO can produce substantial blood levels of COHb.

People with various types of heart condition experience chest pain (angina) that results in cessation of activity at COHb of 2.9 percent and levels of 3-4 percent can produce ischaemia in exercising individuals. Ischaemia is a reduction of blood supply to parts of the body. These losses in activity may not be alarming, yet they result in limited activity for a subset of the population and affect the population and affect the quality of life.

Other effects associated with CO exposure include impaired ability to maintain attention and performance level. At COHB levels of 5 percent, hand-eye activities may be impaired, infrequent events may not be detected, and the ability to perform critical tasks continuously is affected. Effects at this level of COHb may be small, but the consequences potentially catastrophic; such lapses can be serious if exposure occurs during machine or equipment operation. At 5 percent COHb and above, neurological symptoms can occur, such as headache, dizziness, weakness, nausea, confusion, disorientation and visual disturbances. These worsen and intensify as exposure increases until levels equal to 10 percent and above cause unconsciousness and eventually death.

The focus of epidemiological studies has recently turned towards investigating the health effects arising from long term exposure to low concentrations of CO, previously considered to be "safe". Studies carried out in Canada and the US give preliminary evidence that some observable health effects result from long term exposure to average CO concentrations of 2.75 mg/m^3.

2.6 Air Quality Guidelines for CO

The Ministry for the Environment's Ambient Air Quality Guideline is 30 mg/m^3 (one hour average), and 10 mg/m^3 (eight hour average), intended to keep concentrations of COHb in the blood below 2.1 percent. They are based on WHO guidelines for Europe (WHO, 1987) which also included a 15 minute average guideline of 100 mg/m^3, and 30 minute average guideline of 60 mg/m^3. These guideline values remained unchanged in the more recent WHO guidelines (1994) and are typical of those used by a number of countries.

It is likely that many countries may consider developing an annual or longer term guideline, as a result of the further research into long term health effects of CO.

2.7 Concentrations of CO

Regional Councils and NIWA (as part of a SMF project) have undertaken a reasonable amount of useful CO monitoring in New Zealand, particularly adjacent to busy roads, and occasionally in more general urban environments. At several of the roadside monitoring sites, concentrations of CO exceeded the eight hour AAQG, sometimes quite regularly. Guideline exceedances have occurred both in major cities, such as Auckland and Christchurch, and also smaller urban areas, such as Whangarei, Tauranga and Dunedin. The CO eight hour guideline is typically under threat at the roadside when congested traffic, enclosed corridor topography and low/negligible wind speeds occur in combination.

Two particular AQM sites have been confirmed as representative of the worst case traffic pollution environments in New Zealand. These are street level sites located at Khyber Pass Road in Auckland and on Riccarton Road in Christchurch. They are typical of the conditions that give rise to air quality with the highest ambient CO concentrations. They are both main urban arterial roadways in built up and populated areas, regularly carrying high volumes of traffic and are prone to congestion. Incidences of these conditions are widespread in New Zealand's main urban centres.

For Auckland, the Khyber Pass Road carries around 33,000 vehicles, on an "annual average daily traffic" (AADT) basis. The corresponding maxima for the other major arterials are around 40,000 to 45,000. However, a feature of Auckland's natural topography is that the majority of these routes are on more exposed terrain, such as a ridgeline. None is reckoned to have the degree of containment represented by the Khyber Pass route, which is in more of a gully. So, for Auckland, this AQM site is considered to produce roadside pollution measures which are the worst to be expected.

For Christchurch, the typical AADT for the Riccarton Road corridor is around 24,000 vehicles, compared with the maxima for other urban arterials up to 34,000. In general, the containment factor from both natural (the land is flat) and artificial topography tends to be less than for Auckland and also the traffic flows are lower and less interrupted. More dominant, however, is the calming and containing effects of the local winter meteorology, which is the main cause of

the higher pollution levels. The comparison within Christchurch, of Riccarton Road against the other arterial routes, suggests that this AQM site is also a good worst case measure, despite the lower daily traffic flows than for other routes. Riccarton Road is only a two lane roadway, which is prone to rapid breakdowns in the flows with the consequent congestion effects on emission rates. It also features a narrower corridor than most between the roadside buildings. The localised importance of this containment factor is also indicated by the difference in peak levels recorded in two separate Riccarton Road AQM datasets, where the sampling points were laterally separated by only 40 metres.

Whilst this discussion might appear to focus on the Auckland and Christchurch situations, it should be appreciated that the CO pollution problem, at these levels, may not be necessarily confined to these two cities. The potential incidence may more widespread within these traffic networks, but can exist in any urban centre where the particular coincidence of traffic corridor conditions arises.

For CO, the 8-hour, 99.9 percentile maxima encountered to date at the peak kerb-side monitoring sites are 20-27 mg/m^3 as an estimated result for Khyber Pass Road and 24-37mg/m^3 for Riccarton Road (ref. Stage 1 VFECS); the corresponding AAQG limit is 10mg/m^3.

These results indicate that exceedances can arise in CO exposure for people habituating corridor locations, such as living or working close to the roadway in built up arterial traffic corridors. As stated in Stage 1, the VFECS has recognised the need to reduce ambient air concentrations of CO in order to prevent adverse effects on human health, particularly for those who may be sensitive to CO.

Although sites located close to busy roads experience high CO concentrations, it is useful to consider the extent of the area around an intersection or busy stretch of road that is affected by high CO pollution levels. For this reason, Stage 1 VFECS introduced the traffic corridor concept and designed a set of pollution profiling studies to investigate the dispersion of contaminants from roads.

The air quality measurements were undertaken by NIWA, and reported in the "Transport Emissions Study - Final Report". This measured the dispersion gradients of CO away from a number of different roadway locations, with a view to calibrating an atmospheric dispersion model. The monitoring found that:

- on the whole, CO concentrations decreased rapidly in a perpendicular distance away from the roadway

- CO concentrations were directly proportional to vehicle numbers and vehicle emission rates

- CO concentrations had a complex relationship with meteorological factors such as wind direction, wind speed and atmospheric stability

Further work on the spatial characteristics of air pollution within traffic networks is being conducted within the overall MOT VFECS programme, and is reported on separately (ref. Traffic Corridor Air Quality Survey, MOT).

Other recent work has attempted to assess the extent to which people are exposed to concentrations of CO that causes adverse health effects. A preliminary study for Auckland used pollution exposure mapping; initial results suggest that most of the population is exposed to relatively low levels of CO. However, exposure is not even across the city, occupations and age groups, and that in the worst affected area, the Central Business District, peak 8 hour levels of

CO could potentially exceed the guideline, again if in the close vicinity of busy roads and intersections. The meteorological conditions giving rise to these high levels, little or not wind, occur infrequently, but in the event that this occurs, 13,000 people living and working in the area have the potential to be affected. It was concluded that most healthy adults will not be affected and those that are, should recover quickly. However, some people, particularly the young, elderly and those not used to breathing urban air, may experience mild health effects that could emerge as headaches or drowsiness, and possibly exacerbate other conditions.

It should be reiterated that exposure mapping is still a relatively new technique to be used in New Zealand and that further studies in these areas are required. The preliminary conclusions from this work cannot be applied to other pollutants that have different characteristics and guideline values.

2.8   Required Reductions in Emissions from Vehicles

Stage 1 of the VFECS introduced the "Traffic Corridor" airshed concept for CO as a means for isolating the pollution directly associated with vehicle emissions and considering reductions in emissions required to ensure improvements in air quality. The development of this concept is described in greater detail in Appendix A of Stage 1. The relevance of this concept to other vehicle pollutants is considered in the respective pollutant sections.

The traffic corridor airshed corresponds directly with the AQM results from street level, or kerbside sampling, the location of which is designed to represent the worst case of possible human exposure to pollution directly from vehicle traffic. As there are usually no other significant sources within this vicinity, this airshed concept provides a direct correlation between pollution *concentrations*, as measured, and vehicle emission *rates* in the traffic flow. The result is a convenient means for translating the quantified air quality policy targets into the form of measure used to evaluate the emissions performance of vehicles, their individual capability and the collective output from the traffic flow within the corridor.

The currently available monitoring results indicate that a reduction in local emission rates up to 60% is required in the worst case traffic corridor situations, for the air quality to meet the lower threshold of the "alert" category for CO. Ideally, the next goal for vehicle emissions control should be to attain the "acceptable" level, which provides the margin required to prevent exceedances under even the most extreme conditions. The factors in Table 2.1 indicate that, again for these potentially worst case situations, that the emission loading would have to be reduced by up to 70% in a congested traffic network, and by over 80% for the more localised "hotspots", to maintain the "Acceptable" level, under extremes of atmospheric calms.

Table 2.1 - CO Emission Reduction Targets, %

Proposed Indicator Target Level Description	8-Hour Ave.	Peak, 99% ile Auckland Measured, Summer	Low Estimate, Winter	High Estimate, Winter	Christchurch Measured, Location 2
	mg/m3	12	20	27	37
		Percentage Reductions Required			
"Alarm" (Guideline Max.)	10.0	17	**50**	**63**	**73**
"Acceptable"	6.7	44	66	75	82
"Good"	3.3	72	83	88	91

For CO, the AQM results closely reflect the interrelationships between traffic flows, their volumes and degree of interruption, meteorology and the local topographic features in the particular corridor airshed. The sites were originally selected to be typical of the worst case conditions for traffic pollution, but before presuming that this 60% reduction measure is representative of the wider traffic situation, it is necessary to consider the equivalent balances for other main routes, traffic flows versus the "containment" factor. The emphasis is upon areas of sustained traffic flows when in proximity to human activity or residence, rather than potentially extreme and geographically isolated instances, such as a motorway interchange. Reference should be made to the companion studies on traffic corridor pollution gradients, to understand the degree of sensitivity to these factors.

3.0   PARTICULATES

3.1. Introduction

Particulates, emitted by many anthropogenic sources (including motor vehicles) and formed by reactions in the atmosphere involving gases, are pollutants of much concern about their health and environmental effects, especially in the inhalable/respirable size ranges (for which no concentration threshold for the health effects has been identified).

3.2. Characteristics of Particulates

Airborne particulates are very diverse in their chemical composition and physical properties. The principal common feature is that they exist as discrete units ranging in size from 0.005 μm (micrometre, one-thousandth of a millimetre) to about 100 μm in diameter. Particulates can be characterised by size, number, their mechanism of formation or origin, chemical composition, physical properties, or by what is measured by a particular sampling technique. In general, the composition and behaviour of airborne particulates are linked with those of the gas surrounding them.

Particulates can be referred to in various ways: as total suspended particulates (TSP), as visible smoke, or by direct or indirect descriptions of their size. Common size-related terms are the classes PM_{10} and $PM_{2.5}$ (particulate matter, with the numbers referring to the maximum particle diameter in micrometres) and 'inhalable' or 'respirable' particles. Another useful classification is between those particulates that are directly emitted (such as road dust, sea salt and fly ash), referred to as *primary* PM and particulates that are condensed or formed by reactions involving gases in the atmosphere (such as photochemical aerosols and condensed acids), referred to as s*econdary* PM. The most important types of secondary particulates formed by reactions in the atmosphere are:

- sulphates, which derive primarily from sulphur dioxide emissions;
- nitrates, which derive primarily from nitrogen oxides emissions; and
- organic aerosols, which derive primarily from volatile organic compound emissions.

3.2.1   Size Classification

The most common size-related descriptors of particulates, are coarse/fine particulates, deposited/suspended particulates and inhalable/respirable particulates. The 'cut-off' sizes between each of these classifications are not absolute, and often depend on the sampling methodology used. For practical purposes, it is usual to think of coarse particulates as those greater than 2 μm in diameter, and fine particulates less than 2 μm.

Deposited particulates are generally those greater than 20 μm, which are large enough to settle out of the air quickly and become deposited on exposed surfaces. Suspended particulates, usually referred to as total suspended particulates (TSP), are generally those smaller than 20 μm and, as the name suggests, are largely suspended in the air. Within the suspended particulates category there are two other, equally imprecise, classifications – inhalable and respirable particulates. It is these which are of human health significance. Although there is still debate about precise definitions, it is becoming increasingly common to consider inhalable particulates, those able to enter the nose or mouth under normal breathing, as generally less than 10 μm in diameter, and

respirable particulates, those able to penetrate the nasal cavity and tracheobronchial regions to enter the lungs, as generally less than 2.5 μm in diameter. Convenient short-hand terms for inhalable and respirable particulates are, respectively, PM_{10} and $PM_{2.5}$.

3.2.2   Modes

Particulates of different sizes behave differently in the atmosphere, and can be classified within three modes of behaviour – nuclei, accumulation and coarse. The first two modes directly relate to the size classification of fine particulates, whereas coarse mode relates to the classification of coarse particulates.

The smallest, of diameter less than 0.2 μm, are considered to be in the nuclei mode. This mode has the largest number of particulates but they have a short existence as they readily coagulate into the size of the next mode. These particles are primarily formed through either condensation of, or chemical reactions involving, gases.

The second category of fine particulates, in the range 0.2 to 2 μm, are considered to be in the accumulation mode. These are formed by either agglomeration of, or condensation on, nuclei mode particulates and they remain in the atmosphere for 7 to 30 days, and may be transported more than a thousand kilometres in that time. The long atmospheric residence time tends to produce a fairly even distribution across urban areas. This size range is most significant in reducing atmospheric visibility as they both scatter and absorb light.

Particulates greater than 2 μm in diameter are considered to be in the coarse mode. These either settle out or are washed out of the atmosphere within a period ranging from minutes to hours. Coarse particulates behave like a solid, primarily subject to gravitational influence. The larger it is the sooner it will drop out of the air.

3.3.   Sources of Particulates

On a global scale, PM emissions occur from a number of natural sources, such as volcanic eruptions, dust storms, pollens, natural biomass burning and sea salt spray. Although, for example, PM emissions from volcanic eruptions have had regional and, in some cases, global air quality implications, these sources are generally distributed over the entire surface of the earth and the resulting background concentrations are usually quite small.

Particulates are emitted in urban airsheds from motor vehicles, domestic fires, power plants, industrial processes and incinerators. Smoke from land clearing can have wide air quality impacts, and affect communities far removed from the burn site. Particulates formed by reactions involving gases in the atmosphere, such as sulphates, nitrates and organic aerosols, can also contribute significantly to PM pollution levels in urban airsheds. These are sometimes termed "secondary" PM.

Because PM emissions arise from a variety of sources, which differ markedly from one location to another depending upon the presence of industry and the dominant landuse, there is considerable variation in the contribution of various source types to ambient concentrations of particulates. To estimate the proportion of emissions from different sources in an area, an emissions inventory must be compiled. Some regional councils in New Zealand have developed emission inventories for their regions, and the findings are presented below.

In Auckland, the Auckland Regional Council inventory calculates that the TSP emission on an average summer week day is 13 tonnes/day, and rising to 29 tonnes/day during the winter season. For the summer day, the estimate is that 18% of the emission comes from motor vehicles, some 16% is from domestic fires, with the largest anthropogenic source in this total being the 25 % emanating from metal manufacturing processes. Other significant sources include mineral industries, food manufacture and off road and other forms of transport. The source contributions change markedly in the winter, with the domestic heating contribution to TSP emissions rising to 64% of, and accounting for, the increase in the total to 29 tonnes/day. The shares from metal manufacture and motor vehicles (the absolute quantities of which are largely unchanged) become proportionately lower, at 12% and 8% respectively. (Although the Auckland inventory uses TSP, rather than PM_{10}, it is fair to assume that most of the particulates from motor vehicles and domestic heating will be PM_{10}; only industrial sources will have a significant proportion of particles other than PM_{10}.)

In Christchurch, where the extent of domestic fuel burning in winter is more significant than in Auckland, the Canterbury Regional Council estimate home heating gives rise to approximately 82% of the PM_{10} emissions on a typical winter day, with motor vehicles 10% and industry 8%. One would expect a substantial reduction in summer of the total quantity of PM_{10} emissions (down from 13 tonne/day), with the absence of domestic fires for heating hence less chance of PM air quality exceedances.

In Hamilton, Environment Waikato estimate the percentage contribution to ambient PM_{10} from motor vehicles to range from 29% in central Hamilton to 3% in Upper East Hamilton, with home heating responsible for the majority. For Tokoroa and Te Kuiti, motor vehicles were estimated to contribute 3-4% of the PM_{10}. These figures are an annual average, and so the relative contribution from motor vehicles would be higher in the summer and lower in the winter. This inventory has not considered the contribution of PM_{10} from industry, but it is probably relatively minor for the Hamilton area, which is estimated to have total average PM_{10} emission quantity of less than 5 tonne/day, but maybe proportionately higher in towns near major industry (such as Tokoroa).

3.4.   Motor Vehicles as a Source of Particulates

As indicated above, motor vehicles are relatively minor contributors to primary emissions of PM_{10} in the ambient air of urban areas. Although there are differences depending on the presence of other sources, especially major reliance on solid fuel combustion for domestic heating, and there are considerable seasonal variations, motor vehicles are estimated to contribute no more than about 20% of primary PM_{10} emissions. However, it is important to recognise that particulates are also formed from chemical transformation of gaseous pollutants in the atmosphere and, because motor vehicles are the major contributors to most of these gases, their role is probably more significant when taking secondary source particulates also into account.

PM emissions can result from both petrol and diesel vehicles, proportionately more by mass from the latter due to the less volatile type of fuel in use, and a number of emission control technologies are emerging which can directly or indirectly reduce the emission rate. By example, the use of catalytic converters on petrol vehicles reduces particulate emissions together with other pollutants. Also, the removal of lead from petrol, and the accompanying " lead scavenger" additives (such as bromides), eliminates emissions of those types of particulates. Further improvements in petrol quality, such as reducing the sulphur content, also improves the conversion efficiency of catalytic converters. Reductions in emissions of VOCs and NO_x reduce the potential contribution of vehicles to the formation of secondary particulates by reactions in

the atmosphere. Currently, the greater concern with regard to particulates are emissions from diesel vehicles, as this type of emission has only recently come under regulatory control. This is now the main technical challenge in the transport sector within the management of air quality, internationally, along with the control of NOx.

Particulates from diesel vehicles consist of three components – carbonaceous soot formed during combustion, heavy hydrocarbons condensed or adsorbed on the soot, and sulphates/bound water. Primary soot particulates are small spheres of graphitic carbon, and are formed mainly during the diffusion burning phase of combustion, by the thermal decomposition of the fuel, and rapid polymerization of resulting unsaturates, such as acetylene, at moderately high temperatures under oxygen deficient conditions. Poor fuel atomisation and combustion quenching can also contribute. The primary particulates then agglomerate to form chains and clusters of linked particulates, giving the soot its characteristic fluffy appearance. Most of the soot formed during combustion is subsequently burned during the later portions of the expansion stroke; in a modern diesel engine less than 10% of the soot formed in the cylinder survives to be emitted. Soot oxidation is much slower than soot formation, however, and the amount of soot oxidised is heavily dependent on the availability of high temperatures and adequate oxygen during the latter stages of combustion. Poor oxygen availability in the combustion zone, or reduced combustion residence time will reduce the rate of soot oxidation, hence increase the emission rate. The combustion system will be optimised against the emission standards required of it, with the inherent compromises between the different emission types as well as engine performance and fuel efficiency. Perhaps the most significant balance is between the PM and NOx emission species, which are in direct conflict with regards to the optimised combustion conditions. Beyond this there will be the tendency for increased PM emission with poor engine service condition, particularly as affects the proper functioning of the fuel injection process, and air induction. Also, under transient engine operation there will be instantaneously higher particulate formation and emission rates.

Apart from soot itself, most of the particulate mass from a diesel engine consists of heavy hydrocarbons adsorbed or condensed on the soot. This is frequently referred to as the soluble organic fraction, and is derived partly from the lubricating oil, partly from unburned fuel and partly from compounds formed during combustion; the relative importance of each of the sources varies from engine to engine, fuel quality and engine operating mode. The soluble organic fraction of particulates from all combustion sources, such as vehicle engines and domestic fires, include many known or suspected carcinogens and otherwise toxic air contaminants, such as polynuclear aromatic hydrocarbons (PAH), PAH derivatives, aldehydes and other oygenated hydrocarbons.

Diesel fuel has traditionally contained more sulphur than petrol, as only with the recent emissions regulatory attention has there been a drive to refine down the natural petroleum sulphur content. As sulphates comprise a significant proportion of the particulate mass, as measured, removing sulphur from the fuel makes a direct contribution to reducing PM emission The potential for secondary particulates to form from gaseous sulphur oxide emissions will also be reduced as will the formation of various metallic sulphates. Also, this avoids the adverse tendency of oxidation catalysts, now being fitted to diesel engines for VOC control, to actually increase PM emission by promoting the oxidation of fuel sulphur to the more weighty sulphates.

3.5.   Effects of Particulates

Being made up of solid material, particulates differ from gaseous pollutants in a number of important ways. The effects associated with particulates depend on the aerodynamic diameter of

the individual particulates. The adverse effects of deposited particulates, those greater than 20 µm and mainly mineral in origin, are primarily the soiling of structures, which leads to increased maintenance, and reduced plant production or crop damage. Fine particulates are of human health concern and, as previously mentioned, are also associated with reduced atmospheric visibility. Inhalable particulates, those generally less than 10 µm (PM_{10}), may penetrate the upper defenses of the respiratory tract and deposit in the lungs. Respirable particulates, those generally less than 2.5 µm ($PM_{2.5}$), can be carried to the alveoli, and increasing concern is being focused on the health effects associated with these particulates.

3.5.1   Health Effects.

The predominant population groups at risk to exposures of inhalable/respirable particles are:

- healthy children;
- adults with obstructive lung disease; and
- asthmatics.

Over the past decade evidence that human exposure to inhalable particulates (PM_{10}) can result in significant increases in both morbidity and mortality has become overwhelming. Widely dispersed populations around the world have been assessed and usually show similar response patterns in every instance where appropriate statistical analyses have been undertaken. It is now possible to enumerate the health effects that have, on epidemiological, clinical and toxicological grounds, been currently identified as being related to short-term increases in PM_{10}. These associated adverse health effects include:

- Increases in total mortality ('all causes'), as well as in mortality from respiratory or cardiovascular disease;
- Increases in hospital admissions for respiratory and cardiovascular conditions;
- Increases in the daily prevalence of respiratory symptoms;
- Increases in hospital casualty and medical surgery visits for asthma and other respiratory conditions;
- Increases in functional limitation as indicated by restricted activity days or, in the case of children, by increased frequency of absence from school; and
- small decreases in the level of pulmonary function in healthy children, and in adults with existing disease.

International studies have consistently shown a 1% increase in daily mortality (all causes) per 10 µg/m^3 increment in daily PM_{10}. For respiratory and cardiovascular mortality, the observed increases are higher with values of 3.4% and 1.4% per 10 µg/m^3 PM_{10}, respectively. Significant associations have also been observed between PM_{10} and hospital admissions and emergency room visits for respiratory and cardiovascular disease. Increased PM_{10} has also been found to exacerbate asthma.

Table 3.1 summarises the observed health effects associated with PM_{10} and the dose-response relationships.

There are population subgroups which are clearly more sensitive to PM_{10} exposure, in that they experience more severe adverse health effects for a given particulate exposure. These subgroups include the elderly and those individuals suffering from pre-existing heart or lung disease. There is also evidence to suggest that young children may be more sensitive, leading to an increased frequency of respiratory tract infections, coughing and wheezing.

Statistical evidence suggests that the observed adverse health effects of PM_{10} appear to occur independently of the presence of other pollutants such as ozone, nitrogen dioxide and probably sulphur dioxide, although the reverse does not apply. What that means is, that whilst there is evidence to suggest that PM_{10} can impact significantly as a major confounder on the observed responses to other pollutants, there is no satisfactory evidence that the effects of PM_{10} are influenced by the other pollutants.

Based on epidemiological data, there is no evidence that threshold concentrations can be described for PM_{10} below which it is not possible to detect any population health impacts. Currently the evidence that particulates of some size ranges ($PM_{2.5}$ or $PM_{1.0}$), within the PM_{10} fraction, might be more deleterious to health than other size fractions is inconclusive, although there is increasing evidence to suggest that the respirable ($PM_{2.5}$) fraction may be the major area of concern with regard to adverse health effects.

Table 3.1 - PM Health Impacts

Health Impact	Percentage Change in Health Indicator per 10 $\mu g/m^3$ increase in PM_{10} (24 hour average)
Daily Mortality (all causes)	1.0
Respiratory Deaths	3.4
Cardiovascular Deaths	1.4
Hospital Admissions	
Respiratory Disease	2.0
COPD	3.3
Pneumonia	1.4
Heart Disease	0.4
Exacerbation of Asthma	3.0
Increase in Respiratory Systems	
Lower Respiratory	3.0
Upper Respiratory	0.7
Cough	1.2

3.5.2   Effects on Vegetation.

Deposited particles can also adversely affect vegetation. Severe deposits of particulates can result in a decline of photosynthesis with the covering acting as a barrier to sunlight. Most deposited particulates are mineral in origin, rather than of combustion origin, and calcium oxide and calcium hydroxide, for example, have been shown to break down the leaf cuticle, which leads to the release of fatty acids. Fertiliser particles produce similar direct effects, and there is also the possible indirect effect of changes in the alkalinity of the soil, which may result in reduced (or enhanced) plant growth.

Particulates such as elemental carbon may obstruct the stomata of leafs leading to a reduction in plant growth, possibly from the prevention of normal gas exchange. Secondary particulates

formed from reactions in the atmosphere involving gases - sulphates, nitrates and organic acid aerosols - are phytotoxins. Chronic low dose exposures to these pollutants can cause leaf necrosis, nutrient leaching and irregular leaf development.

Particulates, especially acid aerosols, are known to cause discoloration, erosion and leaching of concrete and masonry. Accelerated corrosion of metals is often experienced when particulates have a high concentration of soluble chemicals. Particulates larger than about 5 μm may also lead to the erosion of metals if their transport velocity is significant. The effects of particulates on paints and other surface finishes include discoloration, abrasion, increased drying time and reduced life span. Discoloration is also an impact of particulates on plastics and elastomers, along with cracking and loss of tensile strength. Whilst acid aerosols can cause notable deterioration to textiles, solid particulates create indirect damage through abrasion and more frequent attempts to remove soiling.

3.5.3   Effects on Visibility.

The ability of fine particulates to both scatter and absorb light means that they contribute significantly to reduced visibility in urban areas. Degraded visibility affects the aesthetic value of the environment and can impact on tourist perceptions of New Zealand's "clean green" image. Maximum light scattering occurs when the diameter of the particulates is equivalent to the wavelength of light. Therefore, particulates in the size range 0.1 to 1.0 μm exhibit more light scattering, and hence more visibility degradation, than either smaller or larger particulates. Whilst all particulates scatter light, light absorption is due significantly to the presence of elemental carbon.

A more local air quality issue is the objectionable PM emission in the form of visible smoke from, for example, a smoky vehicle exhaust or from a chimney stack, caused by incomplete combustion of the fuel. Such emissions can invoke justifiable public concern, not only because of the adverse impact on aesthetic values but also by raising the perception over the potential health and environmental effects of the emissions.

3.6.   Air Quality Guidelines for Particulates.

In 1994 MfE established AAQGs for PM_{10} of 120 μg/m^3 (one day-24 hours- average) and 40 μg/m^3 (one year average). These guidelines were based on the then proposed (but never adopted) Victorian EPA air quality objectives for Class 1 indicators, because it was considered they had been developed on the basis of more recent health evidence than the values then being recommended by the World Health Organization (WHO). Since then the situation has changed greatly.

As previously mentioned, over the past decade evidence from epidemiological studies in widely dispersed populations around the world have overwhelmingly found that human exposure to inhalable particulates (PM_{10}) can result in significant increases in both morbidity and mortality. In response to that most jurisdictions have markedly reduced their guidelines/standards for PM_{10}, with 50 μg/m^3 (one day average) increasingly becoming the international norm. For example, the standard for PM_{10} in the proposed Australian National Environment Protection Measure for Ambient Air Quality is 50 μg/m^3 (one day average). Both the UK and the European Union have also adopted that standard, but some care is needed because it is specified as a "running average" (presumably the averaging of some shorter-term, continual measurements), whereas the usual specification (based on versions of the 'hi-vol sampler') is for a calendar day average. The Auckland, Waikato, Canterbury and Otago Regional Councils all observe a one day average

concentration of 50 μg/m^3 to assess the results of ambient air monitoring for PM$_{10}$, and it is expected that this will be formalised in their regional air quality plans.

A notable exception to this emerging international consensus is the World Health Organization (WHO). The absence of a threshold concentration for fine particulates (which, incidentally, is also the case for ozone and lead) led WHO to adopt the position of not being able to recommend a guideline for PM$_{10}$. The United States, amongst others, have addressed the threshold issue (and most jurisdictions have also had no difficulty with respect to ozone and lead). The recently revised United States standards for particles include 65 μg/m^3 (one day average) and 15 μg/m^3 (one year average) for PM$_{2.5}$.

This new interest in PM$_{2.5}$, being led by the United States, is of considerable importance, but at this time it is really only an indicator of the possible area of focus for the future. In the meantime, it is appropriate to use air quality guidelines for PM$_{10}$.

There are three other measures of particulates used in New Zealand, for the purpose of assessing the results of additional air quality monitoring carried out. These are 60 μg/m^3 (one week average) for total suspended particles (TSP), 125 μg/m^3 (one day average) for 'smoke' in association with sulphur dioxide, and 4 g/m^2/30 days for particulate deposition rate.

3.7.   Concentrations of Particulates.

There is an array of different methodologies used in New Zealand to measure ambient concentrations of particulates. A consequence of that is the difficulty in directly comparing results gathered at different locations, by different methods .

The preferred standard methods for measurement of PM$_{10}$ are those set out in Standards Association of Australia AS3580.9.6-1990 and AS3580.9.7-1990. Both are gravimetric methods utilising collection on a large glass fibre filter, and produce calendar day average results, but differ on the sample collection system used. The former is a high volume sampler with a size selective inlet head, whilst the latter uses a dichotomous sampler for collection. The 'hi-vol sampler' without the size selective inlet can be used to collect total suspended particulates (TSP). There is also a scaled down version of the hi-vol sampler (actually a medium volume sampler) which was specifically developed for TSP measurement in New Zealand. This gravimetric method uses a small glass fibre filter and a proportional decrease in the sample air volume (to obtain a similar linear velocity through the collection media), and the sampling period is normally one week.

Various semi-continuous, non-gravimetric devices are also used in parts of New Zealand for measurement of PM$_{10}$ (with a size selective inlet head) and, in some cases, TSP (without the size selective inlet). These include:

- the TEOM (tapered element oscillating microbalance) Monitor, which measures the mass of collected particulates by the change in frequency of oscillation of the tapered element;
- the Beta Attenuation Monitor, which measure particulates by attenuation of beta radiation; and
- the Grimm Monitor, which measures particulates by light scattering.

There are also the long-standing optical measurements of 'smoke', in association with sulphur dioxide, by a British Standard method (BS 1747: Part 2: 1969), which measures the darkness of the stain of collected particulates by its light reflectance. The reflectance is converted to a mass

loading, by means of an empirically derived standard curve. Although the method now calls for use of what is commonly referred to the OECD-curve, this European-derived curve is not particularly relevant to New Zealand conditions. The method is highly dependent of the physical characteristics of the particulates, especially the colour. New Zealand particulates in urban areas are relatively light in colour, comprising more dust than black coal smoke, and although some work was done to develop New Zealand derived curves, it is not apparent what approach in this regard has been taken for recent monitoring by this method, which is continuing at at least one site (Penrose in Auckland). It has been shown that the method measures particulates of a size less than about 4.5 μm.

There is also some monitoring carried out for particulate deposition, usually by resource consent holders of potentially dusty industries such as quarries and mineral processing plants. These generally use the method set out in British Standard 1747: Part 1: 1969.

A great deal of monitoring for particulates has been done, at many sites in New Zealand, some dating back in the 1960s. A major problem, however, in assessing long term trends in ambient concentrations of particulates is that non-standard methods have been until recently, and in some locations are still being, used. The results gained from these methods (which are not specific to PM_{10}) are not directly comparable to the standard methodologies.

A long-standing (since 1988) PM_{10} data set is the monitor located in the inner city suburb of St Albans, Christchurch and operated by the Ministry of Health as part of the World Health Organization's Global Environmental Monitoring System. Prior to 1994 this site used a Beta Attenuation Monitor, which then failed and was replaced with a TEOM Monitor (in 1996 a replacement Beta Attenuation Monitor was installed, and operated for a time in parallel with the TEOM). In 1995 two additional PM_{10} monitors, both using TEOM, were installed in the residential suburbs of Hornby and Beckenham. In 1996 another PM_{10} monitoring station was established, this time using beta attentuation, at Opawa (a residential area adjacent to an industrial area).

Although 1996 was apparently a fairly mild winter and consequentially it was a relatively 'low pollution year', the following Table 3.2 gives the highest peak recordings and number of exceedances of the PM_{10} air quality guideline of 50 μg/m^3 (one day average). The results for the Opawa site have been adjusted downwards, because the comparative study at the St Albans site found the Beta Attentuation Monitor consistently measures higher PM_{10} concentrations than does the TEOM Monitor.

Table 3.2 - PM10 Ambient Air Measurements

AQM Site	Max. 24-hour ave. (99%ile), μg/m^3	Exceedances of 50 μg/m,^{3} no. of days in 1996
St Albans	108 (1995) 96 (1996) 141 (1997)	28
Beckenham	48 (1995∗) 65 (1996)	8
Hornby	45 (1996) 62 (1997)	2
Opawa	125 (1995∗) 132 (1996∗) 101 (1997)	12

∗ 6 months only

In Auckland similar differences in methodologies exist, and a relatively short period of useful monitoring for PM$_{10}$ concentrations has been carried out. PM$_{10}$ monitoring using the standard hi-vol sampler with a size selective inlet head has operated in the industrial suburb of Penrose since 1994. A concentration of 50 μg/m^3 (one day average) is exceeded 2-3 times a year with maximum results of 101μg/m3 and 77μg/m3 occurring at the Penrose site during winter 1994 and 1995, respectively. In 1995 the Auckland Regional Council installed a TEOM Monitor in the residential suburb of Takapuna.

One of the most obvious features of the monitoring results for particulates in New Zealand urban airsheds, irrespective of the measurement method used, is the considerable seasonal variations in the concentrations measured. For example, an analysis of the PM$_{10}$ monitoring data at the St Albans, Christchurch site found an average concentration in spring/summer months (October to March) of 13 μg/m^3, whereas in autumn/winter (April to September) the average is 31 μg/m^3. A concentration of 50 μg/m^3 (one day average) is exceeded only in winter, but, as indicated above, quite frequently. The reasons for this are fairly obvious, being the period during which reliance on fuel burning for home heating is greatest. In addition, the calm weather patterns during those months favour the build-up of pollution because of poor dispersion.

Notwithstanding all of the difficulties with the varying monitoring methodologies etc, the results indicate that ambient PM$_{10}$ poses a significant risk to human health in certain locations in New Zealand, most notably in winter months due primarily to domestic fires.

3.8. Required Reduction in PM Emissions.

Emission inventories show that throughout New Zealand the greatest contributor to ambient PM$_{10}$ is domestic fires. This is confirmed by the "winter smoke" phenomenon experienced in many urban centres, especially Christchurch. Motor vehicles, as sources of primary emissions of PM$_{10}$, are minor contributors. It has been argued that even if there was a 100% reduction in emissions of particles from motor vehicles, ambient levels of PM$_{10}$ would show little change. However, this is too simplistic because other vehicle emission species, that act as precursors to the formation of secondary particles, also need to be considered.

For particulates, it is important to recognise the distinction between reductions in directly emitted PM and reductions in concentrations of PM in the atmosphere. Changes in particulate air quality depend both on changes in emissions of particulates and on changes in emissions of gaseous pollutants, such as sulphur dioxide and nitrogen oxides, which are later converted to particulates through chemical transformation in the atmosphere. This highlights an important and unique feature of particulates as an ambient pollutant. More than any other air pollutant, reductions in particulates are actually largely achieved through reductions in a wide variety of pollutants. In other words, controlling particulates means controlling "air pollution" in a very broad sense. Reductions in sulphur dioxide, nitrogen oxides, volatile organic compounds and directly-emitted particulates, achieved by such things as specifically targeted programmes for motor vehicles and the conditions of air discharge consents to industrial premises, will result in significant reductions in both nation-wide and certain airshed concentrations of particulates.

Degraded visibility caused by fine particulates affects the aesthetic value of the environment and can impact on tourist perceptions of New Zealand's promoted image. Another, more local factor, is the visually objectionable impact of emissions of dense smoke, which tend to be more readily observed when in close proximity to individual vehicles in a traffic flow as opposed to a high level and stationary chimney stacks. It is important that the visible smoke nuisance is also addressed as part of policy to manage emissions from motor vehicles, for its credibility in the eyes of the public. The importance of public support for the success of an emission reduction strategy cannot be understated; failure to effectively control emissions of visible smoke from vehicles may result in public indifference and even opposition to other measures.

Because there is a limited understanding in New Zealand about the formation of secondary particulates and their sources, it is very difficult to establish cause and effect relationships necessary to determine the extent and significance of secondary particulate formation and a specific reduction factor for vehicle emissions of precursor gases. Therefore, at this stage, the VFECS should aim to reduce emissions of precursor gases as far as practicable without compromising the other, more specific reduction targets. For the purpose of reducing nuisance effects of smoky exhausts and for reducing the overall contribution from vehicles to ambient PM_{10}, the VFECS should aim to minimise the occurrence of excessive "visible" exhaust emissions from all vehicles.

4.0   NITROGEN OXIDES

4.1.   Introduction

Nitrogen oxides are important gaseous pollutants in their own right as well as being precursors of photochemical oxidants and particulates. They are primarily formed by the oxidation of nitrogen in air (and also to some extent as is present in fuels) at high combustion temperatures, and are present in elevated concentrations in some urban airsheds mainly as a result of human activities such as from motor vehicles.

4.2.   Characteristics of Nitrogen Oxides

Although there are seven oxides of nitrogen that theoretically may be present in ambient air, nitric oxide (NO) and nitrogen dioxide (NO_2) are the most important in the context of local air quality. Nitrous oxide (N_2O), the only other oxide found in appreciable quantities, plays an important role in the enhanced " greenhouse effect" as well as being involved in other reactions in the upper atmosphere, but it is of far lesser significance in the lower atmosphere.

For most combustion processes nitrogen oxides are emitted primarily in the form of NO. NO discharged into the atmosphere transforms into NO_2. The speed with which this reactions occurs depends on atmospheric conditions, such as temperature and the quantity of ultra violet light, and the presence of oxidants such as ozone. This reaction is considered to be the most important anthropogenic route for NO_2 production. It is therefore important that emissions of NO as well as NO_2 are considered. Of the two contaminants, NO_2 has the greater potential to cause adverse effects on the environment and human health. Wherever possible, ambient air measurements of both NO_2 and NO should be made. Because of the close relationship between NO and NO_2, they are commonly given in combination the symbol NO_x.

In addition to their role as important gaseous pollutants, nitrogen oxides are reactive and have major roles in photochemical reactions which are associated with the formation of photochemical oxidants and particulates. Excess levels of ozone in the lower atmosphere are formed by the photolysis of nitrogen dioxide. Other products of photochemical reactions include nitric acid (HNO_3), peroxyacetyl nitrate (commonly written as PAN) and various organic particulates containing nitrogen. In addition, NO_x in the lower atmosphere plays an important role in forming inorganic particulates by chemical reactions, and these particulates also have impacts on health and visibility. For example, NO_2 reacts with sea salt (NaCl) to form fine particulates such as sodium nitrate ($NaNO_3$).

NO_x is mainly removed from the atmosphere via oxidation to nitric acid (HNO_3), followed by wet precipitation and dry deposition. The addition of nitrate (and ammonia) by rainwater to the plant soil ecosystem constitutes an important source of fixed nitrogen to the terrestrial biosphere. Dry deposition is also important as a sink, NO_x being readily absorbed by materials covering the earth surface. In excess though, wet and dry deposition of HNO_3 are partially responsible for what is called " acid rain".

4.2.1   Nitric Oxide (NO)

NO is a colourless, odourless and tasteless gas. NO is produced during fuel combustion in motor vehicles, thermal power stations and industries which involve boilers and other intensive combustion processes. In the high temperature zones of the combustion process, nitrogen in air

and the fuel reacts with oxygen to form NO. NO is then oxidised to NO_2 primarily through photochemical reactions, more rapidly in the presence of oxidants such as ozone (O_3). NO is also slowly oxidised directly by oxygen and photochemically by hydrogen species such as the hydroxyl radical (OH), hydrogen dioxide (HO_2) and hydrogen peroxide (H_2O_2). NO is not generally considered to cause adverse effects on the environment and it does not have an AAQG. For the purposes of practical air quality management, it is sometimes assumed (as a worst case situation) that all of the NO will be oxidised to NO_2. It is convenient therefore to consider NO as a pollutant directly emitted from sources and NO_2 as essentially a pollutant formed by subsequent reactions in the atmosphere. As a consequence, NO_x emissions are an important consideration in the air quality of regional airsheds, as well as more local air quality issues.

4.2.2   Nitrogen Dioxide (NO_2)

NO_2 is a reddish-brown gas with a pungent, irritating odour. It reacts with water and other compounds in the air to form nitric oxide, nitrogen trioxide, nitrate, nitrogen pentoxide, nitrous acid, nitric acid and peroxyacetyl nitrate. NO_2 is one of the more invidious pollutants. It is irritating and corrosive. NO_2 has the potential to cause adverse effects on human health and on the wider environment.

As discussed earlier, the concentration of NO_2 in ambient air largely depends on emissions of NO and the atmospheric conditions that control its subsequent conversion to NO_2. The rate at which this occurs can vary quite significantly. It has been found in Auckland that the ratio of NO to NO_2, which indicates the extent of conversion from NO to NO_2 at the time of measurement, depended on the proximity of the monitoring site to a road way and the atmospheric conditions. For example, on some summer days at a monitoring site in Penrose, NO concentrations were equivalent to NO_2 concentrations indicating rapid conversion. However, during lower temperatures and lower ultra violet light levels in winter, the conversion to NO_2 was far slower, with the concentration of NO being between 4 to 10 times higher than NO_2.

NO_2 absorbs light in the yellow to blue end of the visible spectrum and the near ultraviolet. The yellow brown haze occasionally seen over Auckland and Christchurch is likely to be due, in part, to nitrogen dioxide and some of the light scattering particulates it helps generate.

4.2.3   Nitrous Oxide (N_2O)

N_2O is a colourless, slightly sweet, non-toxic gas present in the natural environment. Various human activities are causing its concentration to increase rapidly. N_2O has been used as an anaesthetic in minor surgery and dentistry. N_2O is a greenhouse gas, and has been associated with photochemical reactions involving the ozone layer in the upper atmosphere, but because of its low reactivity in the lower atmosphere it is largely ignored in considerations of local air quality management.

4.3.   Sources of Nitrogen Oxides

On a global scale, the majority of NO_x is produced by natural sources including soil bacterial activity, lightening discharges, natural biomass burning, ammonia oxidation, oceans and geothermal activity. However, as these sources are distributed over the entire surface of the earth the resulting background concentrations are very small.

The majority of NO and NO_2 in urban areas comes from the combustion of fuels. This includes combustion of petrol and diesel in motor vehicles, domestic burning of wood, coal, natural gas

and LPG, marine, rail and aviation activities and certain industrial processes (such as the manufacture of nitric acid and arsenic based chemicals). The proportion of NO to NO_2 in the discharge from combustion sources is typically 90-95% NO. There is therefore little NO_2 that is discharged directly into the air.

N_2O emissions result mainly from agricultural soils and combustion processes. Although internationally the use of nitrogenous fertiliser is seen as important, apparently in New Zealand (because of our legume-based pastures) this is not the case. In urban areas emissions of N_2O are minor, being mainly from combustion processes, including trace amounts from petrol motor vehicle exhausts as a result of formation in the oxidation-reduction process of a 3-way catalytic converter.

The proportion of NO_x from different sources will vary spatially and depend significantly on the nature of the sources in a particular area. To estimate the proportion of emissions from different sources in an area, an emissions inventory must be compiled. Some regional councils in New Zealand have developed emission inventories for their regions, and the findings are presented below.

For Auckland, the Auckland Regional Council's inventory estimates that approximately 81% of NO_x emissions on an average summer week day come from motor vehicles. The next most significant source is metal manufacture at 8%. Other minor sources include aviation, rail transport, off-road vehicles, and domestic fuel combustion. The emission proportions are similar in winter months; emissions from motor vehicles remain at around 80%, but there is a minor increase in the NO_x emissions from domestic fuel burning of 1.9% (summer) to 2% (winter).

The Canterbury Regional Council inventory indicates that motor vehicle emissions account for 91% of the NO_x discharged into the air on a typical winter day, in Christchurch. Home heating accounts for 4% and industry 6%. The percentage from motor vehicles is likely to increase in summer with reduced emissions from domestic fires.

In Hamilton, Environment Waikato estimate the percentage contribution to ambient NO_x from motor vehicles to range from 98% in central Hamilton to 88% in Upper East Hamilton, while home heating emissions is responsible for the remainder. Although, these figures are an annual average, the results are not significantly different during the winter months when home heating emissions increase. This inventory has not considered the contribution of NO_x from industrial sources, although they are expected to be relatively minor, except where thermal power stations exist (such as Huntly).

Human exposure to NO_x also comes from other sources such as gas cookers in the home and poorly ventilated fuel burning heaters. Point sources emissions of NO_x such as thermal power station plumes have generally decreased in recent years with the introduction of low NO_x burners; in Auckland, however, they are still considered to be a significant source.

4.4.   Motor Vehicles as a Source of Nitrogen Oxides

As indicated above, motor vehicles are, proportionately, the most significant source of NO_x in the ambient air over urban areas in New Zealand. Depending on the presence of other sources, such as thermal power stations and industry with major combustion processes, motor vehicles are estimated to contribute between 80 to 95% of total NO_x emissions.

Nitrogen oxides from motor vehicles, as with all combustion processes, are formed during coinciding conditions of high temperature and pressure and excess air, and the residence time at these conditions. Peak temperatures and pressures are affected by a number of engine design and operating variables, and so therefore is the quantity of NO_x in the (otherwise uncontrolled) exhaust. There are significant differences in this regard between petrol and diesel engines, with proportionately more NO_2 in the exhaust of a diesel vehicle than a petrol vehicle, due to the excess air combustion system of the diesel engine, but with NO still the predominant form of NO_x for both. Another differentiating feature is that NOx output increases with higher engine load, which is the workhorse role traditionally performed by the diesel engine (as petrol engines tend to be confined to light duty vehicle applications), hence the usual association between NOx and diesels.

Although design modifications and changes to operating variables have significantly reduced emissions of NO_x from both petrol and diesel engines, only for petrol have further large reductions in emissions been achieved by after-engine (that is, exhaust pipe) treatment methods. Oxidation-reduction "three-way" catalytic converters can markedly reduce (by up to 70-90%) emissions of NO_x from petrol engines, but they are not applicable to the lean burn stoichiometry inherent to diesel engines. The control of NOx in diesel engines is a current focus of vehicle emission standards, along with the control of particulate; the two exhibit natural trade-offs in terms of the usual techniques available for their control. However, in responding to the future emission standards other approaches are now being introduced, such as exhaust gas recirculation, specialised "De-NOx" catalysts and fuel treatments.

4.5.   Effects of Nitrogen Oxides

4.5.1   Health Effects

The predominant population groups at risk to exposures of NO_2 are:

- young children;
- asthmatics of all ages, but especially children; and
- adults compromised by chronic cardiac and respiratory disorders.

NO_2 appears to exert its effect on the human organism (namely, the lung) both directly and indirectly. Direct effects lead to an inflammatory reaction on the epithelial surfaces in the human lung. This irritation of the respiratory system causes increased frequency of coughing, wheezing or breathlessness. Asthmatics and people suffering from chronic lung disease are the most highly affected population group due to changes in lung function and airway responsiveness. As for indirect effects, NO_2 in the human respiratory system causes an impairment of immune defence mechanisms in the lung, resulting in an increase in susceptibility to infections and asthma attacks, particularly in young children. It can also increase the severity of such episodes and increase reactivity to natural allergens.

NO_2 appears to contribute both to morbidity and to mortality, especially amongst susceptible groups such as young children, asthmatics, and in individuals with chronic inflammatory airway disease (chronic bronchitis and related conditions). Epidemiological studies have found significant effects of NO_2 on hospital admissions, emergency room visits, and respiratory illness and mortality. In particular, increases in NO_2 have been found to be primarily responsible for increases in admissions for childhood asthma and for heart disease in the elderly. NO_2 has been demonstrated to have synergistic effects with other known irritants, such as photochemical oxidants, sulphur dioxide and particles.

The current Lowest Observed Adverse Effect Level for short-term exposures to NO_2 is in the range 400 to 600 μg/m³, but there is an increasing body of data to suggest that longer term exposures to concentrations of about 80 to 150 μg/m³ during early and middle childhood can lead to the development of recurrent upper and lower respiratory symptoms.

4.5.2   Effects on Ecosystems

NO_2 is a phytotoxin, and is reported to be toxic to plants at short-term concentrations of about 120 μg/m³. If ozone and sulphur dioxide are present, pronounced synergistic effects are observed. Chronic low dose exposures to NO_2 have been shown to produce growth suppression, chlorosis and necrotic lesions in sensitive plant species.

NO_2 can be corrosive to building materials at high concentrations and, in the presence of moisture, through its formation of nitrous and nitric acids. High nitrate levels in dust can also cause metal corrosion.

The reaction products of NO_2, in particular nitric acid (HNO_3), have been a major contributor to the transcontinental "acid rain" problems of North America and most of Europe. Acid rain deposition adversely affects plants through direct exposure and the alteration of soil acidity. Because of it's isolation, New Zealand is considered to be relatively free of susceptibility to acid rain of this nature.

4.5.3   Effects on Visibility

The ability of NO_2 to absorb visible light and produce (through atmospheric reactions) aerosols with high light scattering abilities means that it can contribute significantly to reduced visibility in urban areas and play an important role in the formation of regional hazes and photochemical smog. NO_2 is likely, for example, to be responsible for the brownish colouration of the haze occasionally observed in Auckland and Christchurch.

Visibility degradation is currently the focus of a number of studies in New Zealand. Degraded visibility caused by air pollution affects the aesthetic value of the environment and can have impacts on New Zealand's image. It may therefore have impacts upon tourism and New Zealand businesses. The causes of visibility degradation are known to be fine particles, especially those less than 1 micron in diameter, with other contaminants such as VOCs and NO_2 contributing other characteristics such as the colour of the haze. However, further investigations are required to identify the main sources of visibility reducing contaminants and the atmospheric conditions that give rise to their formation.

4.6. Air Quality Guidelines for Nitrogen Oxides

To protect the New Zealand population from the potential health effects of NO_2, MfE established in 1994 AAQGs for NO_2 of 300 μg/m^3 (one hour average) and 100 μg/m^3 (one day average). These guidelines were based on the then Victorian (Australia) EPA Draft Recommendation for Class 1 indicators, which at the time were more stringent than the values being recommended by the World Health Organization (WHO).

WHO has since revised its Air Quality Guidelines. It now recommends values for NO_2 of 200 μg/m^3 (one hour average) to protect sensitive asthmatics in particular, and a one year average of 40 μg/m^3 to protect all at risk population groups from chronic exposures. WHO also recommends 30 μg/m^3 of NO_x (one year average) to protect vegetation. The Auckland and Waikato Regional Councils have both proposed use of the WHO one hour average guideline, and it is expected that this will be formalised in their regional air quality plans. This value (200 μg/m^3) is increasingly becoming the international norm for one hour average concentrations. Consequently, for the purposes of assessing ambient concentrations of NO_2, it would be prudent to use this value, as well as the MfE AAQGs.

4.7 Concentrations of Nitrogen Oxides

As previously mentioned, NO_x emissions are an important consideration in the air quality of regional airsheds, as well as local air quality issues, which needs to be considered in monitoring protocols. Unfortunately, in New Zealand this does not appear to have been the case, to date. Because it is the measured concentrations of NO_2 that are compared with an AAQG, the location of the monitor is usually extremely important.

Evaluation of NO_x monitoring data is complicated by its atmospheric reactivity. Most NO_x is emitted from combustion processes as NO, which is subsequently oxidised to NO_2. The rate at which this conversion occurs depends on the presence of oxidants in the atmosphere, such as ozone, and prevailing meteorological conditions. Then NO_2 participates in various photochemical reactions, the extent of which again depends on the prevailing meteorological conditions. The international experience is that, under certain weather conditions, NO_2 concentrations can be considerably higher at monitoring sites further away from busy roads than at those directly adjacent.

Although the situation is complex, ambient NO_2 concentrations tend to be more evenly dispersed from major sources such as traffic corridors. This contrasts with carbon monoxide from traffic, which tends to be concentrated in the immediate vicinity of the roadway corridors.

The standard method for measurement of NO_x is that set out in Standards Association of Australia AS3580.5.1-1993. That is, continuous measure by chemiluminescence analysis. An air sample is brought into contact with ozone produced by an ultraviolet light; the reaction between the two produces an emission of light (chemiluminescence). The intensity of the light is proportional to the concentration of NO present. In a parallel stream, a sample of air is first passed through a catalytic converter to reduce all of the NO_x to NO, and then the concentration of NO is measured by the same process as for the untreated air stream. The difference between the NO_x concentration and the NO concentration is assumed to be the NO_2 concentration.

There are only a few sites in New Zealand where NO_x has been monitored on a continuous basis using this standard method, and for sufficiently long-term periods. The most useful information has been collected in Auckland and Christchurch. The monitoring has been done at roadside

sites, industrial sites, residential/light industrial sites, residential/commercial sites and a site on the edge of the urban area. Quite understandably, the highest concentrations of NO_x (but possibly not reflecting maximum concentrations of NO_2) have been recorded close to busy roadways.

There are two monitoring sites in Auckland for NO_x operated by the Ministry of Health as part of the World Health Organization's Global Environmental Monitoring System. These sites are located in Penrose (a predominantly industrial area) and Mount Eden (a residential/commercial area). The Auckland Regional Council also monitored nitrogen oxides on Dominion Road for an 18 month period from fourth quarter 1994 to first quarter 1996. Examination of emission inventory data in the vicinity of these monitoring sites show that over 90% of the NO_x emissions at the Dominion Road and Mount Eden sites are due to motor vehicle emissions. The Penrose site is influenced by industrial emissions in the area, but motor vehicle emissions still account for 80% of the NO_x emissions.

Dominion Road therefore represents a site influenced almost solely by motor vehicles, being immediately adjacent to major arterials, and therefore is probably the most relevant "worst case" situation for considering the impacts of motor vehicles on local air quality. The Mount Eden site is further away from arterials and more represents neighbourhood background levels. The Penrose site represents neighbourhood background levels in a predominantly industrial site. The Auckland Regional Council commenced monitoring for NO_x in 1997 at Musick Point, a site on the harbour edge of the urban area of Auckland (and used previously for the monitoring of photochemical oxidants). The location is 11 km down the prevailing SW wind direction from the Penrose industrial area.

Although they represent the best monitoring data set available, in reality this NO_x monitoring in Auckland provides only a limited amount of useful information. The data for Dominion Road covers only the 18 month period from fourth quarter 1994 to first quarter 1996. For the Mount Eden and Penrose sites there were large gaps (over two-thirds of data) in the period 1991 to 1993, making it unsuitable for reporting. The relatively short time span of much of the monitoring, especially at Dominion Road and Musick Point, makes trend analysis difficult. However, emission inventory projections may be useful as surrogates.

The single monitoring site for NO_x in Christchurch, at St Albans, is also operated by the Ministry of Health as part of the World Health Organization's Global Environmental Monitoring System. As with the two Auckland sites, the standard chemiluminescence method is used. The site is located between Packe Street and Madras Street, in what can be described as a residential/light industrial site. It is about 30 m from a moderately busy road, somewhat closer than the Mount Eden site in Auckland, but it still can be considered to approximate neighbourhood background levels rather than direct emissions from motor vehicles. The existing emission inventory data in the vicinity of the monitoring site indicates that about 90% of the NO_x emissions are due to motor vehicles. The monitoring for NO_x at the St Albans site has been relatively continuous since it commenced in 1988. In recent years the only significant problem was some loss of data in August and October 1995. The level of quality assurance of the monitoring data has been satisfactory, at least for the past half dozen years.

When reviewing the results of NO_x monitoring in the context of considering emission reduction requirements, the 99.9 percentile data is appropriate for the one hour averaging period data. However, one day averages are taken on a calendar day basis (midnight to midnight), meaning there is only a maximum of 365 data points in any one year. Anomalous peaks in one hour data tend to be averaged out, so it is appropriate to use the maximum one day averages recorded in

any year to establish emission reduction requirements. Available peak and 99.9 percentile monitoring data for NO_2 are given in the table on the following page.

As mentioned, the concentrations of NO_2 reported above may not reflect the maxima values in the respective airsheds. It is measured concentrations of NO_2 that are compared with the AAQGs, and concentrations of NO (and NO_x) are relatively ignored. NO_2 is essentially a pollutant formed by reactions in the atmosphere. Unless one adopts the approach of assuming all of the NO will be oxidised to NO_2, which of course it eventually will (albeit then removed by subsequent photochemical reactions), then at least the upper bound of the potential extent of NO_2 concentration levels may not be appreciated. Although the situation is complex, what can be stated with some confidence is that if NO_x is monitored at a site where the NO concentrations are markedly higher than the NO_2 concentrations, then the location may not be optimal in terms of assessing health and environmental effects.

Analyses have been done of the NO/NO_2 ratios for the long-standing Auckland (that is, Mount Eden and Penrose) data. At lower levels of NO_x the ratio is approximately 1:1, but at higher levels of NO_x the ratio can be 3:1 or more. This indicates that there is inadequate time for oxidation of the NO to NO_2 to occur between the source of the emissions (predominantly motor vehicles on the nearby roadways) and the monitoring position, especially at the higher NO_x levels. The results therefore clearly understate the potential peak concentrations of NO_2 at other locations.

The recent siting of an NO_x monitor at Musick Point, a location on the harbour edge of Auckland's urban area, some 11 km down the prevailing SW wind from the Penrose industrial area, is a significant departure from previous practice. As mentioned above, the site has been used for measuring concentrations of photochemical oxidants, but it is possibly a little too remote to be a good site for urban NO_2 assessment. However, the ratio of NO/NO_2 concentrations will be of interest, when a reasonable quantity of data is available.

Table 4.1 - Peak NO2 Measurements

Site	One day Peak	One hour Peak	One hour 99.9%ile
Dominion Road	80	363	200
Mount Eden			
1994	44	73	66
1995	49	71	66
1996	41	89	74
1997	45	85	66
Penrose			
1994	44	67	60
1995	51	83	70
1996	67	114	90
1997	45	97	79
Site	**One day Peak**	**One hour Peak**	**One hour 99.9%ile**

Musick Point	45	75	65
St Albans 1994 1995 1996 1997	 43 51 41 50	 85 132 200 119	 77 88 67 91

Notwithstanding the fairly limited amount of monitoring that has been done, the results indicate that ambient NO_2 poses a risk to human health at certain times and at certain locations in New Zealand. With one year average concentrations approaching 30 μg/m^3, ambient NO_2 levels are also a risk to ecosystems. The potential secondary impacts of photochemical smog formation and visibility degradation adversely affect New Zealand's "clean green" image.

4.8.   Required Reduction in Emissions

The indicators approach to managing air quality, used in Stage 1 of VFECS for CO, can be applied to estimating the required reduction in emissions of NOx from vehicles, as may be necessary to achieve the ambient air quality guidelines and ongoing improvement in ambient NO_2 concentrations. Using the indicators approach to devising reduction targets for NO_2 is more difficult than for CO because of the complex atmospheric factors affecting the conversion of NOx to NO_2, and the fluctuating ratio of $NO:NO_2$. However, based on peak NO_2 concentrations (99.9 percentile for one hour values) an estimate of required reductions can be made to achieve the guideline value (alert) and then the air quality categories of acceptable and good (see below). It is assumed that required reductions in ambient NO_2 are proportional to emissions of NOx. Although this is not always the case (i.e. the ratio of $NO:NO_2$ is not always 1) it does tend to approach unity with the highest NO_2 concentrations. Further monitoring of NO_2 away from roads, where concentrations may be higher than next to roads (due to time allowing conversion to occur), should be undertaken to confirm this required reduction estimate. Three air quality targets can be considered, viz;

- an immediate target of achieving the "alert" level of air quality (0 to 2 years);
- as a short-term target, achieving "acceptable" air quality (2 to 5 years), and
- as a long-term target, achieving "good" air quality 5 to 10 years).

For NO_2, the relevant air quality guidelines are:
- 100 μg/m^3 (one day average) – the MfE AAQG;
- 200 μg/m^3 (one hour average) – "the international norm" and recent proposed regional guideline; and
- 300 μg/m^3 (one hour average) - the MfE AAQG.

On the assumption that reductions in emissions achieve equivalent reductions in ambient concentrations, the percentage reductions in NO_x concentrations can be estimated to achieve the above air quality targets. The emission reductions required are given in Table 4.2.

Table 4.2 – Vehicle NOx Emission Reduction Targets

Site	Peak/99.9% ile Values	Air Quality Guideline	"Alert" Target	"Acceptable" Target	"Good" Target
Dominion Rd					
One day	80 μg/m^3	100 μg/m^3	0%	16%	59%
One hr	200 μg/m^3	200 μg/m^3	0%	34%	67%
		300 μg/m^3	0%	0%	50%
Mount Eden					
One day	49 μg/m^3	100 μg/m^3	0%	0%	33%
One hr	74 μg/m^3	200 μg/m^3	0%	0%	9%
		300 μg/m^3	0%	0%	0%
Penrose					
One day	67 μg/m^3	100 μg/m^3	0%	0%	51%
One hr	90 μg/m^3	200 μg/m^3	0%	0%	26%
		300 μg/m^3	0%	0%	0%
Musick Point					
One day	45 μg/m^3	100 μg/m^3	0%	0%	27%
One hr	65 μg/m^3	200 μg/m^3	0%	0%	0%
		300 μg/m^3	0%	0%	0%
St Albans					
One day	51 μg/m^3	100 μg/m^3	0%	0%	35%
One hr	91 μg/m^3	200 μg/m^3	0%	0%	26%
		300 μg/m^3	0%	0%	0%

The above analysis suggests that, while an immediate reduction target is not called for, in the short-term emissions of NO_x from motor vehicles should be managed down by about 30%, and in the long-term by about 65%, in order to improve progressively the quality of air against the air quality targets. Although those reduction targets are based on peak ambient concentration values, they are appropriate because emission inventories indicate emissions of NO_x could increase with the projected growth in traffic, at least in the short term, notwithstanding the improvements expected in emissions performance with the turnover of the vehicle fleet.

5.0   VOLATILE ORGANIC COMPOUNDS

5.1   Introduction

Volatile Organic Compounds (VOC), emitted by many anthropogenic sources (including motor vehicles), are a very diverse group of gases and vapours. Some are hazardous, many are malodorous, a few are phytotoxins, and most are photochemically reactive, and hence are precursors of other pollutants formed by secondary reactions in the atmosphere.

5.2   Characteristics of Volatile Organic Compounds

Of all the classifications of air pollutants, volatile organic compounds (VOCs) are the most confusing in terms of understanding the terminology, because of the difficulty in separating out distinct groupings. There are numerous organic compounds of which volatile compounds are a part. The principal groups are hydrocarbons, oxygenated hydrocarbons and halocarbons.

An important sub-category of VOCs are reactive organic compounds. The reactivity refers to their participation in photochemistry, and hence it is related to their role as precursors in the formation of other pollutants by reactions in the atmosphere. VOCs in the troposphere are important in controlling the concentration of the hydroxyl (OH) radical – the so-called "detergent of the atmosphere" – and of great importance in photochemistry, resulting in decreased lifetimes of certain species such as methane of stratospheric significance. As such VOCs can have both direct and indirect effects on climate change.

One of the most abundant VOCs is the first of the hydrocarbons, and an important "greenhouse gas", methane. In the lower atmosphere methane is quite stable, and so it is usually considered separately from the other hydrocarbons. One descriptor of a group of VOCs is non-methane hydrocarbons (NMHC), often used to cover the majority of VOCs involved in photochemistry.

There are a host of other organic compounds, mainly associated with industrial processes, which have been included in air quality studies. They include acrylonitrile, 1,3-butadiene, carbon disulphide, 1,2-dichloroethane, dichloromethane, styrene, tetrachloroethylene, trichloroethylene and vinyl chloride. There are also the important halocarbons commonly referred to as 'dioxins and furans'; chlorofluorocarbons (CFCs), of importance in the troposphere both with regard to depletion of the ozone layer and the enhanced "greenhouse effect"; and polynuclear aromatic hydrocarbons (PAHs), of which benzo[*a*]pyrene is the best known.

The terminology becomes confusing because the groupings of compounds are overlapping. For practical purposes, in this discussion related to the air quality management aspects of motor vehicles, VOCs can be considered as the sum of C_2 to C_{10} hydrocarbons and carbonyls (aldehydes and ketones).   A sub-group of VOCs that are of concern in their own right (that is, not just for their photochemical reactivity) are those included in what is increasingly being referred to as "air toxics".

5.2.1 C_2 to C_{10} Hydrocarbons

The most predominant group of VOCs (not including methane) in emissions to atmosphere are the C_2 to C_{10} hydrocarbons. They include the alkanes (ethane, propane, butane, pentane, hexane, heptane, octane, nonane, and decane), the cycloalkanes (cyclopropane, cyclobutane, cyclopentane, etc), the alkenes (ethylene, propene, butene, etc), the alkynes (acetylene, propyne,

butyne, etc), the aromatics (benzene, toluene, xylene, styrene, cumene, etc) and the numerous derivatives of all of those. In each of the series, only the first two or three are gases at ordinary temperatures; the others are liquids which can occur in various isomeric forms, and are vapourised under combustion conditions, such as in a motor vehicle. Of the multitude of derivatives, particular mention should be made to alkadienes (such as 1,3-butadiene), which are similar to alkenes but with two double bonds, and polynuclear aromatic hydrocarbons, which have two or more benzene rings.

5.2.2 Carbonyls

The second most common group of VOCs in emissions to atmosphere are the gaseous oxygenated hydrocarbons – aldehydes and ketones, collectively known as carbonyls. (Some other normally liquid oxygenated hydrocarbons, alcohols and ethers, and strictly speaking also VOCs, sometimes arise when used in their role as blendstocks with petrol, in certain formulations.) The simplest and most common of the aldehydes found in the atmosphere is formaldehyde, which is a gas at ordinary temperatures, whereas other (usually liquid) carbonyls - - acetaldehyde, benzaldehyde, and acetone – are vapourised at combustion temperatures, such as in a vehicle engine.

5.2.3 Organic "Air Toxics"

The term "air toxics", which are made up of both organic and inorganic (metallic) compounds, is becoming increasingly common. Among the many VOCs which are usually included in this group of hazardous air pollutants are acetaldehyde, benzene, benzo[a]pyrene, 1,3-butadiene, formaldehyde, toluene and the xylenes. These organic compounds are to be found in emissions from motor vehicles and other combustion systems, and can also be formed (sometimes in greater quantities) by reactions in the atmosphere.

As previously mentioned, and the source of much of the confusion about terminology, these groupings of VOCs are overlapping. Acetaldehyde and formaldehyde are carbonyls; the others in this abbreviated "air toxics" listing are C_2 to C_{10} hydrocarbons.

5.3 Sources of Volatile Organic Compounds

With such a diverse range of compounds making up VOCs it is difficult to generalise about sources. Methane is largely emitted by natural, mostly biological, processes, but anthropogenic sources (rice paddy fields, grazing animals, biomass burning, natural gas leakage, and coal mining) are becoming more significant, and are the reason why atmospheric concentrations of methane are increasing by about 1% per year. As for the other hydrocarbons, especially the reactive organic compounds, the sources are again a combination of natural (especially from vegetation) and, in urban areas, anthropogenic. The latter are many and varied, and include motor vehicles, industrial processes, fuel storage and combustion, paints, aerosols and solvents.

Formaldehyde is an intermediary in the methane cycle, with low background concentrations in non-urban environments. Anthropogenic sources include direct emissions, especially from the production and use of formaldehyde, and reactions in the atmosphere which form oxygenated hydrocarbons from reactive organic compounds. It is estimated that as much as 85% of the ambient concentrations of formaldehyde, and 95% of acetaldehyde, in urban areas are formed in this way. The major anthropogenic sources of formaldehyde affecting humans are in the indoor environment. Products containing formaldehyde, such as resins, are common. Sources include insulating materials, chipboard and plywood, and fabrics; other sources are cigarette smoke,

heating and cooking. It is also responsible for the noticeable odour that emanates from a poorly tuned gas-fuelled vehicle.

Polynuclear aromatic hydrocarbons, and their nitro derivatives, are generated by the pyrolytic processes of incomplete combustion. Sources include diesel engines, domestic heating (coal/wood combustion), refuse burning, coke production and biomass combustion.

Some VOCs are naturally present in fuels and so can be released to the atmosphere as a result of storage evaporation (fugitive losses) and from incomplete combustion, or are the products or by-products of (largely chemical) industry. Other VOCs are formed in the combustion process, whereas several are produced (or their concentrations are greatly increased) by reactions in the atmosphere.

Because emissions of VOCs arise from a variety of sources which differ from one location to another, there is significant variation in the contribution of various source types to ambient concentrations of VOCs. To estimate the proportion of emissions from different sources in an area, a detailed emissions inventory must be compiled. Some regional councils in New Zealand are developing emission inventories for their regions, and the findings are presented below.

Auckland Regional Council predict approximately 68% of the anthropogenic VOC (not including methane) emissions on an average summer week day come from motor vehicles. Other significant sources are domestic/commercial aerosols (5%), surface coatings (5%), domestic fuel combustion (4%) and service station petrol refuelling (4%). In winter the total anthropogenic quantity of VOCs increases (from 166 tonnes/day to 210 tonnes/day), with an even greater quantity increase from domestic fuel combustion and decreases from storage and evaporation sources. The contribution of motor vehicles to anthropogenic VOC emissions on an average winter week day drops to about 51%, while that from domestic fuel combustion increases to 29%. The other significant sources decrease slightly.

Auckland Regional Council also estimate the VOC emissions from biogenic sources, at 13 tonnes/day and 27 tonnes/day, for an average winter week day and summer week day, respectively.

In Christchurch, where domestic fuel burning in winter is more significant than in Auckland, the Canterbury Regional Council estimate motor vehicles give rise to approximately 64% of the VOC emissions (presumably, not including methane) on a typical winter day, with home heating at 34% and industry 2%. One would expect a substantial reduction in summer of the total anthropogenic emissions of VOCs (down from 45 tonnes/day), and a concomitant increase in the percentage contribution from motor vehicles. It needs to be observed that the Christchurch inventory has less source categories than the one for Auckland, so direct comparisons are difficult.

In Hamilton, Environment Waikato estimate the percentage contribution to ambient VOCs (again, presumably not including methane) from motor vehicles to range from 82% in central Hamilton to 24% in Upper East Hamilton, with home heating emissions responsible for the majority of the remainder. These figures are annualised averages, and so the relative contribution from motor vehicles is likely to increase during summer months and decrease in winter months. This inventory has not considered the contribution to VOCs from industry and domestic/commercial sources other than home heating. These are possibly quite significant, of the order of about 10 to 15% of total VOC emissions.

5.4   Motor Vehicles as a Source of Volatile Organic Compounds

As indicated above, motor vehicles and their fuels are the most significant sources of VOCs in the ambient air over urban areas in New Zealand. Although there are differences depending on the presence of other sources, such as some industry and commercial/domestic coating processes, and there are considerable seasonal variations, especially where there is major reliance on fuel combustion for domestic heating, motor vehicles are estimated to contribute between 60 to 75% of total anthropogenic emissions of VOCs.

One estimate has total annual VOC emissions from the New Zealand motor vehicle fleet of about 240 tonnes/day. There is no breakdown of the contributions to that total from different types of vehicles, but light duty petrol vehicles (which make up about 82% of the total fleet) are the major contributors. That emission estimate, which seems a little low, may only relate to exhaust emissions of VOCs. Evaporative emissions of VOCs from motor vehicles can also be proportionately significant in urban areas, especially in summer.

5.4.1   Exhaust Emissions

There are significant differences in the nature of exhaust VOCs emitted from petrol and diesel vehicles. The main concern about emissions of VOCs from diesel vehicles, apart from the types of VOCs involved, is that they are absorbed or condensed on fine particulates.

Exhaust emissions of VOCs from petrol vehicles, which potentially include thousands of different chemical compounds, are largely the result of incomplete combustion of the petrol. The amounts emitted are related to a multitude of factors concerning the design and control of the combustion system, and its in-service condition, as well as fuel composition. There exists a wide range of techniques for the control of the VOC emission, which can be incorporated to suit the need of emission standards; the use of catalytic converters is an example.

A major influence on the overall VOC emission potential of petrol vehicles is the chemical formulation and properties of the petrol fuel. The volatility required of petrol is also the cause of evaporative losses of VOC from the vehicle fuel system whilst the vehicle is in motion, and also at rest (and also during the tank refuelling process). Fuel specification controls are applied to the volatility property to minimise these losses, along with on-board vapour trap/recovery systems. The trend towards fuel injected engines also removes the potentially significant vapour loss pathway that was the carburettor in older vehicles.

The chemical composition of the petrol plays a great part in the combustion emissions from a petrol engine, and this is the cause of significant changes in the traditional approach to formulation. This concerns many different and complex refining and combustion chemistry relationships. However, one of the more notable changes in recent years is a consequence of the move to unleaded petrols, and the need for alternatives to maintain octane quality. The refining industry has recourse to many such alternatives, but one in particular is to increase the content of aromatic blendstocks, with their naturally high octane values. This can cause an increase in benzene in the petrol, a component which is subject to particular control; although it should be noted that aromatics/benzene have always been present as a natural component of petrols.

In the wake of this, contemporary specifications for petrol include a maximum limit for the benzene content, which are generally progressing downwards as per the perceived degree of need to do so; in some countries specification levels are down to a maximum of 1% by volume, although New Zealand has used a higher level (5% by mass, which is about 4% by volume). For

high octane, unleaded petrol in particular there is a perception that removal of lead, *per se*, causes an increase in emissions of benzene. That is not correct, as an increase in the benzene content of petrol only occurs if the high octane number is maintained through deliberate blending of additional aromatics, or increased refining of the petrol to increase aromaticity, as the particular refining strategy.

Furthermore, benzene in the exhaust emissions from petrol vehicles largely result from benzene formed from the combustion process, and less from the benzene content of the petrol. A reduction in the total aromatics content of petrol (currently limited in New Zealand to a maximum of 48% by volume) produces a more significant reduction in the benzene generated. Also, benzene in exhaust gases is removed at a high efficiency by a catalytic converter.

The exhaust emissions of VOCs from diesel vehicles include polynuclear aromatic hydrocarbons (PAHs), their nitro derivatives, aldehydes and other oxygenated hydrocarbons. VOCs from diesel vehicles occur primarily at light loads, due to poorer fuel atomisation and/or excessive fuel/air mixing which results in some volumes of the air-fuel mix which are too lean to burn. A significant proportion of the smaller two and three-ring PAHs are derived from unburnt fuel in this way. Diesel fuel can contain up to percentage levels by volume of PAHs. Most of the larger PAHs appear to form during the combustion process, by polymerization reactions. The oxygenated hydrocarbons are responsible for much of the characteristic diesel odour.

The fuel quality influences on the VOC emission are many and complex, and interact through the overall optimisation of the combustion system. Of most direct consequence is the volatility of the petroleum fuel fraction that is destined for use by diesel engines, with its heavier molecular weight compounds. Part of this is the content of aromatic structures, the reduction of which contributes to the lowering of exhaust VOCs from diesel vehicles. Significantly chain branched aliphatics in the fuel can also contribute to the formation of PAH in incomplete combustion. Conversely, an advantage of the involatile fuel type is that evaporative VOC emissions from the diesel vehicle are essentially negligible.

5.4.2   Speciation

There are differences in the types of VOCs in exhaust emissions from petrol vehicles and from evaporative emissions of the fuel. There are also significant variations in the types of VOCs in petrol vapour compared with petrol liquid, with the former containing more alkanes and alkenes, and less aromatics.

The fuel in combustion is subject to various reactions, resulting in alkanes being converted to more aromatics and to carbonyls as intermediaries. If not fully combusted the overall photochemical reactivity of the emissions is increased, compared with the initial fuel chemistry.

As part of the Auckland emission inventory study, an attempt was made to define the species involved in both exhaust emissions and evaporative emissions of VOCs from petrol vehicles, and the results are presented in Table 5.1. The evaporative VOC emissions require estimation of the relative contributions of petrol vapour and petrol liquid to emissions, and were taken as respectively 78% and 22%. The VOCs do not include methane.

Table 5.1 - Speciation of Petrol Vehicle VOC Emissions (est.)

Species	%VOC; Exhaust Emission	% VOC; Evaporative Emission

Alkanes	37	77
Alkenes	20	14
Alkynes	7	neg
Aromatics	32	9
Carbonyls	4	neg

5.5 Effects of Volatile Organic Compounds

Again, with such a diverse range of compounds making up VOCs it is difficult to generalise about effects. Some VOCs are hazardous, many are malodorous, a few are phytotoxins, and most are photochemically reactive.

5.5.1. Health Effects

It is usual to focus on a select group of VOCs which are considered hazardous air pollutants, commonly referred to as "air toxics". Not that this list is particularly small – of the 189 hazardous air pollutants listed under Title III of the United States Clean Air Act Amendments of 1990, and not including pesticides and herbicides, 148 of them are VOCs. Those specifically related to emissions from motor vehicles are acetaldehyde, benzene, benzo[*a*]pyrene, 1,3-butadiene, formaldehyde, toluene and the xylenes.

Air toxics are generally emitted in relatively small quantities (and atmospheric concentrations are correspondingly low) compared with the more common pollutants, but they may have more serious health effects. They include substances that are known or suspected to cause acute health effects, cancer or teratogenic effects, or serious or irreversible effects – reproductive dysfunctions, neurological disorders, heritable genetic mutations, or other chronic health effects. The list also includes substances known or suspected to cause a significant adverse effect on the environment due to their toxicity, persistence in the environment, tendency to bioaccumulate, or any combination of these.

Of the small list of VOCs given above, benzene, benzo[*a*]pyrene and 1,3-butadiene are human carcinogens, whereas formaldehyde is a suspected carcinogen. The approach taken with such pollutants is to estimate the carcinogenic unit risks for each; that is the cancer risk estimate for lifetime exposures to 1 $\mu g/m^3$ of the substance. For example, benzene has a unit risk of 4×10^{-6} for leukaemia and benzo[*a*]pyrene has a unit risk of 9×10^{-2} for lung cancer. For some of these substances no threshold concentration has been determined (that is, there appears to be no concentration below which can be considered as providing a 'no observable adverse effects level'). This has not constrained certain authorities from setting air quality standards or guidelines for those substances. The aim is to attain a concentration of these substances in ambient air so the risk to health by way of cancers and other effects is very small.

Short-term exposures to relatively high concentrations of formaldehyde produce eye, nose and throat irritation. The threshold of irritation is about 100 $\mu g/m^3$, but significant increases in symptoms start at levels above 300 $\mu g/m^3$ for most (non-sensitive) people.

5.5.2 Odours

Basic hydrocarbons generally have fairly high odour threshold concentrations, but most of their oxygenated hydrocarbon derivatives and some of the larger aromatics (often present as a mixture) can give rise to odour nuisance impacts. In fact, strict air pollution control equipment on certain industrial processes, such as surface coating of metals, are installed because of the potential of the products of the paint baking process to cause unpleasant odours. As mentioned above, the characteristic odour of diesel emissions is caused by the presence of oxygenated hydrocarbons. A few air quality standards and guidelines for VOCs, including styrene and toluene, are based on sensory effects and annoyance reactions, where these occur at concentrations below other health effects.

5.5.3   Effects on Vegetation

Gaseous alkenes (ethylene), alkynes (acetylene and propyne) and aldehydes (formaldehyde) are phytotoxins to certain plant species. The main effect seems to be a general reduction in plant growth. A significant issue in setting emission limits for a particle board plant in Kumeu, Auckland, was the potential damage to the nearby grape growing industry.

5.5.4   Effects of Atmospheric Reactions

As mentioned above, vegetation is a very significant source of VOCs, especially the reactive organic compounds. Biogenic sources of terpenes and radicals of alkadienes (such as α-pinene, β-pinene – proportionately more prevalent in New Zealand conifers than elsewhere -- and 2-methyl-1,3-butadiene, more commonly called isoprene) from trees are increasingly being recognised as important contributors to total VOCs in ambient air. They can also contribute to regional hazes. For example, the Blue Mountains outside Sydney are so-named because of the apparent blue haze from the eucalypt trees.

As for atmospheric reactions involving VOCs, an important consideration is the relative reactivities of the individual compounds. Although there are significant differences within groups, the general trend is that alkanes have relatively low reactivity, alkenes have much higher, and aromatics fall somewhere between. Carbonyls generally have high reactivities. Of the VOCs commonly present in ambient air, ethene, propene and 1-butene (all alkenes), 1,3-butadiene and 2-methyl-1,3-butadiene (alkadienes), *m*-xylene and 1,3,5-trimethylbenzene (aromatics), and formaldehyde and acetaldehyde (carbonyls) have particularly high reactivities. Benzene has low photochemical reactivity, but not as low as methane.

The point of all this is to observe that the VOC species emitted from motor vehicles, especially petrol vehicles, tend to be those with high potential for participating in reactions in the atmosphere. A very positive development as a consequence, is the recent specification of VOC emission limits for motor vehicles in California, with adjustment of the quantity of the individual species present weighted in accordance with their photochemical reactivity.

Atmospheric reactions dictate the lifetimes of substances in the atmosphere. Returning again to the 148 VOCs which are included in the hazardous air pollutants listed under Title III of the United States Clean Air Act Amendments of 1990, more than 60% of them have atmospheric lifetimes of less than one day. For these, the products of the reactions in the atmosphere are important to any consideration about risk.

VOCs are not only precursors of other pollutants formed by reactions in the atmosphere, they are also produced, sometimes in far greater concentrations, by those atmospheric reactions. An interesting feature is that, with the very important exceptions of formaldehyde and acetaldehyde,

the precursors to formation of hazardous VOCs by reactions in the atmosphere are hazardous themselves. Therefore measures to reduce direct emissions of those VOCs should successfully reduce ambient levels of hazardous VOCs formed by reactions in the atmosphere.

As mentioned, the exceptions to this are formaldehyde and acetaldehyde, which are produced from reactions with alkanes and alkenes (as well as aromatics). Formaldehyde and acetaldehyde are produced by almost every hydrocarbon photooxidation reaction. Estimates in some urban areas have found that as much as 85% of the formaldehyde, and 95% of the acetaldehyde, are the result of reactions in the atmosphere. Once again, it is the VOC species emitted in greatest quantities from motor vehicles, especially petrol vehicles, which largely participate in those reactions.

5.6   Air Quality Guidelines for Volatile Organic Compounds

In 1994 MfE established a list of hazardous air pollutants ("air toxics" in the terminology used above) which includes various VOCs - acetaldehyde, benzene, 1,3-butadiene, formaldehyde, toluene, the xylenes and polycylic organic matter. The supporting text recommends a precautionary approach of minimising emissions of those pollutants. In a draft of the AAQGs there was a guideline for formaldehyde of 100 μg/m^3 (not to be exceeded at any time period of observation), based on the acute irritation effects of formaldehyde. Although at the time this was claimed to be based on the WHO guidelines, the latter is for a 30 minutes averaging period. The 'probable carcinogen' status of formaldehyde, led MfE to remove formaldehyde from the list of ambient air pollutants and include it in the list of "air toxics".

A few countries, mainly in Europe, have established air quality standards or guidelines for individual VOCs. Some of the more relevant ones to local air quality considerations are given in the following table:

Table 5.2 - Overseas Guidelines for Individual VOC

VOC	Country	Period	Concentration in µg/m³
Benzene	Netherlands	One year	30 (no exceedances); 1 (negligible risk)
	Sweden	One year	1.3
	United Kingdom	One year	16 (year 2005); 3.2 (long-term)
Benzo[a]pyrene	Netherlands	One year	0.005 (no exceedances); 0.0005 (neg. risk)
1,3-butadiene	Sweden	One year	
	United Kingdom	One year	0.04-0.35
			2.7 (year 2005)
formaldehyde	WHO	30 mins	
	Netherlands	one hour	100
	Sweden	one year	120 (no exceedances)
			12-60
toluene	WHO	one day	
	Netherlands	one hour	8,000 (irritation); 1,000 (odour)
	Sweden	one year	3,000 (no exceedances); 30 (neg. risk)
			38-380
xylenes	Sweden	one year	
			43-430

Although apparently it never caught on elsewhere, the United States at both a national and state level established many years ago air quality standards for non-methane hydrocarbons, based on a three hour average (6-9 am). The most common standard was 160 µg/m³ (240 ppb), expressed as CH_4, but a few states imposed standards of 100 µg/m³. (Care needs to be taken with these numerical values, because the convention has changed and is now based on the mixture of non-methane hydrocarbons having an average molecular weight of 72, and the concentration is reported on a Carbon weight basis such as ppbC or µgC/m³.) When the formation of photochemical oxidants was first being investigated in Auckland, the intention was to establish an air quality guideline for non-methane hydrocarbons; this was precluded by the limited nature of the investigations.

5.7 Concentrations of Volatile Organic Compounds

In the 1980s attempts were made to measure atmospheric concentrations of non-methane hydrocarbons in Auckland, as part of investigations into the formation of photochemical oxidants, but only limited useful data was obtained. The Auckland Regional Council recently reactivated interest in this area, with the installation of a standard flame ionisation detector instrument for non-methane hydrocarbons.

Although equivalent monitoring has not been done in New Zealand, it is expected that the composition of C_2 to C_{10} hydrocarbons in the atmosphere of urban areas is similar to that found in other cities, with 50-65% alkanes, 10-15% alkenes, 0-5% alkynes and 25-30% aromatics.

The most extensive work on concentrations of VOCs in New Zealand, carried out for the Ministry of Health since 1995, has involved some 20 sites, covering both outdoor and indoor environments, in a range of urban and suburban locations. Samples are collected on activated charcoal tubes or by passive sampling badges incorporating an activated carbon absorption

element, and analysed using gas chromatography/mass spectroscopy. The following are the ranges of the one year average value of the concentrations at the 14 outdoor, residential sites:

benzene	1.0 to 6.2 µg/m^3
toluene	3.4 to 17.1 µg/m^3
ethylbenzene	0.4 to 2.4 µg/m^3
m+p-xylene	1.7 to 10.5 µg/m^3
o-xylene	1.0 to 3.8 µg/m^3

NIWA (for MfE) has carried out a short-term (17 day) monitoring programme at an inner city site in Khyber Pass, Auckland, (actually at a busy intersection of two roads) for a range of pollutants, including the measurement of benzene, toluene and formaldehyde, using an open path monitoring system. The instrument measures ultra-violet light absorption, based on the principle of differential optical absorption spectrometry (DOAS). For comparison, during the 17 day period, non-methane hydrocarbons were measured using a flame ionisation instrument. The following are some of the results, expressed in a form as close as possible to the averaging times usually of interest:

benzene	a 17-day average of 80 µg/m^3
toluene	a 17-day average of 95 µg/m^3
formaldehyde	a range of hourly values of 7 to 29 µg/m^3
	a 17 day average of 12 µg/m^3
non-methane hydrocarbons	a range of hourly values of 29 to 1,756 µg/m^3

It should be noted that the site monitored by NIWA represents a peak inner city site heavily impacted by traffic, measuring through the airspace immediately above the traffic flows at the intersection, and should not be used to indicate general ambient levels in other areas. In addition, the monitoring was undertaken in winter during a period of relatively still wind conditions. Studies have found that measurements of benzene and toluene in winter are generally higher by up to 60% than in summer. Because benzene has a relatively long half life of approximately 19 days, it has the ability to accumulate over time. This may be why the NIWA results, which are for a short period of time, appear higher than the annually averaged results from the other monitoring.

Notwithstanding the limited amount of monitoring that has been done, the results indicate that ambient levels of some VOCs (most notably, benzene and formaldehyde) may pose a risk to human health at certain locations, in New Zealand

5.8   Required Reduction in Vehicle VOC Emissions

Emission inventories show that throughout New Zealand the greatest contributor to ambient VOCs are motor vehicles. This is confirmed by the ambient air monitoring, with much higher concentrations measured near to busy roads. There is a view that emission reductions for VOCs will occur in parallel with strategies to reduce CO emissions from motor vehicles. For the techniques aimed directly at improving combustion efficiency, or exhaust after-treatment this is generally true, certainly as a directional trend if not in absolute rates.

However, the most significant aspect of VOCs as air pollutants continues to be their diversity, and as such it is difficult to generalise about emission reduction strategies. The effectiveness of one strategy over another can only be measured in absolute terms by looking at the impact on the individual VOC components, which in turn should dictate the most appropriate course of action.

For example, measures to specifically control benzene are not synonymous with measures to control formaldehyde, or VOC as a whole. An increasingly common perspective is that a technology-based approach is required, largely in response to the practical difficulty of setting health-based standards for VOCs. The relatively crude approach of Rule 66 of the Los Angeles County Air Pollution Control District, which put blanket restrictions on the quantities of organic solvents discharged to the atmosphere from industrial and commercial premises, has achieved much in the 25 years since it was promulgated, and has forced the development of cost-effective technology. Motor vehicles have proved more difficult, only partly because of the greater complexity of the problem, but there are several approaches available for technology-driven emission limits and fuel quality improvements, from which to find the most cost-effective solutions in response to the VOC emission targets required. However, setting the appropriate targets is the conundrum, to justify the level of technical control.

Given the difficulty in setting an appropriate target at this stage, it is inappropriate to apply the indicators approach to estimating desirable reductions in VOC emissions from vehicles. However, because the monitoring carried out to date indicates that there may be adverse health effects from VOC emissions, the aim of VFECS should be to minimise emissions as far as practicable, without compromising the more certain reductions required for emissions of other contaminants.   Further monitoring is required and the development of a guideline for benzene, and possibly other VOCs, should be investigated.

6.0 PHOTOCHEMICAL OXIDANTS

6.1 Introduction

Photochemical oxidants, of which ozone is the most prevalent, are a mixture of gases formed (along with some other gases and particulates) by reactions in the troposphere involving nitrogen oxides and reactive organic compounds with the action of sunlight, and are pollutants of concern about their health and environmental effects.

6.2 Characteristics of Photochemical Oxidants

Because photochemical oxidants are a mixture of gases, formed from precursors under certain meteorological conditions, their main characteristics are those of the species formed, the photochemical reactions which produce them, and the meteorological conditions that permit the reactions to occur. The initiation of photochemical air pollution, if not always its point of maximum impact, is essentially an urban air quality issue. Even then it is really only produced in significant quantities in those urban areas which are both of a sufficiently large size (that is, with a sufficiently large and continuous quantity of the precursors) and have the mix of meteorological conditions which are conducive to photochemical reactions. The development and point of maximum impact of photochemical air pollution can be remote from (tens of km downwind of) the initial urban sources of the precursors.

Ozone and other photochemical oxidants which form in the troposphere, near the ground, should not to be confused with ozone in the stratosphere, some 15 to 50 km above ground level. The stratospheric ozone, a natural product formed by the photolysis of molecular oxygen, is the major filter of biologically harmful ultraviolet (UV-B) light. There is concern about reactions involving emissions from anthropogenic sources which are depleting that ozone layer. On the other hand, the concern about ground level ozone and other photochemical oxidants in the troposphere is the urban air quality issue of elevated concentrations of those gases.

6.2.1 Species

Although ozone is the most prevalent of the photochemical oxidants it is not the only one. Other oxidants include peroxyacetylnitrate (usually written as PAN), other peroxyacylnitrates, nitric acid and hydrogen peroxide. In addition to the oxidants, the photochemical processes also produce ambient concentrations of formaldehyde, other aldehydes, formic acid, fine particulates (sulphates, nitrates and organic aerosols) and an array of short-lived radicals.

The focus in recent years has been on ozone alone, to the exclusion of the other photochemical oxidants. In 1979, when the United States EPA decided to change the one hour photochemical oxidants standard of 170 $\mu g/m^3$ to an ozone standard of 210 $\mu g/m^3$ (it subsequently went up to 260 $\mu g/m^3$) concern was expressed about this change in specification from photochemical oxidants to ozone alone. The fear was that if ozone is accepted as the standard, the impetus to identify the other photochemical oxidants and to study their particular effects would be lost.

As the name suggests, photochemical oxidants – ozone, PAN, nitric acid and hydrogen peroxide – are all powerful oxidising agents.

6.2.2   Photochemical Reactions

Photochemical reactions are complex. One listing has 684 chemical reactions, involving 384 chemical species. The most important reactions though are the photodissociation of NO_2 by sunlight, to form NO and $O(^3P)$ – atomic oxygen in its lowest energy state ("triplet oxygen") -- followed by reaction of the $O(^3P)$ atom with molecular oxygen, in the presence of any third molecule (usually designated 'M') needed to stabilise the exited intermediate formed by the addition reaction, to produce ozone (O_3). In addition to these two ozone-formation reactions, there is the equally important ozone-removal reaction of O_3 with NO to form NO_2 and O_2.

Thus, the mechanisms of ozone formation during sunlight irradiation of polluted air and removal during night-time are simple in outline (formation by the interaction of molecular oxygen with the photoproducts of nitrogen dioxide, and removal by reaction with nitric oxide), but complex in detail. In its steady state, the ozone concentration can be defined by the ratio of the NO_2 concentration to the NO concentration. In daylight hours the formation reaction predominates and in the night-time, with no sunlight irradiation, the removal reaction prevails.

However, the steady state conditions described above, which would achieve a fair balance of ozone, are upset by real-world urban atmospheres, which contain significant concentrations of various reactive organic compounds. These photochemically reactive compounds (sometimes referred to as the "catalysts" of the reactions) are also dissociated by sunlight, to form peroxy radicals ($R-O_2$), which have the important property of reacting with NO to convert it to NO_2. The significance of this is that the conversion of NO to NO_2 during daylight shifts the equilibrium of the formation/removal mechanisms to be very much in favour of ozone formation. A second point of significance regarding reactive organic compounds is that they are involved in reactions which produce some of the other photochemical oxidants, as well as many of the other products of photochemical reactions. Peroxyacylnitrates, such as PAN, are formed by reactions between derivatives of $R-O_2$ radicals and NO_2. Formaldehyde, and other aldehydes, are produced by almost every hydrocarbon photooxidation reaction.

Photochemical reactions involving ozone are also important. The photolysis of O_3 produces $O(^1D)$ – the second lowest energy state of atomic oxygen ("singlet oxygen") -- and molecular O_2. The $O(^1D)$ rapidly reacts with water vapour to form the hydroxyl radical (OH). The hydroxyl radical – the "detergent of the atmosphere" – initiates the majority of organic oxidations in the troposphere, and thus is a controlling element in atmospheric chemistry. For example, reaction of OH with NO_2, to form nitric acid (HNO_3), is a major chain termination step.

6.2.3   Meteorology

For them to occur, photochemical reactions require a mix of meteorological conditions which favour them. Those conditions are generally accepted to include at least moderately high levels of sunlight radiation, warm temperatures and low wind speeds. Sea/land breezes, formed as a consequence of those other conditions, also seem to be important.

During summer anticyclonic conditions, when there is maximum solar heating and winds are light, daytime sea breezes develop around coastlines. At night these winds reverse, to produce light offshore winds (land breezes). These coastal winds can significantly affect atmospheric dispersion. Also, recirculation of pollution in the sea/land breeze has been found to be strongly linked to the occurrence and distribution of photochemical incidents. The recirculation permits photochemical oxidants to form over several hours, and then be carried back over the urban area at some later time.

6.3   Sources of Photochemical Oxidants

There are no significant direct emissions of ozone, peroxyacylnitrates or the other photochemical oxidants, and all are formed by chemical reactions that occur in the atmosphere. The ozone in the stratosphere can be transported by atmospheric circulation into the lower atmosphere, and as such small concentrations of ozone (at present about 80 $\mu g/m^3$) are found globally throughout the lower atmosphere.

These levels, which appear to be increasing, arise from a combination of injection from the stratosphere and photochemistry involving biogenic sources of reactive organic compounds, especially terpenes and radicals of alkadienes (such as α-pinene, β-pinene and 2-methyl-1,3-butadiene, more commonly called isoprene) from trees.

As mentioned above, ozone, peroxyacetylnitrates (such as PAN), nitric acid and hydrogen peroxide are formed in the lower atmosphere by reactions between nitrogen oxides and an array of photochemically reactive organic compounds. The reactivity of the organic compound largely determines its role in the formation of photochemical oxidants. Table 6.1 gives reactivities of some common volatile organic compounds (VOCs), most of whom (but not methane) are included in the sub-group of reactive organic compounds.

Table 6.1 - VOC Reactivity

VOC	Reactivity, in mg O_3 formed per mg VOC
Methane	0.015
Ethane	0.25
Propane	0.48
n-butane	1.02
ethylene	7.29
propene	9.40
1-butene	8.91
acetylene	0.50
1,3-butadiene	10.89
benzene	0.42
toluene	2.73
m-xylene	8.15
formaldehyde	7.15
acetaldehyde	5.52

There are also particulates - sulphates, nitrates, and organic aerosols - formed by reactions in the atmosphere. Although they are primarily derived from, respectively, emissions of sulphur dioxide, nitrogen oxides, and volatile organic compounds, it is the photochemical reactions that actually convert them from gases to particulates.

Emission inventories in Auckland, Hamilton and Christchurch estimate that between 80 to 95% of total NO_x emissions in New Zealand are from motor vehicles, with domestic heating responsible for most of the remainder. There are significant differences between areas, depending on the presence of other sources such as thermal power stations and industry with large combustion processes. There are also seasonal variations, especially those urban areas with a major reliance on fuel combustion for domestic heating.

Those same emission inventories estimate that between 60 to 75% of the total anthropogenic emissions of VOCs (not including methane) in New Zealand are from motor vehicles, and about 10 to 15% each result from domestic heating and from various industry and other commercial/domestic sources. Again there are significant differences between areas, depending on the presence of certain sources, such as some industry and commercial/domestic coating processes. Not unexpectedly, domestic heating is much more significant in winter months, especially in those urban areas with a major reliance on fuel combustion for domestic heating, whereas evaporative emissions of VOCs from petrol vehicles, fuel storage, etc quite logically decrease in winter. One estimate has the biogenic sources of VOCs (not including methane) in an urban area at approximately 15% of the anthropogenic emissions in summer, but down to about 5% of those emissions in winter months.

6.4   Motor Vehicles as a Source of Photochemical Oxidants

As mentioned earlier, motor vehicles are responsible for the greatest proportion of NOx and VOCs (not including methane) in the urban areas in New Zealand. Those estimates, however, probably understate the true influence of motor vehicles to the formation of photochemical oxidants. Motor vehicles emit, especially in exhaust emissions, a much greater quantity of photochemically reactive organic compounds than other sources, including alkenes (ethylene, propylene, butene, etc), alkadienes (especially 1,3-butadiene) and some of the aromatics (toluene and xylene), as well as the important gaseous/vapour oxygenated hydrocarbons (formaldehyde and acetaldehyde).

Secondary particulates, formed by (photochemical) reactions in the atmosphere, from direct emissions of sulphur dioxide, nitrogen oxides and volatile organic compounds, are relevant to emissions of air pollutants from motor vehicles. These gaseous emissions largely result, in the cases of NO_x and VOC predominantly so, from motor vehicles. There is also the "soluble organic fraction" of soot based particulates from such as diesel engines and domestic fires which, beyond being an air pollution emission source of concern in its own right, is also likely to be the subject of photochemical reactions in the atmosphere, to form other particulates of at least equal concern.

6.5   Effects of Photochemical Oxidants

Stated earlier, photochemical oxidants are all powerful oxidising agents, and their effects are largely related to that property. Only fluorine, atomic oxygen, and oxygen fluoride have higher redox potentials than ozone.

6.5.1 Health Effects

The predominant population groups at risk to exposures of ozone are:

- those with asthma and chronic lung diseases;
- healthy young adults undertaking active outdoor exercise over extended periods; and
- the elderly, especially those with cardiovascular disease.

There is strong supportive evidence from clinical, epidemiological and controlled exposure studies, of health effect associations at ambient ozone levels normally encountered world-wide in large cities. Health effects associated with exposure to ozone include minor changes in lung function and increased symptoms consistent with upper and lower airway irritation, leading to increased requirement for additional medication and increased requirements for medical and hospital services. There is also evidence of a slight but definite increase in mortality, chiefly from cardiovascular causes, particularly in the elderly. The mortality increase is of the order of 1.2% per 10 $\mu g/m^3$ (short-term average) increment in ozone.

International studies have found that there does not appear to be a threshold exposure level for ozone. There is a monotonic relationship between ozone concentration and adverse health effects, and so (unlike, for example, NO_2) it is not possible at this time to define either a No Observed Effect Level or a Lowest Observed Effect Level for ozone.

There is consistent evidence to suggest that there are specific subgroups within the population which are more susceptible to the adverse health effects of ozone, in particular, asthmatics. In addition, there is an increasing body of literature which details the various interactions between the air pollutants ozone, nitrogen dioxide, particles, and sulphur dioxide. In particular, there is robust statistical data which supports enhancement of the effects of ozone, as a result of prior or concurrent exposure to particles, nitrogen dioxide, airborne allergens, and to sulphur dioxide, collected in a wide range of environments in many countries. Meteorological factors such as temperature have also shown an influence. The coherence of the relationships of the pollutants and the many associations of effects, including increased mortality, leaves little doubt as to the validity and strength of assumptions of causality.

Animal toxicological evidence is supportive of the human clinical observations which suggest that the primary mechanism of action of ozone is the induction of vigorous inflammatory responses, which in turn lead to acute adverse respiratory effects.

Peroxyacetylnitrate (PAN) is far less toxic than ozone, but because it and the other photochemical oxidants (nitric acid and hydrogen peroxide) are strong oxidising agents, they also are irritating substances at high concentrations capable of significant effects on various parts of the respiratory tract and mucous membranes. The range and severity of the effects on health are dependent on the pollutant concentration, exposure duration, and individual sensitivity.

6.5.2 Effects on Vegetation and Materials

Photochemical oxidants are serious phytotoxins. Along with sulphur dioxide, the two photochemical oxidants ozone and peroxyacetylnitrate (PAN) are the most widely studied air pollutants in terms of their effects on plants. One study of crop losses in the United States found that short-term exposures to ozone levels of about 100 $\mu g/m^3$ resulted in up to 22% yield losses. However, because commercial crops are mainly grown in areas of relatively low concentrations

of photochemical oxidants, a more significant factor on the outskirts of most urban areas are the effects on market gardens, domestic fruit and vegetables, and ornamentals.

Ozone affects plants by reducing the photosynthetic rate, thereby lowering the production potential. It also interferes with the respiration rate, first reducing it until visible injury occurs, then speeding it up, depleting the plant's hard-earned energy reserves. Ozone interferes with growth and reproduction. For example, in geranium and carnation, ozone prevents or reduces the amount of side branching, retards flowering and generally depresses both growth and the amount of flowers. As little as about 200 μg/m^3 for 5 to 7 hours daily will do this. It has been established that most sensitive plants, such as lucerne cereals, soybeans and tobacco, will sustain injury if exposed to O$_3$ concentrations of about 100-250 μg/m^3 for 2 to 4 hours.

Just like human health effects, for most plant species there is a monotonic relationship between ozone concentration and adverse effects, and so no threshold concentration is apparent. An exception to this is corn, which has the plant physiological equivalent of a Lowest Observed Effects Level to short-term exposures to O$_3$ of about 160 μg/m^3.

The effects of PAN on plants are similar to ozone, except that it is more deadly; only about 50 μg/m^3 (short-term average) being required to induce injury. Thus PAN concentrations in excess of about 250 μg/m^3 for 2 to 4 hours are regarded as serious levels for phytotoxic effects. PAN is more likely to damage young plant tissue than is ozone, and its action is favoured by different physical and physiological conditions.

Nitric acid has been a major contributor to the transcontinental "acid rain" problems of North America and most of Europe. Acid rain deposition adversely affects plants through direct exposure and the alteration of soil acidity. Because of it's isolation, New Zealand is relatively free of susceptibility to acid rain of this nature. In some other countries also, the deposition of nutrients such as nitrates from the air environment to water bodies can be significant, and can aggravate algal blooms and potentially eutrophication.

Photochemical oxidants are corrosive to most materials at high concentrations, including plastics, metals and fabrics. This causes practical difficulties in the atmospheric sampling of these gases, and teflon or glass sampling systems have to be used for reproducible results. Some rubber products are particularly vulnerable to damage by ozone, and in fact the Los Angeles County Air Pollution Control District for many years used measurement of the crack depth in specially formulated strips of natural rubber as a standard method for ozone.

6.5.3   Effects on Visibility

Photochemical reactions form fine particulates, such as sulphates, nitrates and organic aerosols, which scatter light, so they contribute to reduced visibility. White haze is common in high concentration photochemical pollution episodes in major cities overseas. Degraded visibility affects the aesthetic value of the environment and can impact on tourist perceptions of New Zealand's image.

6.6   Air Quality Guidelines for Photochemical Oxidants

In 1994 MfE established AAQGs for ozone of 150 μg/m^3 (one hour average) and 100 μg/m^3 (eight hour average). These guidelines were based on the World Health Organization (WHO) air quality guidelines for Europe of 1987.

In response to the results of recent health effects studies, presented above, especially the confirmation of there being no threshold concentration for ozone, those jurisdictions who have reviewed their air quality standards/guidelines for ozone have tended to come out with recommendations to revise them downwards. Examples of that include the European Union, United Kingdom and Australia, although only the European Union has to date accepted the recommendation and made the change, or imposed the standard

Current international air quality standards and guidelines for ambient concentrations of ozone are as in Table 6.2. For simplicity, the numerical values of the concentrations have been converted to μg/m^3, even though in Australia and the United States they are actually described in terms of ppm.

Table 6.2 - Ozone Guideline Values in ug/m3

Country/Authority	One hour average	four hour average	eight hour average
Australia	210	170	
European Union	150		100
USA – Federal	[260]		160
-- California	190		
Japan	120		
WHO	150		120

The one hour average standard for the United States is in parentheses, because it is to be phased out.

The position of WHO on guidelines for photochemical oxidants/ozone is appears to be at odds with the view taken on particulates, as another class of air pollutant with no apparent threshold concentration. The 1987 guidelines were actually ranges, 150-200 μg/m^3 (one hour average) and 100-120 μg/m^3 (eight hour average), although those countries which adopted them (including New Zealand) tended to use the lower values in each case. The European Union is a recent example. WHO are now recommending slightly revised values, but with no ranges, these being 150 μg/m^3 (one hour average) and 120 μg/m^3 (eight hour average).

However, this appears contrary to the situation regarding particles, where the absence of a threshold led WHO to adopt the position of not being able to recommend a guideline for PM_{10}, although having no such difficulty with setting guidelines for ozone. There have been only minor changes to the ozone guidelines; in fact the numerical values of the concentrations have become more definite.

The concern still exists, introduced earlier, that air quality standards and guidelines for photochemical oxidants have been expressed solely in terms of ozone, and not photochemical oxidants.

For the purpose of assessing ambient concentrations of ozone in New Zealand, it would appear reasonable to use the MfE AAQGs for ozone of 150 $\mu g/m^3$ (one hour average) and 100 $\mu g/m^3$ (eight hour average).

6.7 Concentrations of Photochemical Oxidants

There has been very little monitoring for photochemical oxidants in New Zealand. In the late 1970s/early 1980s attempts were made using fairly basic technologies to understand the formation of photochemical oxidants in Auckland, and to a lesser extent in Christchurch. Routine monitoring of ozone only commenced in Auckland in 1995.

There is an array of different methodologies used in New Zealand to measure ambient concentrations of photochemical oxidants and ozone. The standard method for measurement of atmospheric concentrations of ozone is that set out in Standards Association of Australia AS3580.6.1-1990, and is based on ultra-violet spectroscopy. This method, specific for ozone, is what is being used for the recently reactivated monitoring in Auckland, and for some limited monitoring during the 1996/97 summer in Christchurch. In the past, other methods have been used. The standard method in the 1970s, when standards/guidelines were specified in terms of photochemical (or "total") oxidants, was a chemical reaction with neutral-buffered potassium iodide. After first passing the gas sample over glass fibre filters impregnated with chromium trioxide, to remove reducing agents such as sulphur dioxide, the photochemical oxidant gases (ozone, nitrogen dioxide – often then included as a photochemical oxidant – and peroxyacylnitrates) are brought into contact with the potassium iodide reagent, to form iodine. Sometimes, a crude attempt was made to correct for NO_2.

Another method used to measure photochemical oxidants in Auckland and Christchurch was an instrumental version of the above chemical method, also with a chromium trioxide filter for SO_2. This electrochemical method measures the current required to regenerate a hydrogen layer around an electrode previously depleted by reaction with iodine. The iodine is produced by reaction of the photochemical oxidants with a potassium iodide solution. NO_2 is detected by the method with an efficiency of about 10%, so it should be corrected for. Also, ozone was measured in the late 1970s/early 1980s with an instrument based on the chemiluminescent reaction of ozone and ethylene. For some aircraft flights over Auckland in the summer of 1996/97 an instrument based on the chemiluminescent reaction between ozone and an inorganic dye was used.

The monitoring in Auckland during most summers between 1975 to 1982 gave a reasonable picture for its time of the potential for photochemical formation in that city. A similar pilot study was carried out in Christchurch in the summer of 1977/78. The general conclusion reached was that photochemical reactions occur in Auckland on up to about fifteen days per summer. Only on two days did the one-hour concentrations of photochemical oxidants exceed the MfE air quality guideline for ozone of 150 $\mu g/m^3$, and on eight occasions the then air quality guideline for photochemical oxidants of 120 $\mu g/m^3$ (one hour average) was exceeded. Not unexpectedly, the highest concentrations were measured at sites located more distant from the city, approximately 30-35 km to the north and south of downtown Auckland. The recently reactivated monitoring in Auckland is being carried out at similar sites, and also includes a monitor on the Skytower to investigate the effect of elevation.

As for Christchurch, the early work and some more recent work in the summer of 1996/97, using a mobile monitor, found photochemical reactions do occur in that city also. On occasions the concentrations in Christchurch exceed the equivalent concentrations in Auckland, although the air quality guideline has not been exceeded (possibly because of the limited nature of the monitoring). The four flights to measure profiles of ozone concentrations across Auckland carried out between 14 February and 27 March 1997 produced results in accordance with the general conclusions previously reached.

There is a view that concentrations of nitrogen oxides and reactive organic compounds in Auckland are high enough any day for photochemical reactions to occur, although adequate data sets for those precursors do not exist. The predominant factor would therefore be the prevalence of meteorological conditions favourable to photochemical reactions. In 1996 an assessment was made of the potential for photochemical air pollution to occur in New Zealand, focusing on the cities of Auckland, Hamilton and Christchurch. The analysis found that the meteorological conditions conducive to the formation of photochemical oxidants equivalent to an ozone concentration in excess of the one-hour average air quality guideline might be expected to occur downwind of Auckland, Hamilton and Christchurch on average about 3, 9 and 1 days per summer, respectively. There is likely to be large variations from year to year, and so it is possible that such events may occur as often as 10, 15 and 4 days per summer, respectively.

On the basis of meteorology alone, the highest potential for the formation of photochemical oxidants is in Hamilton, followed by Auckland, then Christchurch. However by virtue of its size, Auckland probably is the most likely city to have significant regional photochemical pollution episodes, but only adequate monitoring programmes in Christchurch and Hamilton will assess the actual situation in those cities. The meteorological assessment mentioned above made the relevant observation that the occurrence frequencies of elevated concentrations of ozone for the three cities are of a comparable magnitude to cities overseas, where air quality monitoring, research and policy have been a much higher priority than in New Zealand. Photochemical reactions producing lower, but still significant, concentrations of ozone might be expected to occur more frequently.

To return to the concern over the use of ozone as the indicator of photochemical oxidants, it is a reality that monitoring for photochemical oxidants in recent years has focused solely on ozone, as a result of the methodologies used (partly in response to the change in specification in standards/guidelines from photochemical oxidants to ozone). However, with the development in Australia of the "Airtrak" instrument a return to monitoring the specific pollutants of interest is now feasible. Airtrak provides information about photochemical oxidants and precursor conditions, in a form that is particularly useful to developing effective control strategies for photochemical oxidants.

The limited monitoring data for New Zealand of both photochemical oxidants and their precursors makes it difficult to assess the degree of risk posed by current levels, and therefore to estimate the emission reductions required.

6.8   Required Reduction in Emissions

It may be interpreted that controlling emissions of the precursors will achieve equivalent reductions in ambient concentrations of photochemical oxidants. The formation of photochemical oxidants in the atmosphere is more complex than that, and this makes decision-making on the most appropriate and effective air quality management strategy for photochemical oxidants difficult.

As well as the concentrations of the precursors, the ratio of the reactive organic compounds (ROC) and NO_x concentrations is also important. Only at values for the ratio of around 8:1 does reducing emissions of both ROCs and NO_x achieve equivalent reductions in ambient concentrations of photochemical oxidants. When ROC/NO_x ratios are considerably less than 8:1 (which is where New Zealand urban areas are estimated to be, although this is very much a first approximation), reducing emissions of ROCs have a larger impact on ambient concentrations of photochemical oxidants than reducing emissions of NO_x. The converse applies for ROC/NO_x ratios much greater than 8:1.

That does not mean, for example, that reductions in emissions of nitrogen oxides are not important in this regard (if indeed, a low ROC/NO_x ratio is where New Zealand urban areas lie on the ozone "isopleths"). It indicates that, depending on the nature of the urban airshed conditions, reducing emissions of one of the precursors may achieve more in terms of ambient concentrations of photochemical oxidants than would reducing emissions of the other precursor. As the precursors are air pollutants in their own right, the appropriate strategy needs also to consider the extent to which their own AAQGs are under threat.

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