Ministry for the
Environment
Manatu Mo Te Taiao

Review of the Ambient
Air Quality Guidelines

Effects of Air Contaminants on Ecosystems and Recommended Critical Levels and Critical Loads

Final Report

Prepared by Stevenson *et al,* for the
Ministry for the Environment's Review
of the *Ambient Air Quality Guidelines*

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Air Quality Technical Report 15

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Foreword by the Ministry for the Environment

This technical report has been prepared by Stevenson *et al.* for the Ministry for the Environment's review of the *Ambient Air Quality Guidelines* (1994) (1994 Guidelines). The report discusses the potential effects of air contaminants on ecosystems in New Zealand, and recommends guideline values to assist those responsible for monitoring and managing the impacts of air pollution on ecosystems. National guidance on how to assess and manage the effects of air pollutants on ecosystems was identified as an important part of revised air quality guidelines for New Zealand.

The Ministry for the Environment's (the Ministry) investigations into the effects of air pollution on New Zealand ecosystems began in 1998 with a series of reports (MfE 1998a, 1998b, 1998c) and a focus group meeting in June 1998. This initial work:

- reviewed the relevance of international research to New Zealand
- investigated whether current air pollution levels have the potential to affect New Zealand ecosystems and
- recommended priorities for further investigation.

The priorities for further investigation were to:

1. Prepare national guidance on how to determine significant adverse effects on ecosystems.
2. Investigate the suitability of international guidelines for New Zealand.
3. Research the sensitivity of native species, to develop guidance on assessment techniques (such as calculating deposition rates) and to monitor contaminants (particularly ozone) where they have the potential to affect ecosystems.

The Ministry decided to pursue priority one – to prepare national guidance. This report presents the results of this investigation and recommends guideline values for determining whether air pollutants are likely to cause adverse effects on ecosystems. Methods for calculating pollutant deposition rates from predicted or ambient monitoring results, and guidance for assessing whether a discharge is likely to cause adverse effects on ecosystems are also presented. This work therefore also goes some way towards achieving priority two - *to develop methods for assessing effects on ecosystems*.

Because guideline values for ecosystem protection should be considered at the same time as those for health protection, the recommendations in this report form part of the proposed changes to 1994 Guidelines that are summarised in the Ministry's discussion document – *Proposals for Revised and New Ambient Air Quality Guidelines for New Zealand* (MfE, 2000). Specific comments on this technical report can be made within your submission on the Ministry's Discussion Document.

The initial reports on the effects of air pollution on ecosystems and other technical reports prepared for the review of the 1994 Guidelines can be downloaded from the Ministry's website at http://www.mfe.govt.nz/monitoring/epi/airqualtech.htm.

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This report has been peer reviewed by the Ministry for the Environment and Dr Dave Doley of the Department of Botony, University of Queensland, Australia.

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Summary

This report has been prepared by Stevenson et al. for the Ministry for the Environment's review of New Zealand's *Ambient Air Quality Guidelines* (1994). It examines research and policy approaches to assessing and managing the effects of air pollution on ecosystems and recommends possible guideline values that could be adopted to assess such effects in New Zealand.

Scope and general approach

In this report, an ecosystem is considered to include all the living organisms within natural and semi-natural systems and the environments in which they live and on which they depend. The work specifically excludes the direct effects of pollutants when people inhale them. The scope of the assessment is potentially enormous, particularly given the range of potential pollutants, organisms and impact pathways that may affect an ecosystem's function. On the basis of current scientific evidence it is only be possible to assess a fraction of the organisms and impact pathways, and a limited number of common contaminants. Even for the various impacts that have been documented, there is still a high degree of uncertainty, particularly when compared with human health effects studies.

However, as a general principle, protecting the fundamental components of an ecosystem protects the ecosystem as a whole. The most fundamental of those components are the climate and hydrology, and the physical and chemical characteristics soils and substrata. As the primary photosynthetic producers, plants are the next most fundamental component of ecosystems. To a large extent, plants determine and exemplify the nature, diversity and health of ecosystems. Accordingly, if the characteristics of the fundamental components are protected, and substantially unaltered conditions for plant growth are assured, the health and quality of the ecosystem is also assured.

Animals are likely to be protected from direct toxic effects of air pollutants by standards or guidelines established to protect human health, although the possibility of some exceptionally sensitive species being adversely affected by such levels cannot be ruled out.

The discharge of toxic components, such as heavy metals or persistent organic toxins, into the environment can adversely affect animals in an ecosystem without adversely affecting plants. Toxic components are therefore a possible exception to the general principle that protecting the fundamental ecosystem components and plants protects the ecosystem. Such effects are considered briefly in this report. At this stage, the available information indicates that current deposition rates of such contaminants are generally too low to cause adverse effects. One exception would be localised impacts of some large emission sources.

Recent research and guideline values

There has been considerable research in Europe and North America to determine critical levels and critical loads of air pollutants for a variety natural and semi-natural ecosystems and species. Critical levels relate to toxic effects of ambient air pollutants on plants. They are available for sulphur dioxide, oxides of nitrogen, ozone and ammonia. Critical loads relate to the toxic effects of deposition of air pollutants into ecosystems. These are available for acidity, (which relate to the acidifying effect of sulphur and nitrogen air pollutants on ecosystems, particularly on soil/plant systems and natural waters), and nitrogen (associate with the effects of nutrient enrichment).

Currently, the most comprehensive approach to ecosystem management has been developed by the United Nation Economic Commission for Europe (UNECE) as part of the Convention on the Long

Range Transboundary Air Pollution. The UNECE has used two principal measures for protecting natural and semi-natural ecosystems;

Critical levels:	*The concentrations of pollutants in the atmosphere above which direct adverse effects on receptors such as plants, ecosystems or materials, may occur according to present knowledge*
Critical loads:	*A quantitative estimate of an exposure, in the form of deposition, to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.*

Generally, critical levels are based on relatively short term (e.g. hours to a year) effects of a single pollutant species (e.g. NO_x, SO_2 or O_3). Critical loads involve assessing the effect that several different pollutants may have over longer time periods (e.g. 1 year to decades). Currently, UNECE has defined critical loading for acidity deposition and nitrogen deposition. Both critical load and critical levels vary from traditional air quality guideline values established for the protection of human health in several significant ways including;

- Critical loads/levels are developed for the protection of both single organisms and ecosystems
- Critical loads/levels are established as close to the threshold point as possible with little or no margin of safety
- Critical loads/levels consider both direct and indirect impact mechanisms - they are effects-based approaches to environmental management
- Critical loads consider impacts over a longer time frame than critical levels
- Both critical loads and critical levels are defined in terms of their environment (e.g. ecotype)

The critical load and critical level concept has subsequently been adopted by the World Health Organisation (WHO) Proposed Air Quality Guidelines for Europe (1996). Due to their comprehensiveness and international acceptance this approach seems to be a valid method for New Zealand to consider, using these concepts as a management tool.

However, current UNECE/WHO (1996) guidelines have been established only for central and northern European conditions. Therefore, in the absence of detailed specific New Zealand research, particularly for native species, it is difficult to accurately gauge their applicability here. European ecosystems have developed with human influences at varying the degrees of intensity over many centuries, and have almost certainly adapted to some degree to this situation. On the other hand, most New Zealand ecosystems have developed under conditions of low nitrogen supply, and have been subject to increased nitrogen supply only over about the last century, or less in many cases. Therefore, New Zealand should take a careful approach to applying these guidelines.

Implications for New Zealand

Critical Levels

The recommended critical levels for the different airborne pollutants are presented in Table I. The critical levels in Table I are based upon the UNECE/WHO (1996) and Australia and New Zealand Environment and Conservation Council (ANZECC) guideline levels. The fluoride guidelines presented with Table I are the same as those include in the Ministry’s 1994 Guidelines.

Table I. Recommended Critical Levels

Contaminant and land use	Critical level	Averaging period	Additional requirements
Sulphur Dioxide (SO_2)			
- Agricultural crops	30 µg/m^3	annual & winter average	
- Forest and natural vegetation	20 µg/m^3	annual & winter average	
- Forest and natural vegetation	15 µg/m^3	annual & winter average	ETS[i] <1000°C days >5°C.
- Lichen	10 µg/m^3	annual	
- Forests	1.0 µg/m^3 [ii]	annual	ground level cloud present>10% of time.
Nitrogen oxides (NO_X)	30 µg/m^3 [iii]	annual	
Ammonia (NH_3)	8 µg/m^3	annual	
Ozone (O_3)			
- Forests	21,400 µg/m^3-h [iv]	6 months[v]	
- Semi-natural vegetation	6,420 µg/m^3-h [iv]	3 months[v]	
- crops (yield)	6,420 µg/m^3-h [iv]	3 months[v]	
- crops (visible injury)	428 µg/m^3-h [iv]	5 days[v]	Mean daytime vpd[vi] below 1.5 kPa
	1,070 µg/m^3-h [iv]	5 days[v]	Mean daytime vpd[vi] above 1.5 kPa
Fluoride			
- Special land use	1.8 µg/m^3	12-hr	
	1.5 µg/m^3	24-hr	
	0.8 µg/m^3	7-day	
	0.4 µg/m^3	30-day	
	0.25 µg/m^3	90-day	
- General land use	3.7 µg/m^3	12-hr	
	2.9 µg/m^3	24-hr	
	1.7 µg/m^3	7-day	
	0.84 µg/m^3	30-day	
	0.5 µg/m^3	90-day	
- Conservation areas	0.1 µg/m^3	90-day	

[i] - Effective Temperature Sum
[ii] - sulphate particulate
[iii] - Assumes that either O_3 or SO_2 are also present at near guideline levels
[iv] - AOT40 values
[v] - Only measured during daylight hours with a clear global radiation of 50 Wm^{-2} or greater
[vi] - Vapour pressure deficit

Generally in areas where sensitive ecosystems are likely to be located (i.e. rural and forest environments), current background pollutant levels are unlikely to breach these critical level guidelines. Concern may arise if valued ecosystems are located near large point sources or urban environments. It is difficult to make this same broad statement with regard to ammonia, since emission sources, emission rates and ambient concentrations in New Zealand are generally not well known. Intensive agriculture is a potentially significant ammonia source in rural areas where sensitive ecosystems may also be located, although what little information is available suggests that the critical level for ammonia is unlikely to be exceeded.

Of particular interest is the high sensitivity of forests and lichen to long exposures to sulphur dioxide. It is also important to note that the critical levels adopted by the WHO (1996) are much lower than the 1994 guideline value for human health protection of 50 µg/m^3 (annual average).

Critical loads

Critical loads for acidity are defined in terms of the acid neutralising capacity of the soil, which depends on the nature of the parent material and texture of the soil. Estimation of probable critical loads for acidity for a range of New Zealand catchments selected to indicate the likely lower ranges of critical loads are presented in this report, and these, combined with estimates of the possible range of acidity deposition, indicate that problems of soil/ecosystem acidification are unlikely here. Accordingly, it is suggested that critical loads for acidity can be ignored unless it is known that the area requiring protection is likely to be sensitive to acid deposition, as indicated by very low levels of alkalinity in water draining from the area (for example less than 10 mg/l as calcium carbonate), or from other information

The lack of information about nitrogen inputs to potentially sensitive New Zealand ecosystems makes both the application of European critical loads for nitrogen and the recommendation of New Zealand-specific critical loads very uncertain. Because of the development of most New Zealand native ecosystems under low nitrogen supply conditions, the "background" level of nitrogen inputs is probably about 1-5 kg N/ha-yr. It is unlikely that a total atmospheric input (including "background" concentrations of nitrogen species and additional contributions from anthropogenic emissions) below 5 kg N/ha-yr would result in significant ecosystem nutrient enrichment effects. In other words, a critical load for nitrogen of 5 kg N/ha-yr is the likely to protect any local ecosystem.

However, because plants growing on fertile soils are a significant source of ammonia in air, sensitive ecosystems adjacent to agricultural land may already be subject to nitrogen loads above this conservatively recommended critical load. This situation may make it possible to determine approximate nitrogen loads which either have detectable effects on sensitive native ecosystems, or below which effects have not been detected. The investigations required to obtain at least some preliminary, but very useful information would be quite modest.

Meanwhile, the UNECE critical loads for nitrogen could be used to give some guidance on possible nitrogen loads which might be acceptable for equivalent New Zealand ecosystem types, although with decreasing certainty the higher the anticipated load above 5 kg N/ha-yr. It does appear reasonable to consider the upper limit of the UNECE critical load range to be a level at which nitrogen enrichment effects in equivalent New Zealand ecosystem types are very likely. As far as possible, the report provides guidance on likely New Zealand equivalents of the European ecosystems.

Where the potential effects of acid deposition and nitrogen enrichment need to be assessed the report suggests that acid deposition and nitrogen enrichment can be estimated using approximate relationships between ambient air concentrations and their deposition rates for the pollutants of concern. This enables ambient air monitoring data (modelled or monitored) to be used to estimate the worst-case deposition situation. The results can then be compared with the critical load for the appropriate ecosystem. If the ambient air concentrations suggest that there may be problems from acid deposition or nitrogen enrichment (using the specified relationships), further investigations may be required, such as measuring actual deposition rates and soil acid neutralising capacity.

Table II sets out the ranges of acidity and nitrogen deposition rates corresponding to annual average concentrations of 1 $\mu g/m^3$ of the various contributing pollutants.

pTable II. Annual acidity and nitrogen deposition estimates for ambient air with annual average pollutant concentrations of 1 µg/m^3

	Dry gaseous	Wet deposition	Dry gaseous	Wet deposition
	Acidity (equiv/ha-yr)		Nitrogen (kg N/ha-yr)	
NO_2	25	Nil	0.3	Nil
HNO_3	100	75	1.4	1.1
NH_3	370	400	5.2	2.8
SO_2	200	<<40	-	-

These estimates almost certainly over-estimate the acidification resulting from air pollution. They do not take account of deposition of alkaline materials that may be present in particulate material (for example from wood ash), which may reduce or completely balance out the overall acidification, and other factors, such as harvesting or denitrification that may also decrease ultimate effects. Nevertheless, because these estimates are likely to be high, they do provide a basis for assessing whether acidification is a potential issue that requires further, more detailed assessment.

Because of the low probability of significant soil acidification in New Zealand and the uncertainties about the nitrogen sensitivities of New Zealand ecosystems, it is not recommended that regulatory limits be established for critical loads. However, it is appropriate for councils to identify valuable ecosystems and to determine whether existing or predicted ambient air quality has the potential to affect them via nitrogen loads. Similarly, it would be appropriate for such assessments to be undertaken as part of the assessment of environmental effects for consent applications for discharges to air.

Further local investigations are also desirable to refine the relationships between ambient air concentrations of nitrogen and sulphur compounds and deposition rates of acidity and nitrogen.

1. Introduction

The Ministry for the Environment (the Ministry) is currently reviewing the *Ambient Air Quality Guidelines* (1994) (the Guidelines). These Guidelines primarily address human health effects. Only fluoride has guideline values aimed at protecting ecosystems. This report contributes to the review process by examining research and policy approaches for assessing and managing the effects of air pollution on ecosystems. Recommendations made in this report will be used as a basis for possible guideline values and guidance that may be used to address such effects in New Zealand.

This report builds on previous work by the Ministry detailed in Ministry for the Environment, 1998a, 1998b, 1998c, and 1998d and the submissions made on those reports. These initial reports reviewed current research (both here and overseas), identified the most critical mechanisms involved and prioritised areas for further work. This present report focuses on priority one, which was to develop national policy for managing air pollution effects on ecosystems. It introduces and recommends approaches to managing impacts on ecosystems in New Zealand through the use of critical levels and critical loads of airborne contaminants.

Since 1994, there has been considerable research in Europe and North America to determine critical levels and critical loads of air pollutants for a variety natural and semi-natural ecosystems and species. Critical levels, which relate to toxic effects of pollutants on plants, are available for sulphur dioxide, oxides of nitrogen, ozone and ammonia. Critical loads which relate to damaging effects of deposition of pollutants onto land, are available for acidity, (which relate to the acidifying effect of sulphur and nitrogen air pollutants on ecosystems, particularly on soil/plant systems and natural waters), and nitrogen (which relate to the effect of nutrient enrichment).

Critical loads strongly depend on the characteristics of the ecosystem. They may require site-specific investigations to establish particular ecosystem characteristics (in order to select appropriate critical load values) and to determine existing and/or predicted acidity and/or nitrogen loads (for example to decide appropriate limits to be placed on discharges). Such investigations, particularly for establishing existing loads, require relatively long-term investigations to obtain annual or longer-term average deposition rates. In Europe, these investigations are major, long-term, regional research programmes that involve extensive mapping of ecosystem characteristics and deposition rates.

The previous reports investigated whether loads of acid deposition and nitrogen enrichment are likely to cause adverse effects in New Zealand. With the possible exception of some enrichment-sensitive ecosystems, they found that adverse effects here are unlikely. However, there may be instances when the potential effects of acid deposition and nitrogen enrichment need to be assessed. To do this, the report suggests that estimates of acid deposition and nitrogen enrichment can be calculated from the approximate relationship between ambient air concentrations and their deposition rates. This enables ambient air monitoring data (modelled or monitored) to be used to estimate the worst-case deposition situation. The results can then be compared with the critical load for the appropriate ecosystem. If the ambient air concentrations suggest that there may be problems from acid deposition or nitrogen enrichment (using the specified relationships), further investigations may be required, such as measuring actual deposition rates and soil acid neutralising capacity.

1.1 Overview of air quality effects on ecosystems

In this report, an ecosystem is made up of all living organisms within natural and semi-natural systems and the environments in which they live and on which they depend. The scope of the assessment is potentially enormous, particularly given the range of potential pollutants, organisms and impact pathways that may affect an ecosystem's function. On the basis of current scientific evidence it will only be possible to assess a tiny fraction of the organisms and impact pathways for a limited number of common contaminants. Even for the various impacts that have been documented, there is still a high degree of uncertainty, particularly when compared with studies of human health effects.

However, as a general principle, protecting the fundamental components of an ecosystem also protects the ecosystem as a whole. The most fundamental of those components are the climate and hydrology, and the physical and chemical characteristics soils, and substrata. Subject to the introduction of exotic species (which is beyond the scope of this review), all life forms develop such that the ecosystem attains a state of dynamic equilibrium, within the constraints of the fundamental components. As the primary photosynthetic producers, plants are the next most fundamental component of ecosystems and to a large extent determine and exemplify the nature, diversity and health of ecosystems. Accordingly, if the characteristics of the fundamental components of an ecosystem are protected and substantially unaltered conditions for plant growth are assured, the health and quality of the ecosystem is also assured.

Animals are likely to be protected from direct toxic effects of air pollutants by standards or guidelines established to protect human health, although the possibility of some exceptionally sensitive species being adversely affected by such levels cannot be ruled out.

Introduction of toxic components, such as heavy metals or persistent organic toxins, can adversely affect animal members of ecosystems without adverse effects on plants. Therefore these are a possible exception to the general principle that protection of the fundamental ecosystem components and plants protects the ecosystem. Such effects are discussed briefly in section 12 of this report.

The primary ecosystem impacts of air pollution on ecosystems result from the deposition onto or entry into organisms (e.g. plants and animals), soil and water. Since plants are sessile organisms with large biologically active surface areas, they are generally the principal receptors of airborne pollutants. Plants are not only affected by air pollutants and the effects of air pollutants on soils, they are also a primary pathway through which air pollution is transferred into soils. They are commonly one of, or the major mechanism by which, sulphur and nitrogen species are taken up from air and introduced to soils. This further reinforces the importance of examining the effects of air pollution on plants.

Plants respond according to their seasonal nutrient requirements and nutrient availability, climatic conditions, and the properties of the contaminant. For example, in some instances deposition of nitrogen or sulphur compounds can be beneficial and will act as a fertiliser stimulating growth. However, if pollutant deposition causes a pH imbalance in the plant, altered metabolic processes associated with the repair of damage and adaptation to new conditions deplete resources which otherwise would have been used in normal development. The pathway used depends on the type of plant, the level of pollutant deposition and availability of base cations from the soil. The ultimate result may be reduced overall growth, leaf damage, die back, and/or reduced reproduction i.e. seed set or viability.

Where plant communities experience chronic exposures to air pollution, the resultant stresses may produce a gradual selection against pollutant-sensitive individuals and a change in the species' genome. Annual or short-lived varieties are particularly at risk from this process, but even longer-living species (for instance trees) may be susceptible to changes when affected by exposure to air pollutants over many decades. In addition to changes in genome, changes in species distribution and dominance occur as those plants that are able to cope with the ambient air pollution survive and replace plants that do not.

Long-term flow-on effects from ecosystem acidification include acidification of soils and waterways. The degree to which acid deposition causes acidification is largely determined by the acid neutralising capacity of the soil, which in turn is largely determined by the parent material. Soils that are the products of weathering of acidic or silica-rich rock have less acid neutralising capacity than soils derived from basic material. Acidification effects can release aluminium into soil solution and surface waters causing serious losses of flora.

Acidification of soils and waters causes similar effects on animals as on plants but often over a shorter time scale. This leads to dominance of species that are tolerant of the changed conditions. Further changes in succession processes follow from impacts on the consumers and decomposers of the community. Such flow-on effects can be devastating - for example, the acidification of North American lakes, which has resulted in crystal clear waters almost devoid of fish, and the consequent decline in other species that relied on the fish as a food source.

1.2 Critical loads and critical levels concepts

Much of the current knowledge about the effects of the ‘guideline’ pollutants in ecosystems arises from studies of the effects of acid rain, including forest die-back and acidification of surface waters, with consequent decline in aquatic ecosystems. The concepts of critical loads and critical levels have arisen from this and are now widely accepted as an appropriate tool to provide estimates of target levels/loads for decision makers. The intention of critical loads/levels is to directly link adverse impacts on the environment with targeted source control initiatives. This concept was originally utilised by Canadian government in the early 1980s but has since been adopted and developed by the United Nations Economic Commission for Europe (UNECE) Convention of Long Range Transboundary Air Pollution (LRTAP). The World Health Organization (1996) (WHO) drew heavily upon this work (Umweltbundesamt, 1996; Bull, 1992) when defining and evaluating critical loads and levels included in the widely distributed pre-publication summary of the 1996 Air Quality Guidelines for Europe.

The UNECE Workshop on Critical Loads for Sulphur and Nitrogen at Skokloster, Sweden in 1988 defined critical levels and loads as follows:

Critical levels:	*The concentrations of pollutants in the atmosphere above which direct adverse effects on receptors such as plants, ecosystems or materials, may occur according to present knowledge.*
Critical loads:	*A quantitative estimate of an exposure, in the form of deposition, to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.*

Currently critical levels have been established for sulphur dioxide, ozone, ammonia, fluoride, and nitrogen oxides and are expressed as threshold average ambient air concentrations for specified averaging periods. Critical loads have been defined for the total deposition of acidity and nitrogen expressed as deposition fluxes.

The critical load and critical level concept varies significantly from the criteria used to establish conventional ambient air quality guideline values for human health protection. A comparison between conventional human health ambient air guidelines and critical loads and critical levels is presented in Table 1. An important difference between critical loads and critical levels on the one hand and conventional guideline values on the other is that ecosystem guideline values are established as close to the threshold point as possible (i.e. there is little or no safety margin).

Table 1: Comparison of conventional human health guideline values, critical levels and critical loads (Source: adapted from WHO, 1996)

Conventional Guideline Values	Critical Levels	Critical Loads
Objectives are set well below known effects to provide some safety of margin for especially sensitive receptors or unknown consequences	Objectives are set as close to the effects thresholds as possible.	Objectives are set as close to the effects thresholds as possible.
Adverse effects are experienced and evaluated at an organism level (e.g. human health)	Adverse effects may be experienced and evaluated from an organism to ecosystem level	Adverse effects are generally experienced and evaluated at an ecosystem level
Adverse impacts associated with exceedances are usually observed within a short time (i.e. between hours and a year)	Adverse impacts usually result from short to medium term exceedances	Adverse impacts usually result from long term (years to decades) exceedances and may be cumulative
No beneficial effects occur at any levels	Some potentially beneficial changes may occur	Some potentially beneficial changes may occur

Critical loads and critical levels are intended to represent a threshold point at which *some* change occurs in the function and/or structure of an individual plant or ecosystem. Each criterion may be based on one of many different possible impact mechanisms and the threshold point at which the first adverse change occurs is invariably uncertain due to the complexity of the system.

Accordingly, critical load and critical level thresholds are based upon a subjective assessment of when a change is sufficient to be classified as an ‘adverse impact’. This is particularly evident for nitrogenous pollutant deposition since these compounds can have multiple effects on plant development, some which are potentially beneficial, and all which are moderated by environmental and biological factors. Consequently, critical levels and critical loads generally represent ambient air concentrations and deposition rates below which most the most sensitive components of an ecosystem will be protected, given the current level of understanding. However, in many instances the scientific basis for determining accurate levels is limited (Fangmeier et al., 1994).

The critical levels and loads approach is largely based upon the UNECE approaches to controlling emissions in relation to transboundary pollutant transport, through regional scale dispersion modelling and mapping processes. They have therefore been primarily developed for northern European conditions.

2. Critical levels for nitrogen oxides and ammonia

2.1 Environmental effects of nitrogen oxides and ammonia

Short term phytotoxic responses of plants to NO_x and ammonia (NH_3) are predominantly associated with foliar uptake of the pollutants through stomata, although a limited amount of NO and NO_2 also penetrates through the cuticle and epidermal layers of plants. Their uptake is highly correlated to changes in stomatal conductance (aperture), which varies with irradiance, microclimate, internal CO_2 concentration and plant water status. Uptake is highest for ammonia, while that of NO_2 is larger than NO. For lower order plants, like bryophytes and lichen that do not have waxy cuticles and stomata, foliar uptake is potentially greater (Van Der Eerden, 1998).

The impacts of NO_x and ammonia on plant foliage depend upon the pollutant solubility or decomposition in the cell sap and its reactivity with cellular components. Therefore, due to different chemical properties and plant biochemistry, assimilation/detoxification rates and mechanisms vary between pollutants. In general, plants take up NO_2 and NH_3 readily due to the pollutant's high solubility in cell sap. Ammonia dissolves in the sap to form NH_4^+, and NO_x forms nitrate (NO_3^-) and nitrite (NO_2^-) (Bytnerowicz and Fenn, 1996; Stulen et al., 1998; Wellburn, 1990).

Short term exposures to high ambient nitrogen pollutant concentrations cause nitrite and ammonium ions to accumulate within the plant. In turn, this causes stress as the plant resists cellular acidification and interference with critical enzymes and regulatory mechanisms. The response to pollutants varies significantly depending upon environmental factors (climate and soil conditions) and plant species (Luger et al., 1998; Yin et al., 1998; Pearson and Soares, 1998; Wellburn, 1990).

Currently no in-situ studies have demonstrated a significant toxic effect associated with dry deposition of NO_x on semi-natural ecosystems at realistic ambient concentrations (Lee and Caporn, 1998). However, in combination with O_3 and SO_2, considerable synergistic effects have been demonstrated. Nitrate and nitrite are the main products of NO_2 and NO assimilation, and Wellburn's (1990) review of effects indicates that SO_2 may disrupt the detoxification rate of nitrite within plants. At elevated levels of both NO_X and SO_2, plants are subject to simultaneous damage by both nitrite and sulphite in various ways. Nussbaum, Geissmann and Fuhrer (1995) suggest that nitrogen oxides may enhance the toxicity of ozone rather than having a directly toxic effect.

Although ammonia is toxic in isolation, a few experimental studies have also demonstrated synergistic effects of ammonia in combination with other pollutants. However, the interacting effects of these pollutant mixtures upon plant physiology are complex and possibly antagonistic. Effects have also been found to vary significantly between plant species (Fangemier et al., 1994).

In addition to directly toxic effects, nitrogenous air pollutants are also a potential source of growth-stimulating nutrients for plants. While initially beneficial for individual plant species in isolation, an enhanced supply of nitrogen may, over extended periods, also have a negative effect upon individual species' plant physiology ecosystem function and resistance to environmental stresses (refer to Section 6.4.1 of this report).

2.2 Nitrogen oxides ecosystem guideline values

The UNECE and WHO critical levels for nitrogen oxides are presented in Table 2. The annual mean of 30 µg/m^3 (15.7 ppb) for nitrogen oxides has been adopted as a European limit in the Air Quality Daughter Directive (DETR, 1999). Because ambient concentrations of nitrogen oxides are unlikely to be phytotoxic in isolation, the critical levels presented in Table 2 are set on the assumption that O_3 and/or SO_2 are also present at concentrations close to their critical levels, when growth inhibition from the combination would be expected. The WHO (1987) guidelines were set at the same levels as those in Table 2, but applied to nitrogen dioxide only. More recent evidence indicates that at low concentrations typical of ambient conditions, NO is more toxic than NO_2 (Umweltbundesamt, 1996).

Nitrogen oxides in isolation stimulate growth at concentrations below those of the critical levels.

A quantitative differentiation between ecosystem sensitivities is uncertain, but the UNECE have proposed that natural and semi natural ecosystems are the most sensitive to nitrogen oxide levels, followed by managed forests, and then agricultural crops.

Table 2. Critical levels for total nitrogen oxides in air

Organisation	Critical Level*	Averaging Period
UNECE (1996) and WHO (1996)	30 µg/m^3	Annual
UNECE (1996) and WHO (1996)	95 µg/m^3	4-hour

*Critical Levels for NO_X (NO and NO_2 added in ppb), expressed as NO_2 (µg/m^3)

2.3 Ammonia ecosystem guideline values

The UNECE (1996) and WHO (1996) critical levels for ammonia are based upon the Van der Eerden et al., (1991) ecotoxicological model for European heathland ecosystems. The UNECE critical levels presented in Table 3 are intended to be conservative enough to protect most vegetation types (Fangemier et al., 1994). Although a strong biochemical basis exists, the UNECE and WHO still considered the data base insufficient to justify the establishment of more species-specific guidelines (Fangemier et al., 1994; Pearson and Soares, 1998). However, the UNECE suggest that the relative sensitivities of ecosystems to ammonia is the same as that for nitrogen oxides - natural and semi-natural ecosystems the most sensitive, and managed forests more sensitive than crops.

Table 3. Critical levels for ammonia in air

Organisation	Critical Level	Averaging Period
UNECE (1996) and WHO (1996)	8 µg/m^3	annual
UNECE (1996)	23 µg/m^3	1 month
UNECE (1996)	270 µg/m^3	24 hour
UNECE (1996)	3300 µg/m^3	1 hour

2.4 New Zealand ecosystem nitrogen oxide and ammonia exposure

Annual average concentration of NO_x recorded at the Auckland, Mt Eden and the Christchurch, Madras St ambient air monitoring sites are approximately 40 µg/m^3 and 90 µg/m^3 respectively . However, these sites are located within dense urban areas and are representative of the higher range of NO_x concentrations within New Zealand. For rural locations, situated some distance from combustion sources, current monitoring data indicate typical annual concentrations of approximately 2-

3 µg/m^3 (Shooter et al., 1993). Therefore it is unlikely that NO_x critical levels will be exceeded in New Zealand except near major point or urban sources where both NO_x and either SO_2 or O_3 may be present in sufficient concentrations to cause problems. It is also unlikely that many sensitive ecosystems would be located in such urban environments. Further monitoring around urban areas is needed to determine the spatial extent and magnitude of NO_x, identify potentially sensitive ecosystems and to assess potential impacts.

Currently there is very little information about ambient ammonia concentrations and emission rates in New Zealand. The most common source of ammonia within New Zealand is likely to be from productive farmland. Plants growing on fertile soil release significant amounts of ammonia (Harrison et al., 1989) and animal excreta may also be a significant source. Therefore, there may be instances where potentially large rural sources could be located near sensitive ecosystems. However, overseas data (Harrison et al., 1989) and the few local concentration and wet deposition studies available (Section 6.5) indicate that the critical level is unlikely to be exceeded in New Zealand.

3. Critical levels for sulphur dioxide

3.1 Environmental effects of sulphur dioxide

Sulphur dioxide is toxic to plants, and its ability to bleach chlorophyll is a key factor in this toxicity. In plants and plant communities, resistance to sulphur dioxide pollution effects varies according to the plant species, the plant's stage of development, and other external factors such as soil, season and temperature. These differing degrees of sensitivity can result in changes in interspecies competition, the reduced abundance of sensitive varieties, and the alteration of the structure and function of the community. The secondary succession processes that follow will then impact on the consumers and decomposers in the ecosystem and animals that have specialised habitat requirements (WHO, 1987).

Plant metabolism of sulphur dioxide may follow either reductive or oxidative pathways. In reductive metabolism, the sulphur is used as a nutrient and the level of sulphur dioxide uptake at which metabolism changes from the reductive to the oxidative pathway varies with species. Herbaceous plants have higher sulphur:carbon ratios than woody species (Heber and Huve, 1998), and can therefore take up more sulphur dioxide per unit of biomass before adverse effects occur. Oxidative metabolism of sulphur dioxide in the plant generates acidity, requiring uptake of base cations from, and release of hydrogen ions into, the soil in order to maintain the internal pH of the plant. This contributes acidity to soils immediately on metabolism, and also renders the plant potentially susceptible to the effects of soil acidification in sites with low acid neutralising capacity. Acidification decreases the supply and availability of base cations from the soil, adversely affecting both nutrient balances (for example between nitrogen and magnesium) and the plant's ability to maintain internal pH.

Sulphur dioxide uptake by plant leaves occurs via the stomata, so that highest rates of uptake occur when moderate to high light conditions coincide with high plant water availability and low water vapour pressure deficits in the air. Stomatal transfer is limited under conditions of water deficit or at high temperatures. Consequently, stomatal opening and sulphur dioxide uptake may be greatest during winter, when ambient sulphur dioxide concentrations are likely to be highest.

In the Northern Hemisphere extensive damage has resulted to high altitude coniferous forests from high levels of transboundary sulphur and nitrogen pollution occurring particularly during the winter months. During winter, these evergreen trees exhibit low photosynthetic activity, but sulphur dioxide and oxides of nitrogen dissolved in cloud droplets impact on foliage, and the ions are absorbed directly through the cuticlar surfaces. Under cold conditions, there may be insufficient metabolic activity to de-toxify sulphur and nitrogen oxides. Further, substantial levels of wet deposition occur as snowfall, which releases acid pulses to the soil during the spring snow melt. The net result has been severe damage to the forests.

3.2 Sulphur dioxide ecosystem guideline values

Critical levels for sulphur dioxide are set out in Table 4 (Umweltbundesamt, 1996). The effective temperature sum (ETS) used in the determination of appropriate exposure levels is defined as:

$$\mathrm{ETS} = \Sigma d_i(T_I - 5^{\circ}\mathrm{C})$$

where Σ is over the 365 days of the year
$d_i = 1$ if $T_I > 5^{\circ}\mathrm{C}$
$d_i = 0$ if $T_I < 5^{\circ}\mathrm{C}$
T_I is the mean daily temperature.

Table 4. Critical levels for sulphur dioxide in air

Vegetation category	Critical Level (μg/m^3)	Averaging period	Constraints
Agricultural crops	30	Annual and winter mean	-
Forests and natural vegetation	20	Annual and winter mean	-
Forests and natural vegetation	15	Annual and winter mean	Effective temperature sum <1000^{O}C days >5^{O}c.
Lichens	10	Annual mean	-
Forests	1.0 sulphate particulate*	Annual mean	Where ground level cloud present>10% of time.

* Applies only where calcium and magnesium concentrations in cloud or mist are less than the combined ionic concentrations of H^+ and NH_4^+.

The Critical Level of 1.0 μg/m^3 for sulphate particulate is a surrogate measure for acidity of mists and clouds. Acid mists with pH of less than 3.5 (acidity greater than 150 μmol/l sulphate or 300 μmol/l hydrogen ion) have been shown to damage young trees and leaves.

3.3 New Zealand ecosystem sulphur dioxide exposure

Generally New Zealand sulphur dioxide concentrations are relatively low. Annual sulphur dioxide concentrations measured in Christchurch are typically around 7 μg/m^3, and for Auckland annual concentrations are about 1-2 μg/m^3. The Christchurch concentrations are likely to be representative of the upper end of the scale in urban New Zealand. Even at these levels SO_2 concentrations do not exceed any of the WHO (1996) critical level guidelines, suggesting that sensitive ecosystems are unlikely to be subject to significant direct effects from SO_2 in the unlikely event that they are located in urban areas.

Sensitive ecosystems may be more likely to be adversely affected by elevated sulphur dioxide concentrations if located near large industrial point sources (e.g. coal fired boilers), some of which. are located in rural areas.

Some New Zealand species may be more sensitive to sulphur dioxide than their European counterparts, as indicated by preliminary studies on lichens at Waikato University. However, further work is needed to confirm this indication.

4. Critical levels for ozone

4.1 Environmental effects of ozone

Ozone is a natural component of uncontaminated air, being present in air over our oceans at concentrations in the range of about 15-35 ppb (30-75 µg/m^3). Elevated concentrations of concern because of human health or phytotoxic effects are formed predominantly from photochemical reactions of the volatile hydrocarbons and nitrogen oxides emitted from dense urban areas. The rate of formation and ambient concentrations of ozone is highly influenced by precursor pollutant emission rates, radiation intensity and airshed ventilation characteristics. Because ozone is a secondary pollutant, peak surface concentrations can occur some distance from emission sources. Therefore under the right atmospheric conditions, high ozone concentrations have the potential to adversely affect crops and natural ecosystems located in relatively isolated (and in other respects 'clean') areas.

Ozone is potentially one of the most phytotoxic of the major air pollutants. Typical symptoms of the adverse effects of ozone include visible leaf injuries (chlorosis and accelerated senescence), reduced growth and yield, and altered sensitivity to abiotic and biotic stresses (e.g. susceptibility to pathogens and pests) (Bobbink, 1998). Ozone effects on plants vary, according to the degree of exposure. Generally, short term high concentration episodes will result in visible injury, and chronic long term exposures have more effect on the plants' metabolic processes, leading to a reduction in growth or production.

The predominant pathway for ozone uptake by plants is through open stomata so that environmental factors that influence the stomatal conductivity also significantly affect the absorbed ozone dose. Soil moisture deficit and atmospheric vapour deficit have been highlighted by UNECE as the most important of these factors, and have been included as qualifiers in the critical level assessment (Umweltbundesamt, 1993).

Other factors influence plant response to ozone. Among these are the potential synergetic effects of ozone with other pollutants (e.g. nitrogen oxides, ammonia, carbon dioxide and sulphur dioxide). The response of plants to these pollutant mixtures is known to vary considerably with species, climatic conditions and pollutant mixture. At present there is limited data from which to draw definite conclusions (Fangmeier et al., 1994; Umweltbundesamt, 1993).

4.2 Ozone ecosystem critical levels

The UNECE and WHO (1996) critical levels for ozone are expressed as a cumulative exposure over a concentration threshold. This exposure index is referred to as the AOT40 (Accumulative exposure Over a Threshold of 40 ppb (85.6 µg/m^3 at 0 °C)). The AOT40 is calculated as the sum of the difference between hourly ambient ozone concentration (expressed in ppb) and 40 ppb when ozone concentrations exceed 40 ppb.

The concentration threshold used by the UNECE (40 ppb) was established from the analysis of open-top chamber experiments in Europe. The experimental evidence indicated a linear relationship between yields for wheat, beans and pasture with exposures above a threshold ozone concentration. The review of data at the UNECE Egham (UK) workshop in 1992 recommended the use of 40 ppb as a suitable threshold value.

The specific AOT40 critical levels for crops were developed from the wheat yield response to ozone fumigation experiments over an approximate 3-month period. It was decided to retain this 3-month duration criteria in the definition of the UNECE and WHO (1996) critical levels. The 3,000 ppb-h (6,420 µg/m^3-h) critical level corresponds to an 'acceptable' yield loss of approximately 5 percent. Critical levels for longer periods may differ but cannot yet be supported by strong experimental evidence.

Little is currently known about impacts of ozone on natural and semi-natural vegetation. The studies that have been conducted indicate that for the more sensitive species, reductions in shoot biomass, relative growth rate and seed production occur at approximately the same AOT40 level as for crops (3,000 ppb-h). The critical levels for semi-natural ecosystems therefore reflect changes in individual plant performance and also in ecosystem composition. However, a degree of uncertainty is attached to this criteria due to the limited duration, species, and climatic conditions in the experimental studies from which it is derived (Bobbink, 1998; Umweltbundesamt, 1993).

The critical level for forests is based on open top experiments for beech seedlings, but is intended to cover both broadleaf and conifer forests. The UNECE have adopted this value as a *provisional* critical level for ozone evaluated over a growing season of 6 months. Although the basis of the ozone critical level is related to adverse impacts upon tree growth, the uncertainties in derivation of the critical level preclude any quantitative specification of loss of biomass yield decrease.

The short-term visible injury thresholds for crops have been established from white and subterranean clover response data. Although visible injury affects the economic marketability of some crops, the UNECE regards short-term acute injury as less significant than yield loss associated with extended exposure.

The UNECE critical levels for ambient ozone exposure to sensitive vegetation are presented in Table 5. The critical level values are only applicable when nutrient supply and soil moisture conditions are not limiting, since these factors influence stomatal conductivity and ozone flux into the leaf. For example, if water availability is restricted, the resultant closure of stomata will tend to lower the ozone damage predicted by the AOT40 dose-response function. This is particularly relevant to ozone since these conditions are most likely to coincide with the dry, sunny months of summer when the ozone potential is highest. These qualifications of the critical level assessment procedure were intended to relate the critical level more closely to a dose-response model (Umweltbundesamt, 1996).

Table 5. UNECE and WHO (1996) critical levels for ozone predicted by the AOT40 model

Vegetation Type	Ozone Critical Level		Time Period[1]	Constraints[2]
	ppb-hr	µg/m^3-h		
Forests	10,000	21,400	6 months	-
Semi-natural vegetation	3,000	6,420	3 months	-
Crops (yield)	3,000	6,420	3 months	-
Crops (visible injury)	200	428	5 days	Mean daytime vpd < 1.5 kPa
	500	1,070	5 days	Mean daytime vpd > 1.5 kPa

Notes:

1 Only measured during daylight hours, defined as hours with a clear sky global radiation of 50 W m^{-2} or greater

2 vpd = water vapor pressure deficit

4.2.1 Limitations of the UNECE guidelines

The UNECE critical levels were intended specifically for mapping purposes. They were developed to indicate the level at which potential adverse impacts upon vegetation may be experienced. The UNECE acknowledges that variation in environmental conditions and species can significantly influence the dose-response characteristics, and that to accurately assess the ozone impacts in any locality requires the consideration of additional factors.

The current critical level criteria have been based mainly on well-nourished plants in a limited number of central and northern European open-top chamber experiments. Assumptions or qualifications have to be made concerning variation due to climatic conditions, plant species (i.e. limited tree and natural plant types, and mainly annual crop species), exposure methodology, dose-response relationships, and synergistic effects between ozone and other pollutants.

It is also important to note that, in the determination of critical levels for ozone exposure, an adverse effect is evaluated in terms of yield or visible injury (and to a lesser extent changes in species composition). These parameters might not necessarily protect plants from reductions in quality or sensitivity to pathogens.

4.3 New Zealand ecosystem ozone exposure

McKendry's (1996) analysis of the potential for photochemical pollutant in New Zealand, indicated that Auckland, Hamilton and Christchurch have either source and/or meteorological conditions that may facilitate the occurrence of several significant ozone episodes each year. However, as McKendry acknowledges, without accurate continuous ozone monitoring and meteorological data it is not possible to fully evaluate the risk.

Currently only a limited amount of ozone monitoring has occurred within New Zealand, mainly within or near Auckland City. Results from these studies showed that relatively high ozone concentrations can be observed intermittently. The photochemical 'incidents' are generally in the range of 40-80 ppb (86 to 170 $\mu g/m^3$), although rarely over 60 ppb (128 $\mu g/m^3$), and may last for two to three hours. Typical background ozone concentrations are normally below 30 ppb (64 $\mu g/m^3$) (Brasell, 1982; McKendry, 1996; MfE, 1997; Nicol and Harvey, 1996). The mean southern hemisphere levels are 14-20 ppb (30-42 $\mu g/m^3$) over the oceans and this is regarded as probably applicable to the majority of rural New Zealand (MfE, 1998a; Scheel et al., 1992).

Therefore, if it is conservatively assumed that during a typical New Zealand photochemical incident ozone concentrations reach approximately 60 ppb (128 $\mu g/m^3$), then over 150 1-hour ozone episodes would need to occur within a three month period to exceed the long term AOT40 critical level for crops (3000 ppb-h, 6420 $\mu g/m^3$-h). Similarly to exceed the 'visible injury' critical levels (200 ppb-h, 428 $\mu g/m^3$-h) at typical ozone event concentrations, a total of ten events would need to occur within five days. On the basis of present information, these situations seem extremely unlikely, indicating that ozone is unlikely to be a significant risk to vegetation within New Zealand. However, assessment of ambient ozone concentration ranges and frequency distributions is still limited, particularly in areas outside the Auckland Region. Given the trend for increasing vehicular traffic in this region, it is very likely that ozone levels will continue to rise.

Biochemical changes have been demonstrated at lower ozone concentrations than those of the Critical Levels, and the thresholds for adverse effects upon crop quality and abiotic and biotic stress sensitivity have yet to be quantified. Therefore although the UNECE guidelines are unlikely to be exceeded, it is difficult to state definitely that current or possible future New Zealand ambient ozone concentrations will have no adverse impact.

4.4 Overview

There is currently no information available on the sensitivity of native New Zealand plants to ozone exposure, or the possible adaptive capacity to ozone of northern hemisphere species upon which the critical levels are based. Although there remains a possibility that some species may be more sensitive than northern hemisphere plants, the UNECE guidelines most likely provide a reasonable guide for control of possible yield and visible injury ecosystem effects in New Zealand.

It is not immediately obvious whether adoption of guidelines or standards, such as the UNECE Critical Levels, is necessary or desirable for New Zealand. Such standards or guidelines, if established, would be used much less frequently in situations such as resource consent applications than those for pollutants such as sulphur dioxide or NO_x. Whereas the concentrations of sulphur dioxide and NO_x can be predicted with some reliability from a combination of ambient monitoring data and dispersion modelling of point sources of interest, prediction of ozone concentrations requires much more complex airshed modelling techniques, including photochemical modules, and covering all significant sources of NO_x and volatile organic compounds (VOC). Accordingly, management of air quality with respect to ozone must be carried out on a whole airshed basis, rather than on a source-by-source basis.

Although it appears unlikely that the Critical Levels will be reached in the foreseeable future, or that standards or guidelines for ozone will be referred to frequently in resource management decisions, establishment of such standards or guidelines would nevertheless provide a valuable point of reference for assessment of the ozone concentrations in monitoring programmes and those predicted from airshed modelling. The form of expression of the Critical Levels, in itself, also provides guidance on what approaches to monitoring will provide data useful for assessing the likelihood of possible effects from concentrations and their temporal patterns. On balance, it appears useful to capture and communicate the information implicit in the Critical Levels by establishment of a standard or guideline for ecosystem effects of ozone.

5. Critical levels for fluoride

Fluoride has in the past been a major driver in the recognition of the potentially severe effects that air pollution can have on ecosystems. Fluoride is one of the most phytotoxic of the common air pollutants, and produces comparable environmental effects at concentrations 10 times lower than other more common pollutants. However, its importance as an air contaminant has diminished over the last 20 years as improvements in industrial pollution control technologies have significantly reduced emission levels. Concerns still remain regarding fluoride emissions, particularly from large facilities. Principal sources of fluoride in New Zealand include aluminium smelters and phosphate fertiliser works (MfE, 1998a; MfE, 1998b).

5.1 Environmental effects of fluoride

Fluorine is not an essential plant nutritional element, although it can be accumulated either from air where it occurs as hydrogen fluoride, or from soil with low buffering capacity, where it moves as a simple halide ion. As a result of its extensive combination with divalent cations, it forms compounds of low solubility and which do not move readily through soil solution. Therefore, it is viewed largely as an air pollutant rather than a soil pollutant (Doley 1986).

Gas transfer processes between the air and a plant's wet cell wall regulate the intake of fluoride. Fluoride has a relatively high vapour pressure, and may volatilise or diffuse back through the stomata when ambient air concentrations of fluoride are lower than those on the plant cell walls. Of that which is retained in the transpiration stream, some can be carried to the extremities of the leaves, or it may diffuse into cells and can accumulate in organelles. Transportation in the phloem of plants does not appear to be an important mechanism of transport, thereby redistribution from leaves to other organs is limited.

Fluoride is an accumulative plant toxin that can affect tissues at average concentrations as low as 20µg/g. Because of the low solubilities of calcium and magnesium fluorides, fluoride interferes with chlorophyll formation and cell wall synthesis, and this results in some of the most sensitive visible injury symptoms (chlorosis and deformation of expanding leaves). It also reacts with some cell membranes and enzymes.

Where animals graze plants that have accumulated fluoride, fluorosis of the animals' skeletons occurs, with potentially lethal results. In severe cases, the skeleton becomes so weakened that fractures and resultant immobilisation occur.

Doley's investigations (unpublished) have indicated that the range of sensitivities found in New Zealand vegetation is similar to those of other regions. Taxonomic grouping or life forms are not reliable guides to plant sensitivity to fluoride, nor is leaf or plant size and consequently care is need when generalising plant responses to fluoride exposure (Doley, 1986; MfE, 1998a).

5.2 Fluoride ecosystem guideline values

Ambient air quality guideline values for fluoride were established by ANZECC (1988), recognising three land use categories for which different guidelines should apply. The General Land Use category adopted the standard applied in several states of the USA, notably the Washington standard. To assist evaluation of these guidelines, the 90-day average concentration of 0.5 µg/m^3 will be used.

A Specialised Land Use guideline was established to protect commercially valuable plant species that have been demonstrated to be very sensitive to fluoride, including grapevines and stone fruits. The guideline values were established at half of the General Land Use values, i.e. 0.25 µg/m^3.

A third guideline was introduced to protect plant species in conservation areas *"… where the sensitivity to fluoride of a number of plant species is not known …"*. This guideline is set at 0.1 µg/m^3, or one-fifth of the General Land Use value.

As noted in the 1994 Guidelines, *"Neither the guideline nor the test method specifies whether total fluorides or gaseous fluorides are to be measured. From discussion with Australian authorities, it appears that the guidelines were meant for gaseous fluorides."* The 1994 guideline values for fluoride are set out in Table 6.

Table 6. Guideline values for fluoride

Averaging period	**12 hour**	**24 hour**	**7 day**	**30 day**	**90 day**
General Land Use	3.7 µg/m^3	2.9 µg/m^3	1.7 µg/m^3	0.84 µg/m^3	0.5 µg/m^3
Special Land Use	1.8 µg/m^3	1.5 µg/m^3	0.8 µg/m^3	0.4 µg/m^3	0.25 µg/m^3
Conservation Areas					0.1 µg/m^3

The current understanding of the potential for fluoride to affect plants in New Zealand is limited to investigations associated with the aluminium smelter at Tiwai Peninsula; and studies at three South Island locations on the effects of fluoride on New Zealand native species. These have found similar sensitivities to those of Australian plant species. These works are discussed in MfE 1998a and MfE 1998b, and without further evidence to indicate that any change is needed the current guidelines appear to be adequate to provide protection of New Zealand ecosystems.

6. Critical loads

6.1 Development and application of critical loads

In Europe, one of the important objectives of air pollution control has been the protection of sensitive and highly valued ecosystems identified by the various member nations of the EC. Typically, these sensitive ecosystems have developed on soils of low acid neutralisation capacity and/or where the supply of nitrogen has been limited, leading to plant communities adapted to low nitrogen supply.

Critical loads have been developed as a means of setting limits on the affects of air pollution on these ecosystems, and are estimates of exposure, in the form of deposition of pollutants into natural or semi-natural ecosystems, below which harmful effects are not expected to occur. Critical loads have been developed for control of acidification of soils and ecosystems resulting from deposition of sulphur and nitrogen pollutants (critical loads for acidity), and for control of nitrogen enrichment (critical loads for nitrogen). The critical loads vary between different areas, depending on the weathering characteristics of the soil for critical loads of acidity, and the ecosystem type for critical loads for nitrogen.

It is important to recognise that critical loads are usually applicable only to substantially undisturbed ecosystems, largely in their natural state. On managed land, whether for agriculture, forestry or residential use, management processes such as use of rye/clover pasture, cropping and fertilisation or soil pH adjustment impose changes on soils and their associated ecosystems, which are very much larger than any possible long-term changes resulting from acidity or nitrogen inputs from air pollution.

For example, commonly recommended rates of lime application for home gardening are equivalent to about 10 times or more the levels of acid deposition considered to be of possible concern in Europe. Commonly recommended applications of nitrogen fertiliser are about 10-50 times critical loads for nitrogen for sensitive European ecosystems. For New Zealand rye/clover pasture grazing land, underlying ground waters commonly contain nitrate-nitrogen concentrations in the range 5-10 mg/l. If it is assumed that ground waters originate from annual drainage of 300 mm of water out of the root zone, these nitrate concentrations correspond to soil acidification in the range of about 1000-2000 equivalents/ha-yr. This is towards the top of the critical acidity loading ranges considered in the European work. This acidification occurs because nitrogen fixation (by clover) is a neutral process, whereas subsequent nitrification produces acid.

Accordingly, critical loads will not be of concern for the great majority of land uses.

6.1.1 Applicability of critical levels and critical loads to New Zealand

For New Zealand, the concepts and general approach of critical loads are applicable, but local assessments of the levels at which those critical loads are set are needed. The following sections make preliminary assessments of the likely critical loads for acidity for a number of New Zealand catchments, and this indicates that it is unlikely that possible exceedance of critical loads for acidity will be a concern in New Zealand.

The situation for nitrogen enrichment is less straightforward. European ecosystems have developed with human influences at varying the degrees of intensity over many centuries, and have almost certainly adapted to some degree to this situation. On the other hand, most New Zealand ecosystems have developed under conditions of low nitrogen supply, and have been subject to increased nitrogen supply only over about the last century, or less in many cases. Ammonia emission from fertile pasture is likely to be a significant contributor to increased nitrogen supply to adjacent native ecosystems and it is likely that many of the native remnants in the fertile lowlands will have adapted to some degree to this situation. For example, there is good evidence that remnant stands of kahikatea in the Waikato contain an increased abundance of higher fertility, broadleaf species. However, there is very little information available about the level of nitrogen inputs via air to New Zealand ecosystems, and essentially none for ammonia, which is probably the most important nutrient gas.

The probable situation, that there may already have been substantial adjustments of ecosystems in farming areas to increased nitrogen supply, highlights the question about what ecosystem condition is desirable to protect. Is this the ecosystems judged to be of significant value, in their current state, or is there a desire to return (if possible) to a lower nitrogen status? Where developments are proposed which might expose ecosystems not yet subject to significantly increased nitrogen supply to such an increase, is the desire to retain the original condition?

Obviously, these are difficult questions with potentially significant economic, political, conservation and biodiversity implications.

The development of appropriate critical loads for nitrogen depends on the answers to such questions, and also on information not currently available about the response of the various New Zealand ecosystem types to increased nitrogen supply. In these circumstances, it is not possible to recommend, with any certainty, critical loads for nitrogen for New Zealand ecosystems. This report brings together the nitrogen critical load recommendations for Europe, with identification of rough equivalent New Zealand ecosystems. However, because of the different development history and environment of the New Zealand ecosystems, it is uncertain whether the European critical loads are appropriate to the New Zealand ecosystems, because of differences in climate, species composition, structure and function of the local equivalents.

Current "expert judgment" suggests that significant changes in local ecosystems may not occur below total nitrogen inputs of about 5 kg N/ha-yr, which is also about the lowest critical load for nitrogen recommended for protection of European ecosystems. This figure can be used as an interim indication of what is probably a low enough total nitrogen input via air for significant ecosystem changes not to occur. However, if possible increases in nitrogen inputs are being considered, it would be necessary to establish the existing level of nitrogen input for the ecosystem(s) under consideration, to determine what the total nitrogen input including the increase would be. The little information currently available suggests that current inputs from some farming areas to adjacent, possibly sensitive ecosystems may exceed 5 kg N/ha-yr.

If useful guidance on critical loads of nitrogen for New Zealand ecosystems is to be developed, it is important that at least preliminary studies are undertaken to determine the levels of nitrogen species in air in some selected, potentially sensitive ecosystems adjacent to fertile farming areas. Such studies would both indicate the levels of transfer of nitrogen species from farmlands to adjacent ecosystems, and also, in combination with assessment of the condition of the ecosystem, provide an indication of levels of nitrogen that do or do not result in identifiable ecosystem effects. Accordingly, the probable importance of agriculture as a nitrogen source for adjacent sensitive ecosystems provides both a potential source of current effects that might or might not be considered adverse, and a means of assessing critical loads of nitrogen for at least some New Zealand ecosystems.

6.2 Deposition mechanisms

The transfer of pollutants from air to ecosystems can occur through a variety of deposition mechanisms as described below, which occur for both sulphur and nitrogen pollutants, and relate to both acidification and nutrient deposition:

- ***Dry gaseous deposition***: Occurs though plant uptake, usually through leaf stomata for pollutants such as sulphur dioxide and oxides of nitrogen, or by dissolution in moisture on vegetation surfaces.

- ***Wet gaseous deposition:*** Arises both from washout, which refers to processes occurring in clouds (contributing to contaminants in rain), and from scavenging which refers to dissolution into rain drops during their fall to the surface. This form of deposition generally contributes mostly to soil inputs, rather than to direct atmospheric uptake by plants.

- ***Dry particulate deposition:*** This mechanism is associated with the settlement of aerosols and particulates onto surfaces as a result of gravitational settling and Brownian motion.

- ***Wet particulate deposition:*** Results largely from rain scavenging in which raindrops wash particulates out of the air during their fall to the surface. This can include deposition of components of aerosols, such as ammonium sulphate and ammonium nitrate aerosols.

6.3 Critical loads for acidity

Acidification results from deposition of both nitrogen and sulphur pollutants by all of the deposition mechanisms discussed in this report. Response of both plants and particularly soils to acid input is critically important in determining whether any particular level of acid deposition will have adverse ecosystem effects.

6.3.1 Soil evolution and response to atmospheric acidity input

The characteristics and management of soils are critically important in determining whether adverse levels of acidification occur as a result of atmospheric acid inputs. Soil is formed from parent rock by both chemical and physical processes that break the rock into fine particles and convert some of the solid minerals into soluble ions. During this process, ion exchange sites form, both on organic material residues from plant growth and on mineral surfaces. This ion exchange capacity is important for retention of base cations (calcium, magnesium, potassium and sodium) in the soil root zone, where these nutrient elements are accessible to plants. Conversion of soil minerals to soluble cations occurs at different rates in different soils, depending on the climate under which the weathering occurs, the nature of the parent rock, and the particle sizes (and therefore surface areas) of the soil minerals. In many natural soils, unaffected by acidification from either atmospheric contaminants or elsewhere, a high proportion of the cation exchange sites in the soil hold base cations (rather than acidic hydrogen ions). These are described as having a ‘high base saturation’ of the cation exchange capacity.

Addition of acids, such as sulphuric acid or nitric acid to the soil replaces some of the base cations from ion exchange sites with hydrogen ions, and allows the base cations to be leached from the soil as sulphates or nitrates. As a consequence the base saturation decreases, the supply of base cations available for plant uptake decreases and the soil becomes more acidic. Ultimately, continued acidification results in increased concentrations of aluminum in soil solution. This can be toxic to plants by damaging root systems, particularly if only low concentrations of calcium (which has a protective effect) are present; and also to animals when released into water bodies. Deposition of nitrogen from air pollution can, under some circumstances, have a fertiliser effect. When this occurs, the plant will respond with increased growth rates for a period. However, this is curtailed on acid-sensitive soils when the reduced availability of base cations (particularly magnesium) leads to mineral imbalances in plants. The mineral imbalance occurs because the increased supply of nitrogen, stimulates growth and therefore the uptake of base cations, effectively resulting in soil acidification.

If the rate of formation of base cations and alkalinity from the soil minerals is greater than the rate of their loss through leaching, no soil acidification occurs. However, if the rate of base cation and alkalinity leaching exceeds their rate of formation, acidification will occur over a period of time determined by the rate of excess acid input, the cation exchange capacity of the soil, and its degree of base saturation.

The loss of base cations through leaching can be exacerbated through cropping practises that have the potential to remove base cations in the harvested wood or other plant material. To illustrate, base cation removal in harvesting of wood over centuries has been a contributing factor to some of the severe forest decline that has occurred in parts of Europe. However, harvesting can also remove sulphur and nitrogen, reducing their contribution to acidification.

6.3.2 Definition and estimation of critical loads of acidity

The critical load of sulphur and nitrogen acidity is defined (Umweltbundesamt, 1996) as:

"*the highest deposition of acidifying compounds that will not cause chemical changes leading to harmful effects on ecosystem structure and function*".

Critical loads of acidity depend to a large extent on the rate of production of alkaline compounds (which can be expressed in terms of base cations or alkalinity) by weathering of the soil materials. One approximate method for estimating base cation weathering rates is based upon general soil type, geological substrate, and climatic trends observed in European forest soils (de Vries et al., 1993 cited Umweltbundesamt, 1996). The approximate method assumes that texture class has a dominating influence on the weathering rate in the various parent material classes, and that there is a linear relationship between weathering rate and clay content (Umweltbundesamt, 1996). Using this method, the WHO (1996) estimated critical loads for different soil conditions (assuming an average soil depth of fifty centimetres) as presented in Table 7.

Table 7. Critical loads of acidity (eq/ha/yr) for selected rock acidity and texture types, from WHO (1996) guidelines

Texture	**Parent Material**		
	Acidic	Intermediate	Basic
Coarse	<250	250-500	250-500
Coarse-medium	250-500	500-1000	500-1000
Medium	500-1000	500-1000	1000-1500
Medium-fine	500-1000	1000-1500	>1500
Fine	-	>1500	>1500

[1] Acidic: Sand (stone), gravel, granite, quartzine, gneiss (schist, shale, greywacke, glacial till)
Intermediate: Granodiorite, loess, fluvial and marine sediment (schist, shale, greywacke, glacial till)
Basic: Gabbro, basalt, dolomite, volcanic deposits

[2] coarse: clay content < 18%; medium: clay content 18-35%; fine: clay content > 35%

Under some circumstances, critical loads for catchments can be derived by assessing the quantity and composition of water draining from the catchment. In this approach, the discharge of base cations and/or alkalinity in the water leaving the catchment is considered to reflect the rate of base cation and alkalinity production from weathering in the catchment soils. However, care is needed to ensure that the drainage from the catchment does reflect processes occurring in the root zone, and not in deeper soil layers or the water table. Water draining from the root zone is usually slightly acidic because of significant carbon dioxide concentrations from respiration and decomposition processes in the root zone. This acidity will dissolve base cations and alkalinity from alkaline minerals (particularly, for example limestone) in deeper strata, potentially giving a falsely high indication of base cation weathering rates in soils.

Table 8 presents estimates of critical loads for a number of New Zealand catchments. These have generally been selected because it is expected that the drainage from the catchment is unlikely to include substantial contributions to alkalinity from strata below the root zone (for example hill country catchments, including Roaring Billy, Sutton Stream, Hutt River and Hunua lakes) and/or they show relatively low levels of alkalinity in waters draining from the catchment. These figures indicate considerably higher levels of acid neutralisation capacity (critical loads) than may be suggested by the maximum of >1500 eq/ha-yr in Table 7. It is possible that the figures in Table 8 may overestimate the critical loads for some of the catchments, either because some of the alkalinity may originate from mineral leaching below the root zone, or because the average alkalinity concentrations may not accurately represent the average concentrations including periods of peak flow (floods). These figures do, nevertheless, suggest relatively high critical loads for many New Zealand catchments. Neither of these possible limitations is likely to apply to the Hunua Lakes, but, in spite of having one of the lowest levels of alkalinity in its drainage waters, the critical load is still estimated to exceed 3500 equiv/ha-yr.

Table 8. Estimation of critical loads for acidity from catchment discharges for New Zealand catchments.

	Alkalinity		Drainage yeild	Catchment Critical Load
	g/m^3 as $CaCO_3$	equiv/m3	m/yr	equiv/ha-yr
Haast, Roaring Billy	30	0.61	6.0	36535
Opuha River, Skipton, Tekapo	17	0.35	0.7	2263
Dunedin, Sutton Stream	13	0.25	0.3	721
Monowai, control gates	12	0.24	1.8	4192
Buller River	23	0.47	1.7	7903
Grey River, Dobson	16	0.32	3.0	9471
Motueka River, Woodstock	41	0.81	1.1	8670
Wairau River Tuamarina	20	0.40	1.1	4260
Hutt River, Te Marua	19	0.38	1.1	4180
Hunua lakes	14	0.28	1.3	3640
Waikato River, Taupo	38	0.75	1.0	7540

Other methods of estimating weathering rates are also available, including methods based on soil types (European), minerals present, total base cation content of soils and geochemical modelling (Umweltbundesamt, 1996).

6.3.3 Acid deposition from sulphur emissions

Dry deposition of sulphur dioxide (via plant uptake, dissolution in moisture on plant surfaces and absorption by soils) is the dominant mechanism of sulphur deposition close to major sources (eg within a few km), but is also a major contributor to total deposition at large distances from sources (e.g.

contributing about 40 percent or more), in regions of relatively high wet sulphate acidity deposition (Sirois and Barrie, 1988).

Wet deposition of sulphur dioxide in the form of sulphuric acid or sulphates is a major mechanism for ecosystem acidification in humid regions subject to significant sulphur dioxide discharges. Sulphate acidity in rain arises primarily from oxidation of sulphur dioxide in cloud droplets, by hydrogen peroxide and ozone. Rain scavenging of ammonium sulphate and sulphuric acid aerosols formed under clear (non-cloudy) air conditions make only a small contribution. The long lifetime of droplets in clouds, compared with the fall time of raindrops, means that most of the sulphuric acid in rain forms in clouds (Seinfeld, 1986). Because considerable distances are commonly required for local emissions to mix to typical cloud heights, rain acidity reflects wide area regional emissions of sulphur dioxide, rather than local emissions.

Dry particulate deposition of sulphuric acid or sulphate aerosols is usually a minor percentage (e.g. less than 15 percent) of the total sulphur deposition.

Plant metabolism of sulphur dioxide taken up via dry deposition may follow either a reductive or an oxidative pathway. In reductive metabolism, the sulphur is used as a nutrient and may not result in immediate acid input to soils. However, oxidative metabolism does contribute acid to soils immediately on metabolism, because oxidation of the sulphur in the plant generates acidity, requiring uptake of base cations from and release of hydrogen ions into the soil, in order to maintain the internal pH of the plant.

The capacity for reductive metabolism of sulphur varies with species, with herbaceous plants having a greater capacity than woody species, because of their lower carbon:sulphur ratio. Reductive metabolism immobilises sulphur in biomass for varying periods, depending on the plant type and species. For example, sulphur in short lived herbaceous species will be “released” sooner than sulphur in the wood of forest trees, which may be immobilised for very long periods.

Over the longer term, the extent to which plant uptake of sulphur contributes to acidification depends on the proportion of sulphur removed from the ecosystem in harvested material. Sulphur inputs remaining in the ecosystem will, in aerobic soils, ultimately, be oxidised to sulphate, whatever the uptake mechanism in the plant, and whatever the temporary immobilisation and/or metabolism by soil fauna. Therefore eventually they contribute to acidification. In anaerobic or partially anaerobic soils, reduction of sulphate may result in long-term immobilisation in the form of sulphides, without contribution to acidification, unless these soils are drained for agricultural or other development purposes.

6.3.3.1 Estimating sulphur acidity deposition from ambient sulphur dioxide levels

An estimate of dry deposition of sulphur dioxide can be obtained from the annual average sulphur dioxide concentration and the dry deposition velocity. As discussed above, wet deposition of sulphur acidity is unlikely to be significant in New Zealand because of its isolation from large regional sulphur dioxide sources. Consequently, little oxidation of sulphur dioxide to sulphuric acid in clouds will occur. The absence of detectable sulphate acidity deposition in the New Zealand measurements of wet deposition that are available (Table 14) support this view.

This assessment indicates that a worst-case estimate of sulphur acidity deposition in New Zealand situations can be obtained with a reasonable degree of reliability from ground level sulphur dioxide concentrations. This approach could not be used in regions where there is significant wet sulphate deposition, such as Europe. At a likely maximum average sulphur dioxide deposition velocity of 2 cm/sec, each 1 $\mu g/m^3$ annual average sulphur dioxide concentration corresponds to sulphur acidity deposition of 200 equivalents/ha-yr, if none of the sulphur is immobilised or removed by harvesting.

Wet deposition of sulphuric acid could make a significant contribution to acid loadings close to a major sulphur emission source if a significant fraction of the emitted sulphur is present as sulphuric acid. However, this would require a large source. For example, wet deposition modelling for a 150 MW power station burning low sulphur coal (about 0.16 percent), with a high (10 percent) conversion of the sulphur to sulphuric acid in the emissions would give acid deposition rates exceeding 250 equivalents/ha-yr (the critical loading for the most acid-sensitive soils) only within about 200 m of the stack. This estimate also makes no allowance for the alkaline ash that would deposit at the same time, lessening, or completely eliminating the acid deposition.

6.3.4 Acid deposition from NO_x and ammonia emissions

As for sulphur dioxide, uptake by plants of nitrogen oxides, nitric acid and ammonia contributes initially to the plant nutrient nitrogen requirement and under these conditions may not immediately contribute to ecosystem acidification. Further, denitrification, immobilisation in soil organic matter and plant uptake of nitrogen species from soil may remove the acidification that would otherwise occur from nitric acid or ammonia deposition (Umweltbundesamt 1996). Nitrogen removed from the ecosystem in harvesting removes potential acidification, but nitrogen remaining in the system, unless removed by denitrification, will ultimately oxidise and contribute to acidification. Natural nitrogen fixation can also contribute to acidification by increasing the nitrogen pool, although fixation itself is a neutral process with respect to acidification.

Neither nitrogen dioxide nor nitric oxide is scavenged to any significant extent by either cloud water or rain. This results from slow rates of reaction in solution at the relatively low concentrations typically present in ambient air (Seinfeld, 1985). However, these oxides of nitrogen are oxidised in clear air to nitric acid by ozone, and the nitric acid can make a significant contribution to acid rain through rainfall scavenging and washout.

Although ammonia is an alkaline compound and decreases the acidity of rain, once it reaches the ground it is nitrified relatively quickly to nitrate by soil micro-organisms. This nitrification reaction produces acid, so that, overall, addition of ammonia or ammonium ions to the soil contributes to acidification. It is also taken up readily by plants, and potentially contributes to acidification through this route, as for nitrogen oxides. Ammonia is highly soluble in water, and is subject to rainfall scavenging and washout as for nitric acid.

6.3.4.1 Relationship between ambient air concentrations and nitrogen deposition

Estimates of dry deposition of nitrogen dioxide, nitric oxide, nitric acid and ammonia can be obtained from their annual average concentrations and typical dry deposition velocities. These loadings assume that none of the nitrogen is removed by harvesting, denitrification or other processes. Based on typical literature values for deposition velocities, Table 9 sets out approximate estimates of the maximum rates of acidity deposition via dry deposition for concentrations of 1 $\mu g/m^3$ of the various nitrogen species in air. In accordance with European practise, the rates of deposition of nitric oxide are considered to be negligibly slow.

Wet deposition modelling has been used to estimate, for a typical annual rainfall of 1 m, the rates of wet acidity deposition of nitric acid, ammonia and nitrate- and ammonium-containing aerosols per 1 $\mu g/m^3$ of nitric acid or ammonia. These estimates are set out in Table 9.

6.3.5 Estimating total acid deposition from ambient air concentrations

Likely upper limits of acidification arising from wet and dry deposition of sulphur dioxide, sulphuric acid, nitrogen dioxide, nitric acid, ammonia and acid aerosols formed from those compounds can be estimated approximately from their annual average concentrations in ambient air. Table 9 summarises the estimated rates of acid deposition resulting from annual average concentrations of 1 $\mu g/m^3$ of each of these species, excluding sulphuric acid, which is considered likely to be negligible in New Zealand.

Table 9. Annual acid deposition estimates for 1 $\mu g/m^3$ concentrations of pollutants in ambient air

	Typical dry deposition velocity	Dry gaseous	Wet deposition
	cm/sec	Equivalents/ha-yr	
NO_2	0.36	25	Nil
HNO_3	2	100	75
NH_3	2	370	400
SO2	2	200	<<40

The estimations presented here, based predominantly on dry vapour deposition mechanisms, may significantly over-estimate the overall acidification resulting from air pollution. Other factors, such as harvesting or denitrification, or deposition of alkaline materials may decrease ultimate adverse effects. Nevertheless, because these estimates are likely to be high, they do provide a basis for assessment of whether acidification is a possible issue that may require further, more detailed assessment.

6.3.6 Methods for monitoring acid deposition

Dry gaseous deposition of sulphur dioxide, nitrogen dioxide, nitric acid and ammonia occurs through entry of the pollutant into the plant, dissolution in the cell sap and metabolism in the plant, and through dissolution in moisture on plant surfaces under wet conditions. It is almost invariably estimated from ambient air concentrations via use of deposition velocities, in the same way in which the acid deposition loads have been calculated from ambient concentrations in this report. Because it is most convenient to work from long-term average concentrations, passive samplers provide a particularly convenient means of determining the concentrations of all of the contaminants of interest.

Dry particulate, wet particulate and wet gaseous deposition are measured by exposing collectors to dustfall and rain (as appropriate to the deposition data required), and collecting the rinsings or (more usually) the rain, draining from the collector. The solutions collected are analysed for pH, calcium, magnesium, potassium, sodium, ammonia, sulphate, chloride, nitrate and nitrite. Sample collection is usually continued over a period of years, to take account of seasonal variations and variations between years.

6.4 Nitrogen critical loads

Nitrogen is the nutrient required in the greatest quantity by plants and its availability in soil is also frequently the limiting factor for vegetation growth. This is particularly true of regions where cold soil temperatures and short growing seasons limit nitrogen fixation and soil mineralization processes (Lee and Caporn, 1998). However, although increasing supply of nitrogen can stimulate growth (potentially desirable), it can also cause undesirable changes in the competitive relationship of species. This can reduce biodiversity and enhance the susceptibility of plants to secondary stress factors.

Cycling of nitrogen within ecosystems is regulated almost exclusively by biological processes. These are influenced by a variety of environmental factors that can contribute to, or mask, potentially adverse effects. Therefore, although there is direct evidence that nitrogen deposition is influencing semi-natural ecosystems, particularly in Europe, it is difficult to assess the scale and importance of the effects, and determine the impact mechanisms. To avoid the complexities of differentiating between effects, nitrogen deposition critical loads are defined in terms of general changes in species survival and dominance in characteristic ecosystem types over extended periods. No singular impact is associated with each critical load.

6.4.1 Chronic effects of increased nitrogen nutrient supply

Enhanced nutrient supply to an ecosystem may occur via foliar uptake of nitrogen oxides, nitric acid and ammonia, and via wet and dry deposition of nitrate, nitrite and ammonia to soils. The deposition of nitrogen may have an adverse eutrophication effect at an individual plant and community level. These changes occur both above and below the ground, and vary in effect over time.

6.4.1.1 Individual plant impacts

When climate and the supply of other nutrients (such as calcium, potassium and magnesium) allow, biomass accumulation can occur in response to increased availability of nitrogen from moderate increases in NO_x and ammonia concentrations in air. However, at higher levels plant die-back can occur if nitrogen-stimulated growth exceeds the availability of other essential elements, such as calcium, potassium and magnesium. Such effects also tend to be associated with long term land management practices, such as wood harvesting from forests. These practices can deplete the soil base cation reservoir. Plant growth ceases when these nutrient levels reach physiological limiting values, at threshold points which vary for different species (Oren, 1995).

It has also been suggested that changes to air borne nitrogen deposition may also influence the biomass allocation between roots and shoots. Increases in the shoot (transpiration surfaces): root (water uptake) ratio reduce plant resistance to drought stresses. Reduced mycorrhizal infection is also linked to high nitrogen deposition that is important in nutrient-poor soil, since myrcorrhizal infections are beneficial to phosphorous acquisition (Bobbink et al., 1998; Erisman et al., 1998).

Secondary impacts include reduced resistance to pathogens as a consequence of increased stress imposed by air pollutants. Other changes observed have included increased herbivory which is most likely associated with nitrogen accumulation in the foliage (Bobbink et al., 1998).

6.4.1.2 Soil process impacts

The accumulation of nitrogen within an ecosystem also influences soil processes. Soil acidification as a consequence of nitrogen deposition is discussed in Section 6.3.4. Other reported soil effects include large changes in bacterial activity and nitrogen mineralisation, thereby increasing the nutrient availability for plants (Lee and Caporn, 1998).

Accumulation of nitrogen in ecosystem soils with a low nitrogen retention and acid neutralisation capacity may also lead to leaching of nitrate and aluminium to freshwater ecosystems. Aluminium may form compounds that are toxic to aquatic organisms (Emmett and Reynolds, 1996; Fangmeier et al., 1994; Lee and Caporn, 1998; Lee, 1998).

6.4.1.3 Ecosystem change effects

This can result in increased growth and biomass accumulation, and have marked effects on the decomposition processes. Gradual accumulation of nitrogen in nutrient-poor soil may confer a competitive advantage to more nitrophilous species leading to an eventual decline in biodiversity. The best-documented example of these ecological effects is the decline of *Calluna* heathland in Europe. Plants adapted to nutrient impoverished ecosystems tend to be more susceptible to eutrophication effects (Lee, 1998).

6.4.2 Nitrogen critical loads

The critical load of nitrogen was defined at the UNECE Skokjlster Critical Loads Workshop to be *"A quantitative estimate of an exposure to deposition of nitrogen as* NH_x *and/or* NO_y *below which harmful effects in the ecosystem structure and function do not occur according to present knowledge'* (cited Umweltbundesamt, 1996). The total nitrogen deposition critical loads are defined in relationship to their eutrophication effect on plants and ecosystems. The impact of soil acidification from nitrogen pollutant deposition is considered separately in the Critical Load for Acidity section of this report.

Empirical estimates of ecosystem critical loads are based on detectable changes in the structure and function of ecosystems, and are intended to define loads below which any change is unlikely. They rely on an assortment of data obtained from experimental, and observational studies and/or dynamic ecosystem models calibrated with available data. The changes detected may be associated with a variety of impact mechanisms and bio-indicators, and might be considered either beneficial or adverse, depending on the viewpoint considered.

There is a high degree of uncertainty associated with critical loads, even for the European ecosystems for which they have been developed. They are based on a variety of different experimental and observation studies, but changes in ecosystems when exposed to realistic quantities of nitrogenous pollutants over extended periods have only recently been evaluated. These and other limitations are formally acknowledged by the UNECE. Critical loads are intended to be a simplified and general guideline for a range of sensitive European ecosystems. Local climatic, biotic, and land management process will invariability influence threshold values. Critical loads are mainly based on changes in higher order plants and may overlook changes in ecosystem components such as soil biota, although only if these occur in the absence of effects from those changes on the higher plants.

The critical load also assumes that nitrogenous pollutant fluxes are relatively constant. Variations in deposition rates will also influence ecosystem sensitivity. Short, but intensive, episodes may be more or less detrimental than lower but continuous nitrogen deposition.

The UNECE and WHO empirical critical loads are presented in Table 10 along with their degree of certainty.

Table 10. Empirical WHO and UNECE critical loads for nitrogen deposition

Ecosystem	CLO (kg N Ha^{-1} yr^{-1})	Impact
Wetlands		
Shallow Soft-water lakes*	5-10##	Decline of isoetid aquatic plant species
Ombrotropic (raised) bogs*	5-10#	Decrease typical mosses, increase tall gramminoids, N accumulation
Mesotropic fens	20-35#	Increase tall gramminoids, decline diversity
Species-rich grasslands		
Calcareous grasslands	15-35#	Increase tall grass, decline diversity
Neutral acid grasslands	20-30#	Increase tall grass, decline diversity
Montane-subalpine grasslands	10-15(#)	Increase tall graminoids, decline diversity
Heathlands		
lowland wet-heathland	17-22#	Transition heather to grass
Species-rich heaths/acid grasslands	10-15#	Decline sensitive species
Upland Calluna heaths	10-20(#)	Decline heather, mosses & lichen; N accumulation
Arctic and alpine heaths*	5-15(#)	Decline lichen, mosses and evergreen dwarf shrubs, increase in grasses
Lowland dry heathland	15-20##	Transition heather to grass; functional change; N accumulation; litter production
Trees and forest ecosystems		
Coniferous	10-15##	Nutrient imbalance (acidic; low nitrification rate)
Coniferous	20-30#	Nutrient imbalance (acidic; mod-high nitrification rate)
Deciduous trees	15-20#	Nutrient imbalance; increase shoot/root ratio
Acidic coniferous forests	7-20##	Changes ground and flora & mycorrhizas; increased leaching
Acidic deciduous forests	10-20#	Changes ground flora
Calcareous forests	15-20(#)	Changes ground flora
Acidic forests*	7-15(#)	changes in ground flora and Leaching
Forest in humid climates	5-10(#)	Decline lichen & increase free-living algae

Notes:

* - Unmanaged, natural system
- Reliable: When a number of published paper of various studies show comparable results
- Quite Reliable: when results of some studies are comparable
(#) - Expert Judgement: When no data is available for type of ecosystem. The N critical load is based upon expert judgement of ecosystems which are likely to be more or less comparable with this ecosystem

The suitability of nitrogen critical loads for European ecosystems for protection of New Zealand ecosystems is very uncertain. Most New Zealand ecosystems have developed in nitrogen limited situations, and it is estimated (Clarkson, personal communication) that typical nitrogen loads in most New Zealand native forests are in the range 1-5 kg N/ha-yr. Table 11 gives the closest equivalent New Zealand ecosystems to those listed in Table 9 for Europe. The European critical loads for the equivalent ecosystems have been omitted deliberately, because of their uncertainty of application. In some cases (for example mesotrophic fens), where the undesirable change is increased invasion by exotic species, the European critical load may be a reasonable guide, but there can be no assurance of this at the present state of knowledge. In other situations, such as increased abundance of higher fertility species in New Zealand native forests, the upper range of current nitrogen inputs (5 kg N/ha-yr) may be the most prudent guideline, until further information is available.

However, situations may arise where estimated nitrogen loadings exceed 5 kg N/ha-yr, and the recommended critical loads for equivalent European ecosystems do provide at least some guidance. Section 6.7 suggests a possible approach incorporating the European critical loads under such circumstances.

Table 11. New Zealand equivalents of European ecosystems

European ecosystem type	NZ equivalent	Possible Impact
Ombrotrophic (raised) bogs	Restiad bogs eg, Waikato	Decreases in restiads, increase in Carex, Phormium, willow
Mesotrophic fens	Manuka, bog coprosma, harakeke, and sedges (*Baumea* and *Carex*) and grey willow eg Whangamarino	Decline in manuka; increases in willow, Phormium, raupo, and introduced grasses and sedges
Montane-subalpine grasslands	Tall Tussock (Chionochloa) grasslands	Enhanced invasion of exotic grasses and weeds
Upland Calluna heaths	Subalpine shrublands dominated by Dracophyllum or manuka; frost flat vegetation with Dracophyllum, manuka etc; gumland shrublands with Dracophyllum, manuka etc.	Decline lichens and mosses; switch to introduced broom etc enhanced; invasion of broadleaved shrubs
Acidic coniferous forests	Kauri and dense podocarp forests	Increase in broadleaved species first in ground cover and understorey; much later in canopy. Canopy trees extremely long-lived
Forest in humid climates	Most of NZ native forest- podocarp-broadleaved, broadleaved forest and beech (Nothofagus) forest and various intergrades between each	Increased abundance of higher fertility species eg broadleaf, mahoe, tawa, tree fuchsia. Possible enhanced invasion of exotics
Forest in humid climates	Most of NZ native forest	Decline in lichen and increase in free-living algae

6.4.3 Estimating nitrogen deposition from ambient air concentrations

The estimates of acidity deposition from nitrogen dioxide, nitric acid and ammonia presented in Table 9 can be converted into nitrogen deposition rates for comparison with critical loads of nitrogen, as set out in Table 12.

Table 12. Annual nitrogen deposition estimates for 1 $\mu g/m^3$ concentrations of pollutants in ambient air

	Typical dry deposition velocity	Dry gaseous	Wet deposition
	cm/sec	kg N/ha-yr	
NO_2	0.36	0.3	Nil
HNO_3	2	1.4	1.1
NH_3	2	5	3

6.5 Estimation of acidity and nitrogen loads for New Zealand locations.

6.5.1 Concentrations of nitrogen and sulphur pollutants in air.

Loads of acidity and nitrogen relate most closely to annual average concentrations of nitrogen and sulphur pollutants in air. Table 13 presents annual average concentrations for several New Zealand locations, obtained either by instrumental monitoring (Christchurch and Auckland) (ESR, 2000) or by passive sampling (other locations) (Petersen et al., 1997). The data given in *Italics* is estimated, while the other data is from measurements.

Passive sampling results are not available for nitric oxide (NO). However nitric oxide makes only a small and uncertain contribution to either acidity or nitrogen loads, and it is not included in the estimates of deposition of either acidity or nitrogen. This is in accordance with the EC modelling approach (Erisman et al., 1994).

Table 13. Annual average concentrations for nitrogen and sulphur pollutants.

Location	HNO_3 /NO_2	Annual average concentrations $\mu g/m^3$			
		NO_2	HNO_3	NH_3	SO_2
Christchurch, St Albans	*0.22*	13.6	*3.0*	-	5.5
Auckland, Mt Eden	*0.15*	19.7	*3.0*	-	-
Rotorua	0.32	6.4	2.0	-	3.3
Invercargill	0.24	12.9	3.1	-	2.2
Hastings	0.18	13.1	2.4	-	1.2
Whangarei	0.24	9.4	2.2	-	0.9
Lincoln	0.21	5.6	1.2	-	1.2
Whakapapa	0.24	1.5	0.3	-	5.2
Arthurs Pass	0.29	1.7	0.5	-	0.6
Baring Head	0.31	1.8	0.6	0.8	0.8

The Whakapapa, Arthurs Pass and Baring Head samples are of particular interest for NO_2, and HNO_3, as indications of the concentrations of these species in remote areas where the protection of relatively undisturbed ecosystems may be an issue. The Arthurs Pass and Baring Head samples are also of interest for sulphur dioixide concentrations for the same reason. The Whakapapa samples included sampling during the 1996 eruption of Mt Ruapehu, and indicate the substantial contribution of sulphur dioxide from this source.

Very little data is available for ammonia. None of the data for concentrations in air can be considered to reliably indicate concentrations in relatively remote areas. Although Baring head is suggested to be a "pristine" site, it is not clear whether this is so with respect to ammonia. The site is about 15 km downwind, in the prevailing wind direction, from the point of discharge of the sewage from Wellington, and the sewage fields from both Wellington and Hutt Valley will, at times be located much closer than 15 km from the sampling site. Because of the slightly alkaline pH of seawater (about 8.3), the effluent field is potentially a large source of ammonia emission. The only other ammonia concentrations in air appear to be for Penrose, which is likely strongly affected by ammonia emissions from the Mangere sewage treatment ponds, and a winter sample collected in Dunedin, which would be strongly affected by domestic heating emissions.

6.5.2 Measured rates of wet deposition

Table 14 gives data from a number of studies that have examined annual deposition of major ions and nitrogen in rainfall. The Puruki site is about 30 km south of Rotorua and the Maimai site is in the catchment of the upper Grey River.

Table 14. Annual wet deposition at New Zealand sites

	Kelburn	Puruki	Lauder	New Plymouth	Taupo		Maimai
					Rural	Urban	
	eq/ha-yr						
Sulphate	369	263	13	1005			<20
Chloride	2901	535	62	9334			
Phosphate	1.9	4	0.9	-			
Nitrate	21	46	7	45	9	40	11
Sodium	2478	478	48	6936			
Potassium	60	48	7.5	385			
Calcium	130	115	20	689			
Magnesium	557	104	17	1623			
Ammonia	43	186	43	22	9	110	<30
Net wet deposition of acid	112	288	33	NC	18	150	<60
Wet nitrogen deposition of nitrogen (kg N/ha)	0.9	3.3	0.7	9.2	0.25	2.1	<0.6

NC – inconsistencies in the data (chloride/sulphate ratios compared with seawater) indicate that the data are not sufficiently accurate for reliable acidity deposition calculation.

Because of the difficulty of reliable measurement of pH, alkalinity and acidity in very dilute solutions, the most reliable indication of acidity or alkalinity (excluding that from ammonia and nitrates which is considered separately) in the rain waters in Table 14 is obtained from the sum of the concentrations of chloride, sulphate and phosphate (in equivalents) less the sum of sodium, potassium, calcium and magnesium (in equivalents). This indicates that, within experimental uncertainty (about ±50-100 eq/ha-yr), there is no net sulphate acid deposition or alkali deposition at the Kelburn, Puruki or Lauder sites. Dissolution in precipitation of nitric acid (to give nitrate) and ammonia (to give ammonium, NH_4^+) increases the acid deposition rate for the Puruki site to a level clearly above the probable experimental uncertainty. The Kelburn results may indicate some acid deposition above experimental uncertainty, but it is doubtful that any acid deposition is demonstrated for the Lauder site. Similarly, the Taupo urban site proabably indicates acid deposition above experimental uncertainty, but the Taupo rural site probably does not.

The ammonia deposition at the Puruki site is significantly higher than at most of the other sites, and its source is not clear. The sample site is 10 m above a forest canopy, and since vegetation on fertile land is known to emit ammonia, it is possible that it may originate from surrounding agricultural land, or may possibly come from the geothermal emissions.

It would be very desirable to be able to cross-check estimates of wet deposition made from annual average concentrations against measured rates of wet deposition, but unfortunately none of the sites for which annual average concentrations are available in Table 13 relate well to the wet deposition sites in Table 14. What indications can be drawn from comparison of these two tables suggest that the estimation factors are in Table 9 and Table 12 are not unreasonable. For example, it might be expected that estimates of wet deposition of nitric acid for Arthur's Pass and Whakapapa might indicate the likely levels of the deposition at Lauder. The wet deposition-only estimates using the Arthur's Pass and Whakapapa nitric acid concentrations are 0.5 and 0.4 kg N/ha-yr respectively. The nitrate-only wet deposition at Lauder was 0.1 kg N/ha-yr suggesting that the factors in Table 9 and Table 12 might over estimate deposition rates. On the other hand, the combination of low rainfall and relative isolation from busy roads at Lauder compared with either Arthur's Pass or Whakapapa may account for the relatively low deposition at Lauder. The rates of wet deposition of ammonia at the Puruki site and the Taupo urban site correspond to annual average concentrations of about 1 µg/m^3, which appears not unreasonable, judging by overseas literature.

It would clearly be very desirable for some co-ordinated measurement of ambient air concentrations and wet deposition to be undertaken at the same locations.

6.5.3 Estimates of acid deposition loads for New Zealand sites

Based on the annual average concentrations in Table 13, Table 15 presents estimates of acid deposition for the various sites.

Table 15. Estimates of annual acid deposition loads for New Zealand sites.

					Equiv/ha-yr per 1 µg/m3				
					25	175	770	200	
	Annual average concentrations µg/m^3				Annual acidity loads equiv/ha-yr				
Location	NO_2	HNO_3	NH_3	SO_2	NO_2	HNO_3	NH_3	SO_2	Total
Christchurch, St Albans	13.6	*3.0*	-	5.5	339	*525*	-	1102	1966
Auckland, Mt Eden	19.7	*3.0*	-	-	493	*517*	-	-	1010
Rotorua	6.4	2.0	-	3.3	159	356	-	653	1168
Invercargill	12.9	3.1	-	2.2	322	550	-	449	1320
Hastings	13.1	2.4	-	1.2	329	414	-	238	980
Whangarei	9.4	2.2	-	0.9	236	390	-	190	816
Lincoln	5.6	1.2	-	1.2	141	212	-	249	602
Whakapapa	1.5	0.3	-	5.2	36	60	-	1041	1138
Arthurs Pass	1.7	0.5	-	0.6	42	87	-	112	241
Baring Head	1.8	0.6	0.8	0.8	44	97	583	158	882

The acid deposition rates are calculated by multiplying the annual average concentrations by the factors from Table 9 for each species. For example, for deposition of acidity from nitric acid at the St Albans site, the estimated annual average concentration of HNO3 is 3.0 µg/m3. The factor for dry gaseous deposition from Table 9 is 100 equiv/ha-yr per 1 µg/m^3 annual average HNO$_3$ concentration, and the factor for wet deposition is 75 equiv/ha-yr per 1 µg/m^3 giving a total deposition factor of 175, as in Table 15. The total rate of acid deposition from HNO$_3$ is then

$$3.0 \times 175 = 525 \text{ equiv/ha-yr}$$

Alternatively, the dry gaseous and wet deposition can be estimated separately as follows:

$$\text{Dry vapour deposition of } HNO_3 = 100 \times 3.0 = 300 \text{ equiv/ha-yr}$$

$$\text{Wet deposition of } HNO_3 = 75 \times 3.0 = 225 \text{ equiv/ha-yr}$$

Similar calculations apply for all of the other acid deposition species.

As discussed at the beginning of this section, ecosystem effects of acid and nitrogen deposition are only likely to be of concern in relatively undisturbed ecosystems, which will commonly be at considerable distances from urban areas. Accordingly, the urban sites in Table 15 are of limited relevance, except insofar as they may indicate likely upper ranges of acid and nitrogen deposition. The most relevant sites are those likely to indicate existing concentrations in relatively remote areas, such as Arthur's Pass for both nitrogen and sulphur species, Whakapapa for nitrogen species and Baring Head for sulphur dioxide, nitrogen dioxide and nitric acid. Unfortunately, there is no site representing likely concentrations for all species of interest in relatively remote locations.

If the ammonia concentration at Arthur's Pass is assumed to be in the range 0.1-0.2 μg/m^3, the total acid deposition at this site would be estimated to be 325-400 equiv/ha-yr. This suggests that "background" acid deposition – estimated here from annual average ambient air concentrations – is probably in the range 200-500 equiv/ha-yr. These estimates make no allowance for processes such as long-term fixation of nitrogen in the biosystem and denitrification, which would decrease the effective acidity input in the ecosystem. Comparison of this figure with the catchment critical loads from Table 8 indicates the expected situation that "background" acid deposition is unlikely to exceed the critical load for acidity deposition for any catchment.

It appears likely that critical loads for acidity deposition will only be less than 1000 equiv/ha-yr in catchments with low rainfall, and therefore low drainage yield, such as the Sutton Stream in the Rock and Pillar Range, north of Dunedin. The critical loads for most catchments appear to exceed 2000 equiv/ha-yr, with many exceeding 3000 equiv/ha-yr. Comparing these estimates of critical load for acidity with the annual acidity loads estimated in Table 15 indicates that, even if an allowance of 500-1000 equiv/ha-yr is made for acidity deposition from ammonia, problems of soil acidification are unlikely even for unmanaged soils in urban areas in New Zealand.

6.5.4 Estimates of nitrogen deposition for New Zealand sites

Based on the annual average concentrations in Table 13, Table 16 presents estimates of nitrogen deposition loads for the various sites.

Table 16. Estimates of annual nitrogen deposition loads for New Zealand sites.

				kg N/ha-yr per 1 u/m^3			
				0.3	2.9	8	
	Annual average μg/m^3			Annual nitrogen loads kg N/ha-yr			
Location	NO_2	HNO_3	NH_3	NO_2	HNO_3	NH_3	Total
Christchurch, St Albans	13.6	*3.0*	-	4	9	-	13
Auckland, Mt Eden	19.7	*3.0*	-	6	9	-	14
Rotorua	6.4	2.0	-	1.9	6	-	8
Invercargill	12.9	3.1	-	4	9	-	13
Hastings	13.1	2.4	-	4	7	-	11
Whangarei	9.4	2.2	-	3	6	-	9
Lincoln	5.6	1.2	-	1.7	4	-	5
Whakapapa	1.5	0.3	-	0.4	1.0	-	1
Arthurs Pass	1.7	0.5	-	0.5	1.4	-	2
Baring Head	1.8	0.6	0.8	0.5	1.6	6	8

The calculations of the nitrogen loads are the same as described above for acidity loads, but using the factors from Table 12.

The major uncertainty in estimating the deposition loads of nitrogen is the lack of data for ammonia concentrations. Harrison et al (1989) have measured ammonia concentrations 1 m above grass and other crops averaging about 1.5 $\mu g/m^3$ (range 0.4-7.8 $\mu g/m^3$) during experiments that demonstrated that the ammonia was being given off by the vegetation. If New Zealand ammonia concentrations over agricultural land are similar to these, the relatively large factor for estimation of nitrogen deposition from ammonia concentrations in air makes ammonia potentially the dominant contributor to nitrogen deposition loads at many sites. The measured wet deposition of ammonia at the Puruki site (Table 14) is consistent with the ammonia concentration in air being about 1 $\mu g/m^3$, similar to that found in the UK experiments by Harrison et al (1989).

The wet deposition information from Table 14 for the Lauder, New Plymouth, Taupo rural and Maimai sites suggests ammonia concentrations in air of about 0.05-0.2 µg/m3, which may be indicative of "background" levels. This, in turn, suggests nitrogen deposition loads from ammonia (including dry deposition) in the range of 0.4-1.6 kg N/ha-yr. Overall "background" nitrogen deposition, as indicated by the data for Arthur's Pass and Whakapapa, and for Baring Head excluding ammonia, would then be in the range 2-4 kg N/ha-yr.

6.5.5 Methods for monitoring nitrogen deposition

Monitoring of nitrogen deposition rates is usually carried out simultaneously with monitoring of acid deposition, as described in Section 6.3.6

6.6 Relationship between critical loads and critical levels

Critical levels and critical loads address different effects, and compliance with one does not necessarily imply compliance with the other. For example, the critical loads for both acidity and nitrogen vary depending on the ecosystem, whereas the critical levels for sulphur dioxide, NO_x and ammonia are set for all systems, and vary only with the averaging periods. Accordingly, ambient concentrations and annual deposition rates must be estimated and compared separately with the respective critical levels and critical loads to assess the likelihood of possible effects of air pollutants on any ecosystem.

In this report, the authors have developed rough, approximate relationships between ambient air concentrations of nitrogen and sulphur species and the likely deposition rates for acidity and nitrogen arising from those ambient air concentrations. This is intended only as a convenient means of providing an approximate guide to whether acidity or nitrogen deposition is likely to approach possible levels of concern for ecosystems in New Zealand. If the rough deposition rate estimates based on monitored or modelled (for example from point sources) ambient pollutant concentrations approach or breach the critical loads, more detailed assessments to calculate the actual deposition loads should be carried out. These should then again be compared with the critical loads.

Table 17 shows the difference between critical levels and critical loads. It contains estimates of the range of acid deposition and nitrogen deposition for nitrogen oxides (NO_x), ammonia and sulphur dioxide at their respective critical level annual average concentrations. The acid deposition and nitrogen loading ranges are excessive for most or all of the sensitive ecosystems covered by the ranges of critical loads from Table 7 and Table 10. Notably, ammonia at its critical level makes the largest contribution to excessive loads of both acidity and nitrogen.

Table 17. Acidity and nitrogen loadings from critical level ambient concentrations

	Ambient concentrations µg/m3	Acidity Equivalents/ha-yr	Nitrogen kg N/ha-yr
NOx	30	1000	14
Ammonia	8	6160	64
SO2	10	2000	
Totals		**9160**	**78**

It should be noted that the critical levels for ammonia and sulphur dioxide correspond to quite high levels of pollution. For example, the 1997 annual average concentration of sulphur dioxide at the Pack St site in Christchurch was 6.8 $\mu g/m^3$. However, during May that year there were several hours during which the sulphur dioxide concentrations exceeded 450 $\mu g/m^3$, and there were over 30 hours during the year when sulphur dioxide concentrations exceeded 100 $\mu g/m^3$.

6.7 Air-shed management in relation to critical loads.

As discussed in Section 6.1, critical loads will usually only be relevant for the protection of identified important natural or semi-natural ecosystems. If there are no such ecosystems within the airshed, no consideration of critical loads is required. Accordingly, the first step is to determine what ecosystems require protection, and their locations. Because of the possibly wide-ranging implications, and the likelihood that a wider range of issues than just acid or nutrient inputs from air will be important for protection of sensitive ecosystems, the obvious vehicle for the identification of ecosystems requiring protection is via a regional plan.

The estimates of critical loads for acidity for a range of New Zealand catchments, presented in Section 6.3.2, suggest that it is unlikely that acidity deposition will be a problem in New Zealand. Accordingly, it is suggested that critical loads for acidity can be ignored unless it is known that the area requiring protection is likely to be sensitive to acid deposition, as indicated by very low levels of alkalinity in water draining from the area (for example less than 10 mg/l as calcium carbonate), or indicated by other information

Because it is not practical, on the basis of existing knowledge, to make reliable recommendations on nitrogen deposition loadings for potentially sensitive New Zealand native ecosystems, any advice on how to address the issue of critical loads for nitrogen is necessarily tentative. However, the following may provide a useful framework.

Once ecosystems requiring protection have been identified, it may be appropriate to categorise them according to the ecosystem types in Table 11, and as follows:

- Ecosystems probably minimally affected by nitrogen deposition from agricultural, urban or industrial sources
- Ecosystems subject to nitrogen inputs from other sources, such as surface water flows, which are likely to be similar to or larger than deposition inputs from air
- Ecosystems probably affected by nitrogen deposition but not subject to changing loads in the foreseeable future
- Ecosystems likely to be subject to changing nitrogen deposition loads in the foreseeable future

It would also be useful to categorise the ecosystems according to whether the likely source of nitrogen inputs is from agricultural, urban or industrial sources.

Although additional information about air quality and probable nitrogen loadings for all of the ecosystems requiring protection would be desirable, the highest priority would be the last category, those subject to change. For these ecosystems it would clearly be desirable to determine both the current state of the ecosystem (“ecosystem health”), and the current level of nitrogen pollutants in air in the vicinity of and within the ecosystem, to assist with determination of the likely levels and effects of changing inputs. It may also be useful to include some of the ecosystems in other categories as part of the assessment, since they may provide examples of similar systems subject to relatively low and relatively high nitrogen loads, to indicate the likely effects of changing nitrogen loads.

Assessment of the current state of the ecosystem(s) would require expert advice. Estimation of the current nitrogen loading could be based on passive sampling results for nitrogen dioxide, nitric acid and, particularly, ammonia as done here in Section 6.5.4.

Assuming that the likely changed nitrogen loading arises from a proposed activity subject to a resource consent, it is recommended that the existing concentrations of nitrogen dioxide, nitric acid and ammonia should be assessed as part of the assessment of affects, and that this information is used to determine the existing nitrogen loading. A combination of this information and the increases estimated to result from the proposed activity could then be used to determine the total concentrations in air, and the estimated total nitrogen deposition load. The estimated total nitrogen load can then be considered according the following possible scale of acceptability:

Total nitrogen loading	Acceptability of effects
Less than 5 kg N/ha-yr:	Acceptably small level of nitrogen loading, unlikely to cause significant ecosystem changes
Greater than 5 kg N/ha-yr, but less than the UNECE critical load for the equivalent ecosystem type	Possibly acceptable, but additional investigation of New Zealand systems desirable to check validity of the UNECE critical loads for NZ. Progressively less acceptable as the upper bound of the UNECE critical load is approached.
Greater than the UNECE critical load for the equivalent ecosystem type	Not likely to be acceptable unless specific information is available to demonstrate the absence of unacceptable effects.

The proposed activity may also be considered acceptable if the increase in nitrogen loading from the proposed activity is a small proportion (say 10-20 percent) of the existing nitrogen loadings either via deposition from air or via other routes, such as surface water movement into the ecosystem. A high existing loading, particularly if there is a good indication that the situation has persisted for a considerable period, may indicate that the ecosystem has already adapted to the relatively high nitrogen loading, and that minor further increases may have little additional effect. However, expert advice may be required to assess such a situation.

7. Additive and synergistic effects

It is very rare for an air pollutant species to exist in isolation. Most often, they occur as associations of nitrogen, and sulphur dioxide and ozone, all of which are phytotoxic at some concentration. Summarised reviews of plant responses to exposure to these combined pollutants show that the effects are most often additive, synergistic or antagonistic (WHO, 1987).

Studies have shown how important climatic conditions are on the overall effect of exposure to mixtures of pollutants in terms of effects on plants. This relates directly to the physiological processes occurring at the time of exposure. Concentrations that are damaging in winter can be negligible or even beneficial in summer conditions. NO_x combined with SO_2 will generally produce an overall reduction in growth, as well as visible foliar injury at concentrations significantly lower than the threshold concentrations of either pollutant alone.

Studies on the combined effects of ozone, SO_2 and NO_2 have suggested a threshold for injury as low as 28.5 $\mu g/m^3$ NO_2 in association with similar levels of SO_2 (40 $\mu g/m^3$) and ozone (60 $\mu g/m^3$).

Peak concentrations of NO_2 are often associated with elevated SO_2 levels, but low ozone, due to the scavenging of ozone by nitric oxide. Under these conditions, it has been shown (WHO, 1987) that sensitive plants are adequately protected from adverse nitrogen dioxide effects if the 4-hour average does not exceed 95 $\mu g/m^3$.

Because NO_X and SO_2 take-up via stomata is not accompanied by an “equivalent” stomatal cation flux, reductive or oxidative detoxification will induce an additional cation demand that must be supplied from the soil. Quantifying this additional cation demand depends on:

- the growth rate of the plant
- their N, S and cation contents, and
- on the relative participation of oxidative versus reductive detoxification pathways (Slovik, 1996).

The additional cation supply must come from the soil. If there is a cation deficiency in the soil, this must be overcome by fertiliser application, or the result is that chronic NO_X and SO_2 pollution will cause mineral deficiency symptoms. This may lead to reduced canopy and root growth rates as the plant diverts available cations to cope with vacuolar sulphate neutralisation demands. Slovac (1996) states that for Norway spruce, SO_2 concentrations of 85 $\mu g/m^3$ will cause massive competition for any available K^+ budget. Slovac’s work did not see an equivalent effect from the ambient NO_2 levels encountered, because ambient NO_2 levels (16 - 33 $\mu g/m^3$) were below those required to induce an effect. He lists the combination of environmental conditions required to produce canopy thinning which would exceed the natural dynamics of around 20 percent as:

- high ambient SO_2 concentrations
- short growth periods (results of climate effect - forests at higher altitudes are more vulnerable than those at lower altitudes)
- poor K^+ or Mg^{2+} depleted soils
- acid precipitation, which leads to leaching of K^+, Mg^{2+} into groundwater
- the “export” of K^+ or Mg^{2+} out of the system by:
    1. harvesting the crop (wood)

2. stimulated growth of herbaceous plants and micro-organisms
3. increase in protein phytophage insects, deer, etc

Those components of ecosystems which are less able to cope with K^+ or Mg^{2+} shortages will not compete, and the result may be a change in species composition ('ecosystem drift') and reduced biodiversity.

8. Effects of hazardous air contaminants on ecosystems

For many of the hazardous air pollutants, carcinogenicity is the major concern from the human exposure perspective. The levels of cancer risk considered acceptable by regulatory agencies aim to restrict additional cancer incidence to extremely low proportions of the population as a result of possible lifetime exposures. The concern is essentially for the health and well-being of the individual human. On the other hand, for ecosystem protection, the concern is for the population as a whole and the levels of additional cancer risk arising from exposure to hazardous air pollutants is negligible compared with other factors affecting natural populations.

Further, for non-cancer health effects, Reference Exposure Level (REL) or Reference Concentration (RfC) levels recommended by the US EPA and the California EPA contain very substantial uncertainty factors which means that they are commonly orders of magnitude below concentrations which have been observed to have effects either in people or animals (usually mammals). Accordingly, if such REL or RfC levels are used as a basis for control of emissions and air quality for volatile and semi-volatile pollutants not subject to significant accumulation in ecosystems, there is very little probability of any effects on an ecosystem's mammal population.

Apart from organochlorine hazardous air pollutants (e.g. dioxins, PCBs and DDE) and some toxic elements (such as heavy metals), most hazardous air pollutants exist in the atmosphere as gases. They generally do not deposit to soils and vegetation to any significant degree and usually break down in natural biological systems such as soils. Accordingly, their principal exposure route for both humans and animals is inhalation.

The main concern in relation to ecosystem effects of hazardous air pollutants relates to those which are persistent and which are likely to express their effects through bioaccumulation. Transfers of persistent pollutants (notably the organochlorines and toxic elements) from air into soil and water, and from there into human food chains can be examined by use of multi-pathway health risk assessment modelling. However, while this provides a basis for estimating concentrations of the various contaminants in the various environmental media, very little information is available on critical concentrations in those media that are likely to affect ecosystems. Some information is available on concentrations of pollutants such as dioxins and PCBs in air in areas where severe effects, for example on bird reproduction, have been attributed to contamination by these compounds. The concentrations are (or were) much higher than found in the New Zealand Organochlorines Programme (MfE), suggesting that effects are unlikely unless very significant increases were to occur in the New Zealand ambient concentrations. It is unlikely that the implied increases in possible dietary intakes for humans resulting from such increases would be considered acceptable, so that measures taken to control health risks to humans are likely also to control possible effects on ecosystems.

From a toxic elements (e.g. heavy metals) perspective, the natural levels present in soils are such that significant changes in existing levels are likely to arise only from very large emissions continuing for very long periods (decades to centuries to millennia), or in the immediate vicinity (tens of meters, as a result of wet deposition) of smaller or better controlled emissions.

If the natural levels of a toxic element in soil are not changed significantly by deposition, adverse effects on soil biota are unlikely. For such a toxic effect to occur, it would be necessary to postulate that the toxic elements deposited from air were in a different and more bio-available form than essentially all of the particular toxic element content of the soil, and that they remain in that form indefinitely. Although it is usual for the major fraction of the natural toxic element content of soils to be bound in forms of low bioavailability, there is almost invariably a significant fraction (typically up to about 10 percent) that is bioavailable. Also, the bioavailability of heavy metals added to soils (for example in sewage sludges) decreases over time, as they become incorporated into mineral fractions forming in the soil.

Accordingly, unless additions of a toxic element to a soil cause a rapid change in soil concentrations, or a substantial increase in the total soil concentrations, the proportions of the toxic element in bioavailable forms are unlikely to change significantly, and effects on soil biota are unlikely. The bioavailable fractions are also those contributing to toxic effects from ingestion of soil or those available for uptake by plants that may be eaten by animals. Therefore, these pathways are not likely to result in toxic effects under conditions where soil biota are not adversely affected.

9. New Zealand Studies

9.1 Introduction

There has been a range of studies carried out in New Zealand, from the early '70's onwards, which have examined the effects of air pollution on plants, animals or other identified ecosystem components. Some of these studies were reviewed in the original reports (MfE 1998a, 1998b, 1998c) and further studies are reviewed below. At the time these studies were carried out, little was known of the effects that could be expected from some of the pollutants, and this is reflected in hindsight, by the lack of good planning, and the inconclusive outcomes. By contrast, the studies relating to fluoride contamination are well planned, defined, and conclusive. The MfE review of effects of the effects of gaseous pollutants on ecosystems includes a comprehensive coverage of the mechanisms of effects as they are currently known. This should provide a valuable assistance in deciding what risks there may be, and how best to address them in the future.

9.2 Marsden Point

9.2.1 Sulphur Dioxide

The construction of an oil refinery in the mid '70's at Marsden Point, Northland, initiated a study on the effects of sulphur dioxide on lichen populations in the area. The programme commenced in 1976 and is still progressing.

The study involves assessing changes in lichen populations and a rigorous photographic record has been established. Studies have been carried out during the following years: 1976, 1979, 1982, 1987, 1988, 1993, 1994, 1995, 1997, 1999, and 2000. Changes in populations and growth patterns are recorded. For the most part, the changes seen in populations are due to natural succession, and differences in growth patterns could be ascribed to a variety of environmental influences, including high SO_2 levels.

The second (1979) survey report details changes such as the death or decline of some or parts of colonies, and notes that sensitive species, such as Usnea, have continued to flourish. It discusses the fact that an early sign of air pollution effect is a reduction on growth rates, and suggests that a pattern of depressed growth rates of abundant foliose species may be related to ambient SO_2 level. The evidence presented does not clearly show any pattern for exposure based on any implied dominant wind direction. There is no mention of what the levels of SO_2 were in the area during the study period. Recommendations in the 1979 report to include the analysis of the levels of sulphur dioxide in lichens taken from colonies close to the study area would have provided more meaning to the study, but apparently was not carried out.

By and large, the remainder of the work documents growth rates and changes in colonies of lichens at the study sites, but fails to establish a link with ambient SO_2 levels.

The more recent work has included statistical analysis of variations, along with the establishment and assessment of a control site. To date, the control site has shown a statistically significant depletion of population, but the explanation for this is not known.

Lichens are a symbiotic association of an alga and a fungus. They lack the protective cuticle present in higher plants, which is of benefit to them in that they can take up nutrients via the epidermis and not through their roots. They have a thick epidermis, which is a biologically active surface when they are metabolically active, but they are readily subject to desiccation, and the ability to dry out rapidly is one of the secrets to their success. When dehydrated, they are dormant and the upper cortex thickens, becoming opaque and effectively blocking the passage of light energy, and also the entry of most gases. A wet lichen can be destroyed by light intensities and temperature extremes which will not harm a dry lichen. Once re-hydrated they become physiologically active immediately, and vulnerable to toxicity. Therefore, their growth rates are dependent on the amount of precipitation, which maintains their metabolically active state, and when in this state they are vulnerable to a wide range of environmental hazards, including high levels of sunlight, which can be very damaging, as well as gaseous pollution (Raven et al., 1982). In the absence of convincing evidence, it is difficult to assign fluctuations in growth rates, or intermittent damage or changes in colonies of lichens, to a particular pollution effect.

The value of the Marsden point study would be greatly enhanced by the inclusion of annual reviews of meteorological records, if changes in lichen populations are to be used as an indication of the impact of SO_2 emissions on the environment.

Surveys of higher plant vegetation have also been commissioned in conjunction with the refinery development, and also the establishment of the Marsden A and B Power Station, approximately 3 km to the south of the refinery, on Marsden Point. Surveys undertaken for the NZ Department of Conservation prior to the industrial development, note that the vegetation of the Whangarei Heads area has been subject to considerable alteration from human activities. Although now the areas affected by the early logging of kauri, totara, rimu and other hardwoods is undergoing effective regeneration, the bush is still severely impacted by possum infestations, and because of inadequate fencing, goats and stray cattle also. An inspection in 1992 by Dr G T Daley for visible signs of foliage damage caused by emissions of sulphur dioxide failed to find any possible evidence, either on the Whangarei Heads, or on Marsden Point (except for the possibility of some foliar damage in the gardens of the refinery). Dr Daley notes that on an earlier inspection in 1975, lichens were rare on Mt. Manaia, but profuse on exposed rocks on Mt. Aubrey. He lists plants sensitive to sulphur dioxide, and also plants which may be resistant. Included in the possibly resistant species are Kanuka, Pohutukawa and mangrove (Daley, 1992).

A report by Kingett Mitchell on a survey undertaken in 1995 and 1997, relates visible signs of stress such as leaf yellowing, blotching, puckering, intercostal chlorosis and some evidence of leaf burn to the possibility that elevated levels of sulphur dioxide in combination with other factors may be the cause; and recommends further monitoring of vegetation, soil and plant tissue (Kingett Mitchell, 1999).

9.3 Tiwai Point

9.3.1 Fluoride

In addition to preliminary background monitoring done prior, a comprehensive monitoring program focusing on the effects of fluoride discharges to air on the receiving environment has been operating since 1971 in Southland, following the commissioning of the aluminium smelter at Tiwai Point. The various studies commissioned have been conducted to:

- Provide data for process control
- Assess the smelter’s effect on the surrounding environment
- Measure compliance with consent limits
- Comply with conditions in consents which require that monitoring be conducted

Overall, the program has focused on the key areas of:

- Effects on agricultural activities, which has included studies on flouride deposited on and taken up by pastoral vegetation. Both managed and unmanaged pasture was studied, in order to determine the contribution to fluoride levels made by the application of superphosphate. An experimental farm project was established in order to provide more information on the effects on sheep. The levels recorded in cattle and sheep, which included sampling urine concentrations of sheep and cattle, examinations for dental defects, jaw bone analysis on ewes when culled, biopsy sampling and analysis of tailbones in cattle, as well as the analysis of metacarpal and metatarsal bone when culled.
- Effects on wild animals. Insects reptiles, worms, birds, possums and mice were sampled and analysed for fluoride concentrations.
- Effects on plants. Both native and exotic vegetation in the vicinity of the smelter were studied and routinely sampled for fluoride effects and concentrations.
- Effects on water supplies. Aquifers in the immediate vicinity have been studied with regard to fluoride levels, as has the water supply sourced from the Oreti River.
- Effects on coastal marine areas. Marine seawater and sediments taken from Bluff Harbour, Awarua Bay and Waituna Lagoon were analysed for fluoride concentrations. Assesments were made of the biaccumulation of fluoride in marine organisms in Waituna Lagoon, and possible effects on the fisheries of Southland. (NZAS, 1993).

Vegetation has been sampled fairly extensively for fluoride levels, and assessments have been undertaken to determine the local effects of fluoride emissions on flora. Sheep and cattle have been monitored for fluoride levels on local farms, out to about 10 km. A variety of birds, insects rodents and possums have also been studied for fluoride and aluminium levels in bones.

Production has increased at the smelter over the years, and this appears to have resulted in increased fluoride emissions, which has shown up in the above monitoring.

Herbage samples from grazed and ungrazed pasture and pine needles have been routinely analysed for fluoride content by the smelter and other labs. A difference between the smelter analysis and that of a government laboratory has led to several inter-laboratory comparisons of analysis methods and results. None of these were conclusive in determining a cause for the difference, where the government analysis showed a marked trend for increasing fluoride accumulation being sampled, over time (Ministry of Agriculture and Fisheries, 1994).

Vegetation surveys of flora surrounding the smelter established that the harsh environment was responsible for much of the stress apparent in a lot of the plants, and that this was variable according to the growing season conditions. Overall, the vegetation was in good condition. However, low level, fugitive emissions were affecting plants up to 400 m from the potrooms. Further out, symptoms of fluoride stress could be determined, which based on modelled ambient air concentrations, would become a combined potroom and stack plume effect, then gradually, an effect form the plume only. This was detectable out to 1.5 km from the plant, in the direction of the prevailing wind (Doley, 1992).

Pasture samples showed considerable variation in fluoride content. Generally, pasture fluoride concentrations ranged from 10-40 mgF/kg dry matter, with some monthly values in excess of 50 mg/kg, which related to period when the smelter exceeded their Discharge permit limit of 80 mg/kg. The highest values were found in samples collected downwind from the smelter, and the possibility that samples may have fluoride contributions from fertiliser cannot be ruled out.

Selected cattle were routinely monitored for dental fluorosis, tailbone biopsies preformed to measure bone fluoride concentrations, and urine samples collected. An increase in dental fluorosis was detected on two farms since 1983 that are E-NE of the smelter (in line with the prevailing winds), and bone concentrations reached critical levels. No lameness or poor growth was recorded in animals on these farms. Other farms included in the monitoring showed no evidence of smelter induced fluorosis.

Sheep monitored as part of the experimental farm project have also displayed dental changes indicative of fluoride damage. Of the two experimental farms established, the one closest to the smelter discharge showed the highest levels of deposited fluoride and dental fluorosis in sheep. Expert opinion confirmed these effects to be in line with the recorded pasture fluoride levels (Laughton, 1995). Ewes farmed on these properties were generally in lean condition, more as a result of constraints on pasture improvement practices resulting from the need to control extraneous fluoride exposure, but were able to maintain consistently good lambing percentages and longevity. There were no skeletal problems resulting from fluoride exposure (Laughton, 1995).

Overall, the smelter operation may be causing teeth wear in sheep and cattle, but there is no evidence of other signs of impaired production (Ministry of Agriculture and Fisheries, 1994).

Soil sampling was carried out by NZAS staff and also by contractors, on and around the smelter site for available aluminium and fluoride. The most recent study showed fluoride and available aluminium levels were higher at the on-site sampling sites than those further out, in the Tiwai Peninsular.

A single study, which analysed the fluoride and aluminium levels in soil fauna, insects and rodents, birds and plants showed increased levels in organisms living closer to the smelter (Bioresearchers, 1995).

These findings tend to be consistent with expected ambient concentrations of fluoride. Ambient fluoride concentrations predicted by air dispersion modelling undertaken in 1993, range from 0.3 $\mu g/m^3$ within 1 km from the smelter, with a high impact of 0.2 $\mu g/m^3$ about 5 km out in the direction of the prevailing winds.

9.4 Ohaaki

9.4.1 Hydrogen Sulphide

The process of undertaking an environmental impact assessment for the Ohaaki Geothermal Power Station raised concerns for the effects that predicted concentrations of H_2S originating from the power station cooling towers may have on the surrounding environment. Modelled predictions of H_2S and its oxidation product, SO_2 highlighted the Rawhiti wetlands and lagoon, 1.5 km to the SE, and Hardcastle Lagoon, 3.5 km NE of the cooling tower, as being areas of significant impact under stable inversions; with the added potential of these conditions persisting overnight and through the following morning, thus resulting in a relatively long exposure to the pollutants. Further the concerns related to the frequency at which hot sunny conditions might result in H_2S concentrations of up to 0.036 ppm 1 km from the tower, and with a slight breeze, 0.018 ppm 2.4 km downwind, the break-up of the inversion resulting to short term higher concentrations of around 0.24 ppm at ground level. At Hardcastle Lagoon, the highest predicted concentrations of 0.012 ppm could occur on 2 or 3 occasions per year; and at Rawhiti Lagoon, the maximum prediction of 0.030 ppm could occur on 13 occasions per year. Further concerns related to the degree of resolution of predicted concentrations calculated by the model used, as it was only likely to be accurate to an order of magnitude; therefore raising the possibility that H_2S and SO_2 levels could be up to five times higher that predicted (Downes and Forsythe, 1988).

Downes and Forsythe reviewed the literature to determine the potential effects of this scenario on the local ecosystems. They concluded that the greatest risk to plants in the areas was from the impact of the SO_2 oxidation product, more so than H_2S. While H_2S has the potential to affect animals, the evidence was that the expected concentrations were unlikely to do so. This was supported by findings in Rotorua of colonies of birds living with no apparent ill effects at Sulphur Bay, and other evidence, where adverse effects did not occur until considerably higher concentrations were reached.

At the time of the review, the level of understanding of the effects of SO_2 on plants was not as developed as it is today, and their findings were largely inconclusive. However, they concluded that, given the worst-case scenario outlined in the modelling of concentrations expected to impact these ecosystems, there was a possibility of visible damage to plants if levels of greater than 0.080 ppm were achieved. However, the result of such an event was not likely to be detrimental to the overall ecology of the region.

9.5 Kumeu

9.5.1 Formaldehyde

Concerns were expressed that the establishment of a particle board factory in the early 1970’s, in close proximity to established grape vines and state forest nurseries. It was recommended that a maximum ground level concentration of 1 ppm formaldehyde be proposed. This seemed to be acceptable, based on the information available at the time, which indicated that some plants, including grapes, could suffer damage if exposed to “concentrated fumigations” of formaldehyde for 12 to 24 hours; and the observation that tomato seedlings occasionally suffered “burn off” when planted in soils previously sterilised with formalin and not completely flushed prior to planting.

More recent studies have shown that exposures of 700 ppb formaldehyde caused foliar lesions in alflalfa, while similar doses produced no visible injury in spinach, beets or oats. Pollen tube elongation was inhibited in lillies at 1400 ppb. When fumigated for the control of fungal infection, stored grape berries developed necrotic sunken lesions in the skin or around the cap stems. When beans were exposed at regular daily intervals to concentrations of 0, 50, 100, 200 and 400 ppb, respectively, those exposed to the highest concentrations produced the greatest leaf area, and it was noted that the leaves appeared thicker in the exposed plants. The 200 and 400 ppb treatment plants produced the highest leaf and stem dry weights, but no difference was seen between the control and treatment plants for root development. Sucrose content was higher in the leaves of the 400 ppb treatment. However, no corresponding increase in carbon content was found (Mutters et al., 1993).

10. Other Contaminants

10.1 Aluminium

Aluminium is one of the most abundant elements in soils. It occurs ubiquitously in silicates, complexed with sodium and fluoride, as well as hydrous aluminium oxides, aluminium hydroxides and impurities such as free silica. It is not found as a free metal because of its reactivity. Transport through the environment is dependent on its coordination chemistry (it has only one oxidation state; +3), and the characteristics of the local environmental system. At pH greater the 5.5, naturally occurring Al exists mostly as undissolved compounds such as gibbsite or aluminosilicates, unless other influences exist, such as high amounts of fulvic acids and humic compounds. These substances bind with Al, and can cause increased levels of dissolved Al in streams and lakes. However, the mobilisation and transport of Al within the environment is influenced by other factors also, such as chemical speciation, hydrological flow paths, spatial and temporal factors relating to soil-water interactions, and the composition of the underlying geological structures. Aluminium is best mobilised in watersheds which have shallow, acidic soils and poor buffering of surface waters which are exposed to acidic deposition.

Both natural and anthropognic activities release Al into the environment, although natrual processes far outweigh anthropogenic processes, due to the abundance of Al in the earth's crust. Anthropogenic releases are primarily into the atmosphere, and are associated with industrial processes such as smelting. Soil derived dusts have high concentrations of Al compounds. Mining and agricultural activities, as well as the combustion of coal contribute to increased levels in dust. Some industrial uses of Al compounds include glass, ceramic, rubber, wood preservatives and parmaceutical production, in waterproofing textiles; and natural Al minerals such as bentonite and zeolite are used in water purification, sugar refining, brewing and paper industries.

However, it is the mobilisation of existing Al in the environment that causes most concern. The common mechanism for this is acid deposition into environments with poor acid neutralising capacity. While aluminium levels are negligible in most natural waters, high Al concentrations will occur in surface waters that have a pH less than 5. Monitoring of Al levels in steams has shown that concentrations can be seasonal, in response to rainfall levels. During periods of high rainfall, pH decreases, resulting in leaching of Al, while during low rainfall periods, pH increased.

Aluminium toxicity in ecosystems can arise as a consequence of soil and water acidification by air pollutants. Although aluminium may be the toxicant causing the adverse affects it is not the primary cause of the problem, which is acid deposition, as discussed elsewhere in this report. The solubility of aluminium in soils, where it is present in large quantities in a wide range of soil minerals and clays, is controlled predominantly by pH and the quantities of natural organic complexing agents, such as humic and fulvic acids. However, the complexed forms of Aluminium are relatively non-toxic, and the primary concern is with soluble aluminium ion (Al^{+3}), and its inorganic complexes, particularly including the fluoride complex. The equilibria between soil minerals and aluminium are generally well understood.

Because of the toxic effect of soluble aluminium on plants, the ratio of the soluble aluminium concentration to either calcium or total base cation concentrations in soil solution is used as a criterion to define the maximum acceptable level of soil acidification in the determination of critical acidity loads.

10.2 Boron

Boron exists only in particulate form in air. It is of possible concern as an air pollutant because some coals contain significant quantities of boron and the possibility exists that excessive levels of boron maybe deposited on plants and soils to result in phytotoxicity, which is well established as a problem for irrigation waters containing high boron levels.

The most likely situation in which phytotoxicity from boron emissions might arise would be close to the point of emission, where relatively high levels of wet deposition can occur. Under these conditions, the emission rate of boron is the critical perimeter, rather than the concentration in ambient air. The most appropriate criterion on which to base a threshold level of boron emission above which adverse affects might occur is the boron concentration equivalent to the total annual annual boron deposition rate dissolved in the total annual rainfall. The most astringent guideline for protection of sensitive crops, such as citrus, from boron toxicity is that the boron concentration in irrigation water should be less than 0.5mg/l.

10.3 Mercury

Emissions of mercury to air are of potential concern principally because of the potential for bioaccumulation in aquatic ecosystems. The principal concern in relation to this is human consumption of fish, but it is possible that other animals at the top of the food chain might also be adversely affected. Direct ecosystem affects from mercury concentrations in ambient air are exceedingly unlikely compared with the potential for effects via wet and dry deposition of mercury, particularly into aquatic ecosystems.

Mercury can exist in at least three distinct forms in emissions to air.

- Elemental mercury vapour.
- Mercuric chloride vapour.
- Mercury absorbed on particulate material.

The behaviour of these forms both in pollution control systems and after emission to air is quite different, and this can greatly affect the levels of transfer from air into other media. Pollution control systems are generally most effective for removal of particulate and mercuric chloride forms, so that if an emission is subject to a high level of mercury removal, for example 85% removal or more using activated carbon, all of the emitted mercury can be considered to be present as elemental mercury.

After emission to air, elemental mercury is not readily deposited. It enters the global mercury cycle, and is only slowly deposited after oxidation in atmospheric water droplets by ozone.

Mercuric chloride, on the other hand, is highly soluble in water, and readily scavenged by rainfall. It is probably also subject to absorption onto many surfaces, including vegetation and soils.

Particulate forms of mercury are subject to both wet and dry deposition, along with the particulate material on which it is absorbed.

The best approach to identifying mercury levels of possible concern in relation to aquatic ecosystems appears to be via wet and dry deposition modelling to determine of mercury inputs to water bodies of possible concern. Assessment of the acceptability of the resulting mercury contibutions to the water body requires consideration of water quality criteria for mercury for protection of aquatic ecosystems and human consumers of aquatic organisms, which is beyond the scope of this report.

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12. Glossary

Bryophytes. *Bryophyta*. Division of plant kingdom Hepaticae (liverworts), Musci (mosses), and Anthocerotae (hornworts). Lower order of plants.

Buffering capacity. Ability to resist changes in pH when acid or alkali is added.

Chlorophyll. Green pigment found in all lower and higher plants (with the exception of a few saprophytes and parasites); located in chloroplasts except in blue-green algae (Cyanophyta) where it is borne in numerous photosynthetic membranes scattered in cytoplasm at cell periphery

Chlorosis. Disease of green plants characterised by yellow (chlorotic) condition of parts that are normally green; caused by conditions preventing chlorophyll formation (e.g. lack of light)

Cuticle Superficial one-cellular layer covering animal or plant; secreted by epidermis. In higher plants, forms a continuous layer over aerial parts broken only by stomata and lenticels; protects against mechanical injury, but chief function is preventing excessive water loss.

Enzyme. A protein which is a catalyst (i.e. a substance which in minute amounts promotes change without itself being used up in the reaction), by virtue of its power of increasing the reactivity of a specific substance or specific substances.

Equivalent. One gram of hydrogen ions. For example, deposition of 100g of sulphuric acid (molecular weight 100) deposits 2 equivalents, because each mole of sulphuric acid contains 2 moles of hydrogen ion (atomic weight 1).

Epidermal Outermost layer of cells of a plant or animal. In plants one cell-layer thick, covered in aerial parts by a non-cellular protective cuticle.

Equivalents (of acidity). A measure of acidity. An equivalent is equal to a single free proton or H^+ ion released by an acidifying compound.

Eutrophication. (Of lakes, water bodies) highly productive in terms of organic matter formed, well supplied with nutrients. Cf. *Oligotrophic*.

Foliar. Of foliage (plant)

Genome. The set of chromosomes found in each nucleus of a given species.

Herbaceous. Having the characteristics of a herb. *(Herb: plant with no persistent parts above ground, as distinct from shrubs and trees).*

Humus. Complex organic matter resulting from decomposition of plant and animal tissue in the soil, which gives to surface layer of soil its characteristic dark colour; of great importance for plant growth; improving texture, water holding capacity, and mineral storage.

Lichen. Lichens, dual organisms formed from symbiotic association of two plants, a fungus and an alga.

Lipophilic. Lipid = fat; philic = with an attraction for. Substances which are taken up by the lipid tissues.

Membranes. Thin pliable sheet-like tissue serving to connect other tissues or to line organs.

Mycorrozal. Mycorrhiza, "fungus root"; an association of a fungus with root of a higher plant. Mycorrhizas are a common occurrence, forming mutually beneficial symbiotic relationship. Mycorrhizal plants benefit from the association by facilitating phosphorus uptake while the fungus obtains sugars and protein from the plant.

Organelles. Persistent structures with specialised function forming part of a cell, e.g. mitochondria or flagellum; an organelle in a cell is analogous to an organ in a whole organism.

Phloem. Vascular tissue that conducts synthesised foods, e.g. sugars, proteins and some mineral ions, through the plant. Characterised by presence of sieve-like tubes, and in some plants, companion cells, fibres and parenchyma cells.

Phytotoxic. Toxic to plants.

Stomata. Pores in the epidermis of plants, present in large numbers, particularly in leaves, through which gaseous exchange takes place.

Transpiration. *Transpiration stream*; flow of water through plant as a result of loss of water (vapour) through stomata. Differs from evaporation in that it takes place from living tissue and is therefore influenced by the physiology of the plant.

Vacuolar. *Vacuole*. Fluid-filled space within the cytoplasm, bounded by a membrane. A single vacuole, taking up most of the cell volume is present in many plant cells; contains solution (cell sap) isotonic with cytoplasm.