AIR POLLUTANT AND DEPOSITION MONITORING NETWORKS IN ALBERTA

A REVIEW AND RECOMMENDATIONS FOR POTENTIAL FUTURE NETWORKS

Alberta Environment

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Prepared by
Centre for Ecology & Hydrology
Edinburgh Research Station
United Kingdom

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WBK & Associates Inc.

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Any comments, questions, or suggestions regarding the content of this document may be directed to:

Air Policy Branch
Alberta Environment
11th Floor, Baker Centre
10025 – 106th Street
Edmonton, Alberta T5J 1G4

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Oxbridge Place
9820 – 106th Street
Edmonton, Alberta T5K 2J6
Phone: (780) 427-2700
Fax: (780) 422-4086
Email: env.infocent@gov.ab.ca

EXECUTIVE SUMMARY AND RECOMMENDATIONS

Alberta Environment commissioned Dr. John Neil Cape from the Centre for Ecology & Hydrology at the Edinburgh Research Station in the United Kingdom (UK) to conduct a review of current air and deposition monitoring in Alberta and provide recommendations for future network development. The review was conducted to support the development of a new Air Monitoring Strategic Plan for Alberta, and considered factors such as existing air monitoring in Alberta and future air emission scenarios. The following are assumptions and recommendations resulting from this review:

1. The theoretical development of air quality monitoring network designs is described with reference to experience in the UK and Europe.

2. Available measurements from Alberta are used to illustrate the application of simple statistical methods to estimate where current information is most uncertain, thereby indicating where future monitoring may provide a better understanding of the spatial patterns of air concentrations and wet deposition across Alberta.

3. For wet deposition, **we recommend:**
   a) At least one more site in central Alberta (in the region of Slave Lake), with additional sites in SW Alberta (Banff, Jasper foothills) and northern Alberta (3-4 sites to provide better spatial coverage, although concentrations here are small). This implies an approximate doubling of the existing network of 9 sites.
   b) One of the key uncertainties is the spatial pattern of precipitation amount, particularly in the foothills of the Rockies in SW Alberta. Additional data or modelled amounts would reduce uncertainties here.
   c) Given the apparent strong north-south gradient in both precipitation amount and concentrations of ions, a short-term (i.e., 3-5 year) study of gradients north-south and east-west would provide confirmation of the pattern across the province. This would entail another 16-20 sites, with the east-west transect bisecting the Calgary-Edmonton corridor and the north-south transect along the Calgary-Edmonton corridor.
   d) Using data from neighbouring Provinces to establish the spatial patterns, particularly in the case of Saskatchewan, where interpolation uncertainties may be less than in the more complex terrain of British Columbia to the west.
   e) The interpolation uncertainties should be evaluated regularly and, if necessary, new sites established where large uncertainties exist. Patterns will change with time as new emission sources are established, and old ones close. In areas of low uncertainty, redundant sites may be closed. Maps with and without potentially redundant sites can be generated to establish the additional uncertainty caused if a particular site is to be closed.

4. Potential measurement methods for wet deposition are discussed, noting the difficulty in measuring deposition in snow.

5. Available data for rural air concentrations of sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3) and fine particulate matter ($PM_{2.5}$) are mapped across the Province, and potential methods for estimating dry deposition are discussed.

6. For dry deposition **we recommend:**
   a) That low-cost denuder/filter samplers be set up at each of the wet deposition network sites, which should already satisfy appropriate siting criteria. The CEH DELTA system or similar would be appropriate to give air concentrations on a two-weekly/monthly basis for SO_2, nitric acid (HNO_3), ammonia (NH_3), and particulate nitrate (NO_3^-), ammonium (NH_4^+) and sulphate (SO_4^{2-}).
   b) In addition, at these sites, passive diffusion monitors for NO_2 and O_3 should be installed.
   c) If full denuder/filter systems are not installed, we recommend that as a minimum, passive diffusion samplers for NH_3 and HNO_3 be used instead. The network could comprise a mixture of active and passive samplers, with some co-location to provide cross-calibration of the techniques (cf. UK ammonia network)
   d) A better but costlier alternative to passive sampling for O_3 would be a battery-powered UV ozone analyzer/data logger that could be supplied from a similar wind/solar-powered generator. This would provide data on peak concentrations measured during ozone 'episodes' which are likely to be important for direct effects on vegetation.
   e) Temporary (3-5 year) installations at the E-W and N-S transect sites of the wet deposition network would also provide useful information on spatial patterns.
   f) An annual study using passive samplers of the variation of O_3 concentrations with altitude in several regions of Alberta. Studies elsewhere have shown a strong relationship between altitude and average O_3 concentrations. If this also applied in Alberta, altitude could be used as a predictive variable for interpolative modelling of regional O_3 concentrations.

7. Air quality criteria for human health are discussed in terms of PM, NO_2 and O_3.

8. For particulate matter **we recommend**:
   a) Installation of 'background' monitoring stations at approximately 100 km from the two major cities upwind and downwind in the prevailing wind direction. These stations would provide information on the proportion of PM (largely secondary) that contributes to the urban PM, but over which the city authorities have no direct control. Secondly, the downwind site will provide data to evaluate the contribution of the urban area to regions downwind, superimposed on the 'background' regional PM concentrations.
   b) Use of one or more mobile monitors that could be installed for relatively short periods of time (i.e., months) at strategic locations around the urban area, both downtown and in the suburbs, to gain a better idea of the quantitative and temporal correlations with the fixed monitors.
   c) Use of one or more mobile monitors installed for periods of months in other built-up areas (smaller towns and villages) or close to major sources where people may be

exposed to high concentrations of PM outside the workplace. Priority should be weighted by the numbers of people potentially exposed.

9. For nitrogen dioxide **we recommend** that where passive monitoring of NO_2 in built-up areas shows significant increases in concentrations above the regional average:
   a) Short-term (i.e., one year) studies be established with a dense spatial network of passive diffusion monitors to identify the likely maximum areas of high exposure, so that long-term monitoring of the NO_2 risk to human health can be established.
   b) Geospatial statistical modelling should be developed as an interpolation tool for high-resolution modelling in urban areas.

10. For ozone **we recommend**:
   a) That the long-term average ozone concentrations, and areas with highest average exposure, be identified from the regional rural measurements, using either passive or active sampling.
   b) The installation of continuous monitors upwind, downwind, and in the residential areas of major towns and cities, to provide information relevant for human health in terms of the evolution of ozone 'episodes'. Monitors could be co-located with the recommended PM monitoring sites (above).
   c) Campaign (week-month) measurements of volatile organic compounds (VOC) concentrations upwind and downwind of major urban areas and local point/area sources, as for PM and ozone, in order to understand the relative importance of anthropogenic and biogenic VOCs on ozone and secondary organic aerosol (SOA) formation downwind of sources.

11. A strategy is outlined for measuring the budget of trans-boundary air pollution into and out of Alberta. **We recommend:**
   a) The deployment of simple denuder/filter samplers and wind speed/direction monitors to control sampling of the well-mixed boundary layer at the boundaries of Alberta.

12. Maps of wet deposition and air concentrations of NO_2 and SO_2 have been produced based on projected emissions by Census district for 2015. These show only small changes in wet deposition, increases in SO_2 and NO_2 concentrations in south-west Alberta, and decreases in SO_2 concentrations in central Alberta.

TABLE OF CONTENTS

LIST OF FIGURES

1.0 MONITORING NETWORKS – BACKGROUND AND PHILOSOPHY

Most air quality monitoring networks have been established in response to a real or perceived environmental threat to the human population or to the natural environment, rather than from a desire to characterise atmospheric composition or deposition as an academic exercise. Historically, both human health and vegetation were major drivers for the establishment of monitoring in the cities of Britain (and elsewhere in Europe) during the latter part of the 19th century. The work of Robert Angus Smith (Smith, 1872) as the 'father' of 'acid rain' has been documented, in terms of the measurements he established to investigate the effects of industrial emissions on air quality in the industrial towns of Britain. However, even a century ago there were detailed measurements of air quality effects on vegetation (Crowther and Ruston, 1911; Russell and Richards, 1919) which relied on making measurements of air concentrations and rainfall composition. Early 'networks' for air quality monitoring were established to investigate obvious problems of smoke and sulphur dioxide, which were clearly related to burning coal or other related industrial and domestic activity and were focussed on cities and human health, but, particularly in Germany, interest was also being expressed in direct effects of air pollution (especially smoke and sulphur dioxide) on forests (Rhine, 1924; Härtel, 1953). In the UK a National Network for smoke and sulphur dioxide was established in 1961 (http://www.airquality.co.uk/archive/monitoring_networks.php?n=history).

Measurements of precipitation quality on a regional scale in the 1950s (Gorham, 1958) picked up RA Smith's early interest in the UK, but were specifically related to ecological effects on the environment, rather than human health, and it was not for almost another decade that a national-scale effort was made in the UK to measure rainfall composition (Stevenson, 1968). At the same time, a major monitoring network for rainfall composition was established across north-western Europe (the European Air Chemistry Network) and provided information for Sweden's case to the United Nations, that Britain's 'acid rain' was causing serious problems to freshwaters in Scandinavia (Sweden, 1971). The acceptance of long-range transport as a reality (Smith and Hunt, 1978) brought with it a realisation that 'invisible' air pollution in precipitation could also have harmful consequences, and needed to be monitored in order to evaluate environmental risks on regional and international scales.

Precipitation monitoring networks were established in northern Britain (Fowler et al., 1982), in Europe (OECD, 1977) and in the United States (Hales, 1982) in the late 1970s. The Convention on Long-range Transboundary Air Pollution (LRTAP) of the UNECE (United Nations Economic Commission for Europe), signed in 1979, established a broad framework for cooperative action on reducing the impact of air pollution and set up a process for negotiating concrete measures to control emissions of air pollutants through legally binding protocols. As part of this process, the EMEP programme (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe) (www.emep.int) was set up to regularly provide Governments and subsidiary bodies under the LRTAP Convention with qualified scientific information to support the development and further evaluation of the international protocols on emission reductions negotiated within the Convention. The role of EMEP can be summarised as follows (http://www.emep.int/):

"Initially, the EMEP programme focused on assessing the transboundary transport of acidification and eutrophication; later, the scope of the programme has widened to address the formation of ground level ozone and, more recently, of persistent organic pollutants (POPs), heavy metals and particulate matter.
The EMEP programme relies on three main elements: (1) collection of emission data, (2) measurements of air and precipitation quality and (3) modelling of atmospheric transport and deposition of air pollution. Through the combination of these three elements, EMEP fulfils its required assessment and regularly reports on emissions, concentrations and/or depositions of air pollutants, the quantity and significance of transboundary fluxes and related exceedances to critical loads and threshold levels. The combination of these components also provides a good basis for the evaluation and qualification of the EMEP estimates.
The EMEP programme is carried out in collaboration with a broad network of scientists and national experts that contribute to the systematic collection, analysis and reporting of emission data, measurement data and integrated assessment results. Four different Task Forces within EMEP provide for discussion and scientific exchange. These are: the task force on measurements and modelling (TFMM), the task force on emission inventories and projections (TFEIP) , the task force on integrated assessment modelling (TFIAM) and Task Force on Hemispheric Transport of Air Pollutants (TFHTAP)."

The role of air quality monitoring networks has progressed a long way from concerns over the effects of air quality on human health in obviously polluted cities, or on vegetation close to significant point sources. Consequently, networks have been established to satisfy many different concerns. For example, in the UK alone there are 4 automatic networks (for gases and particles) and 11 non-automatic networks that have operated, or are in current operation. Each of these has evolved (and continues to evolve), although the reasons for establishing these networks were very different. There is now an appreciation for the need to move towards a more integrated approach, if only on grounds of logistics and cost. However, there will always be problems in any attempts to rationalise networks – the spatial and temporal scales at which measurements need to be made vary depending on the pollutant and the reason for making the measurements. If human health is the issue, then measurements need to be made where people live, and of pollutants that are known or suspected as posing a risk to health. The issue of 'episodes' as opposed to chronic exposure may also need to be addressed. At the other end of the scale, effects on vegetation may be restricted to regions where the underlying geology cannot neutralise acid deposition, or where nutrient supply is naturally low, and the chronic effects on soils, freshwater and vegetation require knowledge of the cumulative annual loading in regions remote from human settlements. Spatial issues are more concerned with the nature of the pollutant; close to sources, high spatial resolution may be required to establish exposure (e.g., NO_2 in cities, or NH_3 in rural areas) whereas precipitation composition and ozone concentrations vary more slowly across a region.

Monitoring networks for air quality can therefore be established for a range of different reasons, not all of which are mutually compatible, because they operate on different temporal and spatial scales. In general, monitoring networks are established to satisfy one or more of the following requirements:

- Establishing spatial and temporal characteristics of air quality (and deposition) so that risk can be evaluated, and mitigating action identified

- Evaluating computer models that link emissions, transport, conversion and deposition of air pollutants, so that scenarios can be tested, and so that estimates of exposure can be made where measurements are not possible (for logistic or economic reasons)
- Evaluating compliance with regulations on human exposure or environmental loads
- Evaluating the efficacy of mitigation activities or the effects of changes in emission patterns
- Public information on air quality, both in forecasting mode and retrospectively
- As input to epidemiological studies on health effects, for both humans and the environment

The evolution of networks over time reflects the acquisition of knowledge (e.g., the apparent temporal stability of spatial patterns) and the requirements changing, particularly in the case where emissions and concentrations are decreasing. A recent review (http://www.airquality.co.uk/archive/reports/cat16/0604041119_UK_urban_network_review_summary.pdf) of some of the longest-running networks in the UK (the Black Smoke/SO_2 network started in 1961, and the NO_2 network) illustrates some of these processes. The number of sites in the Black Smoke/SO_2 network has varied over the years, with a maximum of 68 in 1986. As concentrations have fallen in all urban areas from their peak values, the requirement for maintaining the network has changed from a focus looking at spatial patterns (identifying areas with high exposure), to long-term trends and continued monitoring of 'hot spots'. An additional problem is that the methods originally designed for measurements in the 1960s are no longer appropriate for the much lower concentrations observed today. The recommendations, which have been adopted in the UK, were (http://www.airquality.co.uk/archive/reports/cat05/0706141352_2006_Annual_Report_final.pdf):

1. *That up to 20 sites be retained using existing methods, as the method still has sufficient sensitivity for black smoke measurements. These sites should primarily be in the coal burning areas of the UK.*
2. *As many existing Black Smoke measurement sites are not ideally located for epidemiological studies, some of the sites should be relocated to AURN* [Automated Urban and Rural Network] *locations, which are located to represent general urban background exposure.*
3. *To equip some AURN sites with higher quality Black Smoke measurement systems (e.g., aethalometers) and as an option, to consider the use of two channel instruments to provide an indication of the contribution of local diesel contributions to the black smoke concentrations.*

Note the retention of sites to measure long-term trends, the specific relevance to human health (rather than areas of high concentration) and the move towards improved techniques which also are adapted to a change in emission source (from coal to diesel exhaust). Moreover, the repeal of a European Directive on SO_2 and suspended particulates (80/779/EEC) in 2005 removed any legal requirement for widespread monitoring across the UK.

For sulphur dioxide, the review recommended:

1. *Stopping these measurements, since in almost all areas of the UK, ambient SO_2 concentrations are smaller than the detection limit of the method and SO_2 is no longer a serious air quality issue in UK urban areas.*

2. *There are exceptions, notably in some parts of Northern Ireland and Northern England where some sites need to be maintained until ambient concentrations are no longer considered to be an issue. The monitoring at these sites is not considered to require central support from Defra* [UK Department of Environment, Food and Rural Affairs] *and Devolved Administrations* [Scotland, Wales and Northern Ireland].

Note here several principles: the removal of the general problem (changes in emissions), and the transfer of responsibility from central to local government in terms of continued monitoring activity close to particular 'problem' areas.

The recommendation for the NO_2 network (using passive samplers) was to cease operation as a national network, because the combination of automated samplers and computer modelling of NO_2 spatial distribution was now sufficient to characterise the UK spatial pattern. It was also recognised that the annual target concentration (40 $\mu g\ m^{-3}$) was more than adequate to protect the population on shorter time scales, thereby removing the requirement for detailed temporal data. However, the need for local authorities to monitor compliance with statutory limits and identify 'hot spots' in cities was recognised, and the following recommendations made:

1. *Using Defra and Devolved Administrations resources to encourage a common protocol in NO_2 measurement using Diffusion Tubes. For these measurements to be valuable, it is necessary to establish a standard operating method and demonstrate equivalence with a standard method.*
2. *The adoption of a standard protocol with traceability to a reference method would make the central collation of data useful for trend analysis and wider application of the data for assessment.*

Note here again the transfer from central to local government and the requirement for the inter-comparability and quality assurance of locally-generated data, so that the data could be combined at a national level if a subsequent need arose.

In terms of gases, where the major interest is in human health and compliance with UK and European Directives, the number of automated monitoring stations in the UK has increased from a handful in the late 1970s to around 130 in 2006, reporting hourly concentrations of a wide range of pollutants amounting to over 4 million data per annum, collated centrally (http://www.airquality.co.uk/archive/reports/cat05/0612111534-421_AirPollutionUK2005text.pdf).

For environmental protection, the history and evolution of the monitoring activity in the UK provides an illustrative example of the processes involved. The first measurements, as described above, were based on perceived problems with horticultural crops close to cities. The general nature of air pollution (i.e., an 'academic' interest) prompted the studies in the 1960s as a research exercise (Stevenson, 1968), although the interest may have been driven also by concerns arising in Scandinavia as to the role of UK pollution. Local monitoring by electricity generating companies was conducted from the mid 1970s (Martin and Barber, 1978). Regional concerns over acidification of soils and freshwaters prompted the operation of a wet deposition network in northern Britain (financed by central government) which provided the first large-scale measurements of rainfall acidity in the UK (Fowler et al., 1982). This network included 16 sites

for monthly sampling of bulk precipitation and identified some of the criteria for future monitoring networks across the UK: concentrations of pollutants in rain varied relatively slowly geographically; and wet deposition depended more on changes in precipitation amount, which was much more variable spatially. This network formed the core of the UK national network established in the early 1980s, established by the former UK Department of the Environment on the advice of the 'Acid Rain Review Group' (ARRG) which was comprised of government scientists, independent researchers, academics and the electricity generating industry. This group of stakeholders produced a series of reports through the 1980s and 1990s, with the latest (NEGTAP, 2001) all providing authoritative reviews of the state-of-the-science as well as reporting summary data.

The numbers of monitoring sites appropriate to address the problem was an early focus of interest – the fragmented nature of the monitoring in the early 1980s led to the production of maps with large blank areas – recognising the lack of data, and the dangers of interpolation and extrapolation into the unknown. Even by 1985 there was still very poor coverage across England and Wales. A network of 59 sites was established in 1986 as the UK 'secondary' network, following protocols defined by the ARRG, and providing spatial patterns across the whole UK at 2-weekly time resolution. In addition, 9 sites were established as a 'primary' network with daily sampling, to study episodes or events using wet-only samplers, at which some (rural) gas and particle measurements were also made. The two networks, though complementary and overlapping, served very different purposes: the 'primary' was aimed at understanding processes and testing transport models, whereas the 'secondary' provided the spatial information for evaluating environmental impacts. Both were established to maintain long-term time trends in composition. The use of 59 sites enabled geostatistical approaches to be taken in interpolating and extrapolating from the network to the whole country. Kriging was used to show not just the spatial patterns for annual concentrations, but also the uncertainties in these concentration estimates. For most of the UK the associated uncertainty was below 20%, but the use of kriging also identified regions with high uncertainty, where additional monitoring sites might be located, and areas of low uncertainty, where redundant sites could be closed or relocated. In 1988 the network was reviewed and the number of secondary network sites reduced from 59 to 32, which was recommended as the smallest number of sites that could provide a spatial map across the UK with acceptable interpolation errors (defined as 5-15 $\mu eq\ l^{-1}$) based on the kriging technique (Webster et al., 1991). The number of 'primary' sites was reduced at the same time from 9 to 5, retaining spatial coverage and sites with a long history. By 2001 there was only 1 primary site left, and 39 secondary sites, some additions having been made to close apparent gaps in the spatial network where interpolation estimates were unacceptably large.

At about the same time as the network was being refined (late 1980s) it was recognised that in complex terrain, estimates of wet deposition are complicated by the systematic changes in both rainfall composition and quantity with altitude. The incorporation of cloud water, as an 'orographic enhancement' of both rain amount and rain composition, has been the subject of intense research activity in the UK because the most sensitive ecological areas are also in upland areas of the UK (RGAR, 1997). The enhancement of both rain amount and rain concentrations was shown to lead to wet deposition in upland areas up to 2.5 times that in nearby (within 20 km) lowland areas. The problem of orographic enhancement has been modelled and is incorporated routinely into UK maps of wet deposition (Dore and Choularton, 1992), but is not used routinely

elsewhere. This may be because the UK, having mountainous areas next to the ocean, with prevailing south-westerly winds, is particularly affected by this type of wet deposition.

The use of a slowly-varying concentration field, multiplied by the much more spatially data-rich precipitation field, along with enhancements for orographic processes, forms the basis for the UK-wide mapping of wet deposition. This was originally done late in the 1980s on a 20 km grid, and is now on a 5 km grid with progress expected in 2008 to a 1 km grid across the country. These grid-based estimates do not provide exact predictions of deposition at any given site, because of small-scale variations in climate and possible local sources, but they do provide a statistical approach to estimating the exceedance of critical loads and levels – for example, the proportion of grid squares across the UK in which a particular critical load is exceeded.

Two other contrasting networks are worth highlighting because of their different approaches to sampling: the UK ammonia network and the UK nitric acid network. The ammonia network has around 90 sites across the UK for passive and active monitoring of air concentrations with monthly time resolution (http://www.cara.ceh.ac.uk/nh3network/index.html). Even this number of sampling sites is not sufficient to reproduce the local-scale variability of NH_3 concentrations in the landscape, but captures the main elements and allows studies to be made of temporal changes (e.g., in relation to changes in stock density during and after the recent foot-and-mouth outbreak in the UK). The data are used to validate a model based on emissions and transport, which can deliver high spatial resolution maps of annual average air concentrations. Higher site density is concentrated in areas where there is known to be high spatial variability and large sources (e.g., in the pig and poultry rearing regions of East Anglia). The nitric acid network (http://www.cara.ceh.ac.uk/hno3network/index.html) measures a range of gases and particles using denuders and filters on a monthly basis, and has recently been extended from 12 to 32 sites, many of which are co-located with secondary wet deposition monitoring sites. This network captures the more slowly-varying (spatially) concentrations of secondary pollutants (like nitric acid) and (water-soluble) particles across the country to give spatial and seasonal patterns.

At a European level, EMEP coordinates international monitoring effort across 59 countries (http://www.emep.int/publ/reports/2007/status_report_1_2007.pdf) but at a relatively small number of locations (e.g., around 100 for precipitation) with varied coverage across the region. The main purpose is to establish trans-boundary movement of air pollutants. Not all national sites formally submit data to EMEP, often because of different sampling and analytical protocols. Work has been active within TFMM (the Task Force on Monitoring and Modelling) to incorporate more of the existing monitoring activity, while not relaxing quality. There has been considerable recent discussion on the trade-off between temporal and spatial resolution. Some countries have a long history of daily measurements at a relatively small number of key sites, so have excellent data on long-term trends at sufficiently high temporal resolution to check against modelling activities, but poor spatial resolution. Other countries have large numbers of sites with weekly or longer time resolution, which provide good spatial data, but are less useful for checking against particular transport 'events'. Both types of sampling strategy have their place, and most countries cannot afford both – each state has tended to come to its own priorities over spatial or temporal resolution. Historically, high temporal and poor spatial resolution was more favoured, but increasingly, greater spatial resolution is also seen as important as modelling activities increase their spatial resolution from grids of 50 km to grids of 5 km or less.

On a more local scale, and particularly with reference to human health, issues of spatial heterogeneity have received much attention in urban monitoring, for particulate matter (PM), nitrogen oxides and ozone, all of which are seen as key pollutants in respect of human health effects. Good temporal resolution is also required for time-series epidemiological studies. For example, hospital admissions with heart or chest complaints are correlated against air quality in the preceding few days. These issues are dealt with more fully in Section 3. The following discussion divides the questions to be answered into Environmental Protection, Human Health, and Trans-boundary Issues. However, within each of these, both spatial and temporal scales have to be addressed.

2.0 NETWORKS RELEVANT TO ENVIRONMENTAL PROTECTION

A network established to satisfy the requirements for environmental protection at a Provincial scale should provide regional patterns of air quality and deposition and identify whether regional pollutant levels are approaching critical loads and levels. It also should provide background data for urban and local-area monitoring, so that the influence of cities, industries or local sources can be assessed. The overall objective is to identify areas with highest risks (in terms of potential environmental impacts) so that decisions can be made as to whether further, more detailed, monitoring is required to provide a more accurate estimate of the risk, and whether intervention is required to reduce the impacts.

2.1 Wet deposition – existing data

Wet deposition alone is unlikely to exceed critical loads in Alberta, based on current deposition rates, but makes a significant contribution to total deposition. Direct measurement of wet deposition comprises measurements of precipitation amount (rain and snow) and chemical composition. Based on the current data it appears that concentrations of pollutants in precipitation are relatively slowly-varying across Alberta; as in the U.K. and most of Europe, the largest spatial variability in wet deposition is determined by precipitation amount. Consequently, the best way to estimate wet deposition is to use the measured (and interpolated) concentration field (e.g., Figure 1a) together with the measured precipitation (available at many more sites, Figure 4) to predict the spatial pattern of wet deposition. Geostatistical methods such as kriging can be used to interpolate between measured data if the spatial network is sufficiently dense. This approach also provides estimates of uncertainty in the predicted interpolated values, so that areas of high uncertainty can be identified for 'gap-filling' a network to improve spatial coverage. The current network of 7 sites at which the chemical composition of precipitation is monitored in Alberta is barely adequate for spatial coverage, and not adequate for kriging the concentrations without having to make many assumptions. Consequently the associated uncertainty maps are themselves uncertain, but do give an indication of where gaps need to be filled. Examples are given in Figures 1-3.

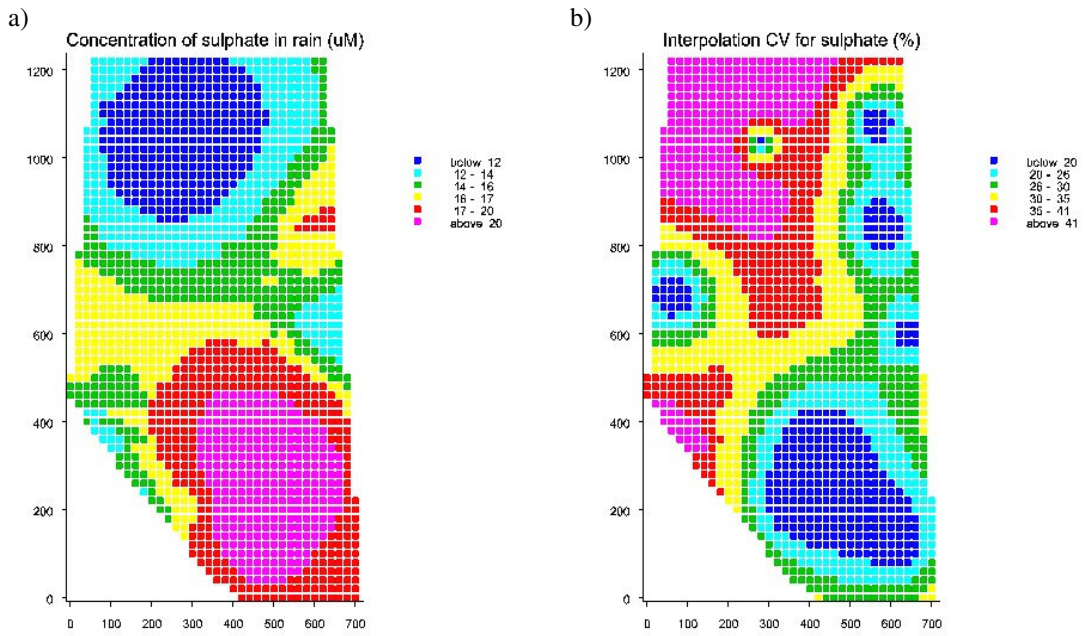

Figure 1 **a) Interpolated sulphate concentrations in precipitation from 7 wet deposition sites in Alberta for 2003-2006, using a simplified kriging approach**
b) Interpolation uncertainty (expressed as coefficient of variation in %); uncertainty is lower closer to measurement sites

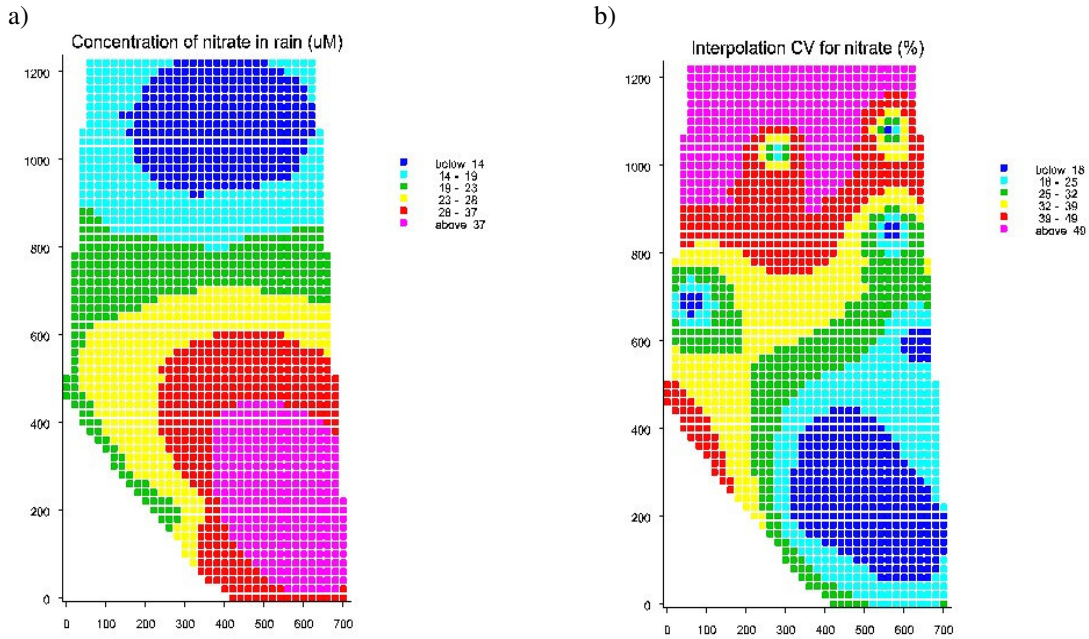

Figure 2 **a) Interpolated nitrate concentrations in precipitation from 7 wet deposition sites in Alberta for 2003-2006, using a simplified kriging approach**
b) Interpolation uncertainty (expressed as coefficient of variation in %); uncertainty is lower closer to measurement sites

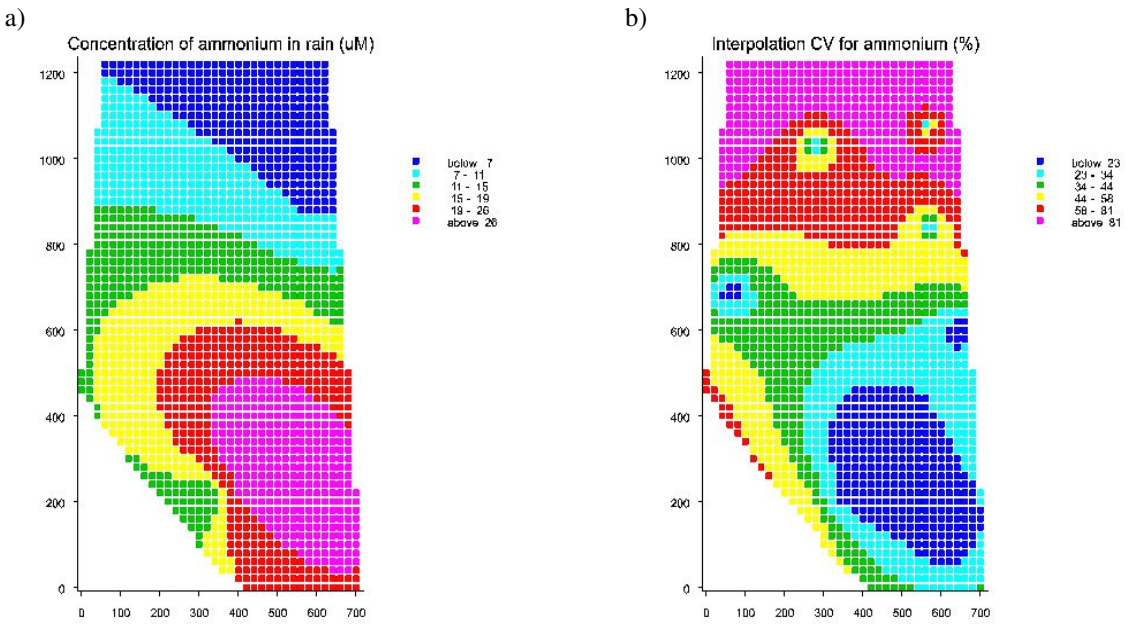

Figure 3 **a) Interpolated ammonium concentrations in precipitation from 7 wet deposition sites in Alberta for 2003-2006, using a simplified kriging approach b) Interpolation uncertainty (expressed as coefficient of variation in %); uncertainty is lower closer to measurement sites**

We have calculated the annual mean precipitation across Alberta from the annual climatic mean precipitation data for 1961-1990 from the Environment Canada website (http://climate.weatheroffice.ec.gc.ca/climate_normals/results_1961_1990_e.html?province=AB&stationID=307&stationName=&searchType=). The interpolated long-term average precipitation field for 1961-1990 for the 98 sites at 20 km grid scale is shown in Figure 4. The precipitation map shows the variation across the province of the 30-year mean, demonstrating the spatial complexity, linked to elevation, and a range of about a factor of 2. The kriging of this data set was relatively straightforward, given the large number of data points available, so that grid-based uncertainties can also be produced.

Combining the concentration and precipitation maps provides an estimate of wet deposition using the best available data and interpolation methods (Figures 5-8). A comparison of the simple interpolation of wet deposited ammonium, using the measured deposition data rather than concentration data at the 7 sites, is shown in Figure 9.

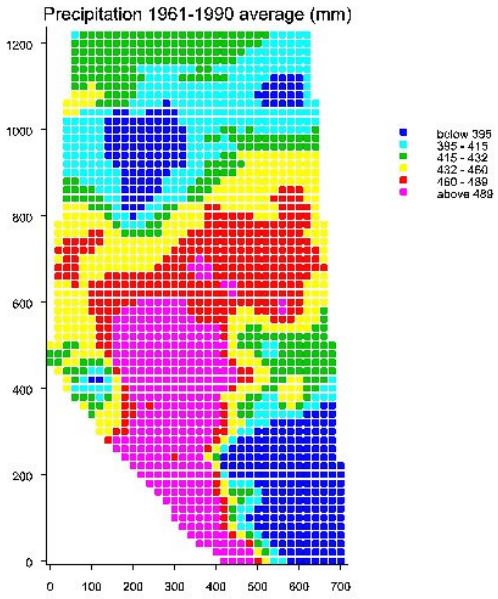

Figure 4 Interpolated precipitation amount across Alberta

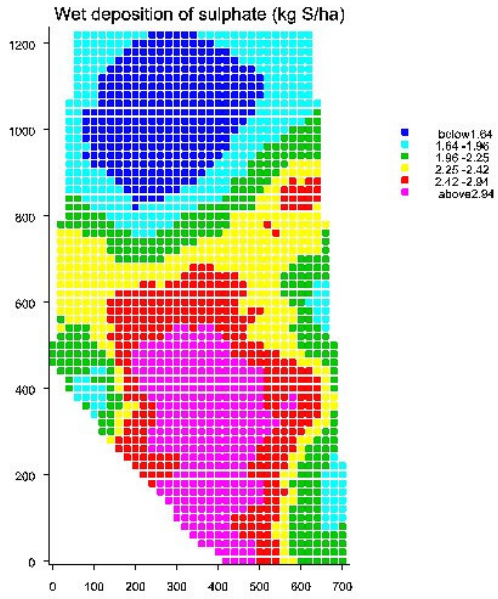

Figure 5 Interpolated wet deposition of sulphate over Alberta

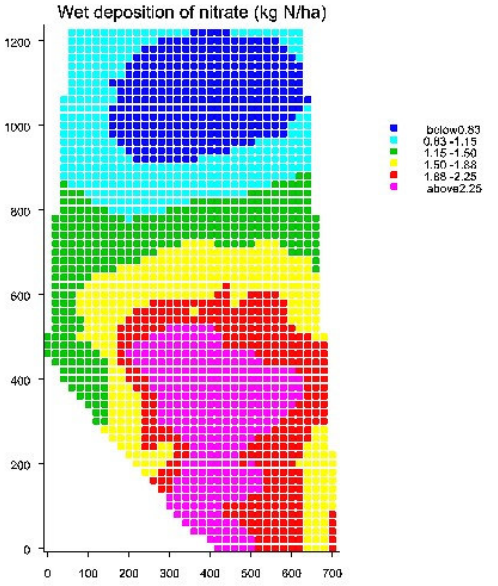

Figure 6 Interpolated wet deposition of nitrate over Alberta

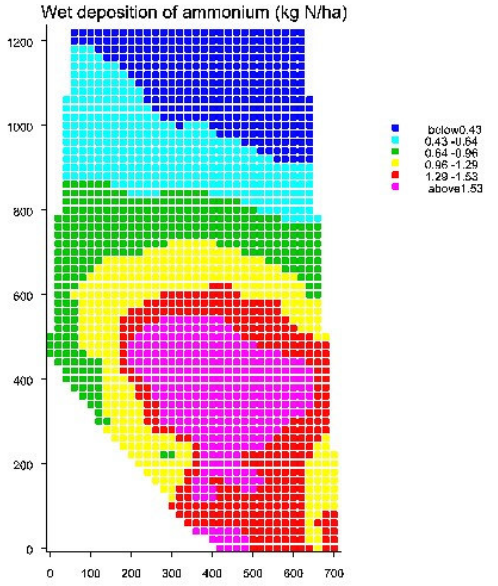

Figure 7 Interpolated wet deposition of ammonium over Alberta

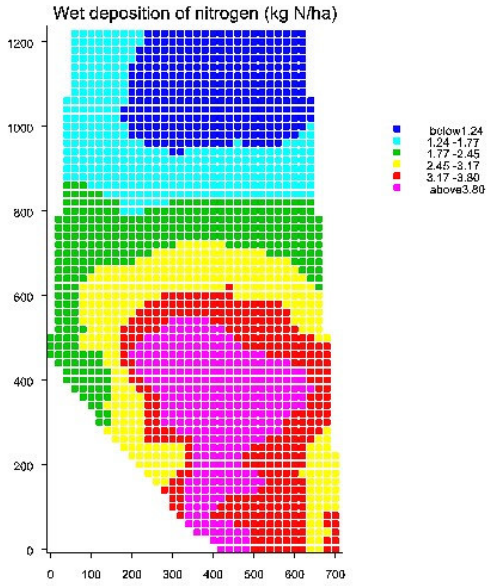

Figure 8 Interpolated we deposition of total inorganic N over Alberta

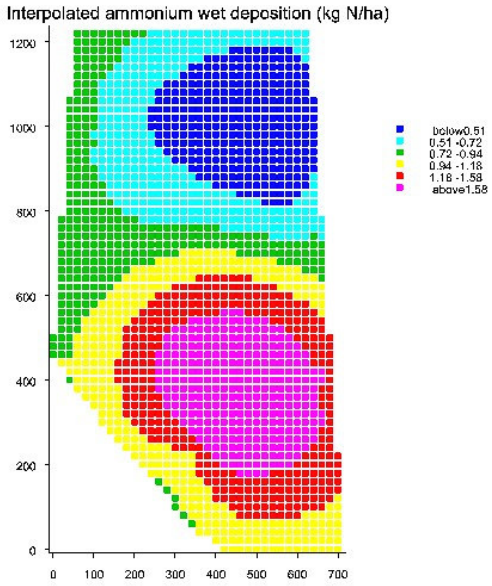

Figure 9 Alternative interpolated deposition of ammonium; interpolating deposition across only 7 sites (cf. Figure 7)

2.2 Wet deposition - recommendations

The uncertainty maps (Figures 1b-3b) show where the areas of greatest uncertainty exist, and on this basis **we recommend:**

1) At least one more site in central Alberta (in the region of Slave Lake), with additional sites in SW Alberta (Banff, Jasper foothills) and northern Alberta (3-4 sites to provide better spatial coverage, although concentrations here are small). This implies an approximate doubling of the existing network of 9 sites.
2) One of the key uncertainties is the spatial pattern of precipitation amount, particularly in the foothills of the Rockies in SW Alberta, and additional data or modelled amounts would reduce uncertainties here.
3) Given the apparent strong north-south gradient in both precipitation amount and concentrations of ions, a short-term (i.e., 3-5 year) study of gradients north-south and east-west would provide confirmation of the pattern across the province. This would entail another 16-20 sites, with the east-west transect bisecting the Calgary- Edmonton corridor and the north-south transect along the Calgary-Edmonton corridor.
4) Using data from neighbouring Provinces to establish the spatial patterns, particularly in the case of Saskatchewan, where interpolation uncertainties may be less than in the more complex terrain of British Columbia to the west.
5) The interpolation uncertainties should be evaluated regularly, and if necessary, new sites established where large uncertainties exist. Patterns will change with time as new emission sources are established, and old ones close. In areas of low uncertainty,

redundant sites may be closed. Maps with and without potentially redundant sites can be generated to establish the additional uncertainty caused if a particular site is to be closed.

2.3 Wet deposition - site selection and monitoring methods

Sites should ideally be more than 20 km from major point sources, and situated in rural districts away from areas of bare soil, ideally over grass or short vegetation. Existing sites that do not satisfy these criteria should be considered for movement, or a new site established in the same region to check for evidence of point-source influence, running both sites in parallel for at least one year to check for systematic influences of site location. If these can be shown to be small (i.e., exact site location is not affecting the sample) then maintaining a historical record for a long-standing site should be preferred over site relocation.

Wet deposition in urban areas is unlikely to be an issue for environmental protection, but it may be helpful to establish whether industrial and urban areas affect the regional pattern defined by the network of rural samplers, and it may be appropriate to establish several short-term monitoring sites for wet deposition (for example, in urban parks) to investigate the magnitude of the effects of urban areas on wet deposition.

Bulk deposition on a weekly or two-weekly basis is adequate for characterising annual deposition in rural areas but may not be particularly useful for validating chemistry/transport modelling of 'events', which require daily sampling. Particular care should be taken over local siting protocols, and sampling of snow, for which protocols are already in place. Care should be taken to site samplers where birds will not cause contamination problems – 'distractors' may be required. The use of biocides (e.g., thymol) may improve estimates of N deposition, but adds to the complexity of sample handling. The simplest way of operating remote sites is for sample volume to be weighed by the local site operator and a small sub-sample of water shipped to a central laboratory for analysis.

'Wet-only' samplers are often used, to minimise bias caused by dry deposition of material to the surfaces of 'bulk' collectors, which are always open. The contribution of dry deposition is likely to be relatively small in remote rural areas (Cape and Leith, 2002), but particularly in regions with high ammonia concentrations it would be prudent to install one or more wet-only samplers alongside the bulk samplers to investigate the potential bias arising from the use of bulk samplers. This would require sites with electrical power available; parallel monitoring need not continue beyond 3-5 years, once any bias had been quantified.

Resin samplers (Simkin et al., 2004) may be useful in providing spatial coverage, because they can be operated over several months. They work by allowing bulk precipitation to pass through a mixed-bed ion exchange resin either to a (calibrated) bucket for estimating sample volume, or through a recording tipping-bucket rain gauge and data-logger. The exposed resin is shipped to the laboratory for extraction and chemical analysis at the end of the sampling period. Although attractive in principle, there is a high risk of sample contamination from birds, and a question over sample stability especially in summer. Snow is also an obvious problem. To reduce the risk of contamination, triplicate samplers may be used, but this obviates the benefit in terms of

numbers of samples to be analysed, although it does reduce the need to visit (remote) sites every 2-4 weeks.

Post-analysis quality control of data to detect contamination from birds or other sources (e.g., biomass burning) is necessary; phosphate and potassium analyses are helpful here, and should be included in the suite of analytes measured.

There are additional uncertainties in wet deposition loading arising from the deposition during winter as snow, which only finds its way into soils and watercourses at the end of the winter, often in more concentrated form than in the original precipitation. The percent of total precipitation that falls as snow may therefore be an important contributory factor that warrants further research. Figure 10 shows the map of percent of precipitation falling as snow, based on climatic (1961-1990) data from 98 sites in Alberta.

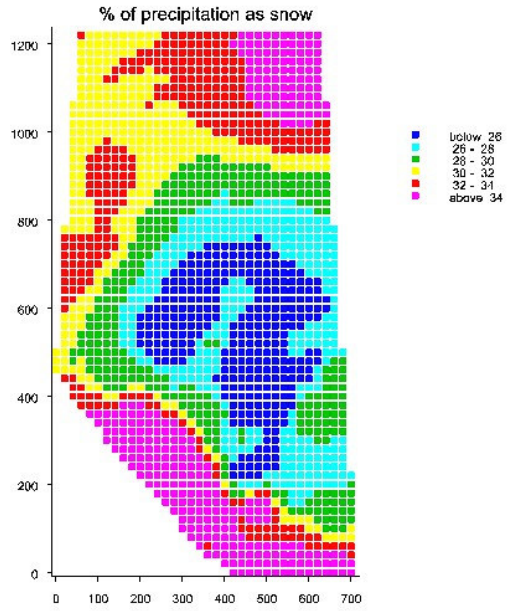

Figure 10 Percentage of annual precipitation falling as snow in Alberta, based on averages from 1961-1990 at 98 sites

2.4 Dry deposition - background

Dry deposition may make a significant input to acid deposition in some regions, and is currently poorly estimated because of lack of data. Inferential methods are likely to be the main route towards dry deposition estimates, rather than direct measurements, because of the time involved in processing flux measurement data. For many gases and particles, especially in rural areas away from point sources, air concentrations have little spatial variability. However, the processes which control dry deposition may vary greatly over very short distances (e.g., at the edge of a forest (Beier, 1991; Lindberg and Owens, 1993; Neal et al., 1994)). This is recognised when estimating deposition to an area, region or country by the use of land use data and other

meteorological data which are important to the deposition process, such as wind speed. Maps of dry deposition may be created for particular land use types (e.g., grassland or forest) or the fractions of different land use in a grid square may be used to estimate total dry deposition to a particular grid square. Such models of deposition, usually based on a simple parametric inferential method (e.g., Brook et al., 1999), can provide from an interpolated concentration field, estimates of dry deposition to different features of the landscape which can be integrated into whole catchment (watershed) deposition or national budgets (Smith et al., 2000; NEGTAP, 2001). When modeling close to sources, such methods fail because the spatial variability in air concentrations is high, and there may be strong correlations between meteorological variables and air concentrations that make estimates based on time-averaged data unreliable; for example, air concentrations decrease as wind speed increases. Both are important in determining rates of dry deposition.

2.5 Dry deposition - review of existing data

The available (sparse) data from Alberta suggest that dry deposition of NH_3, NO_2 and HNO_3 are of similar importance. The much smaller concentrations of HNO_3 and NH_3 than of NO_2 are offset by much greater rates of deposition. Where measurements have been made, for example at Beaverlodge (Aklilu, 1999), the contribution to N deposition from HNO_3 and NH_3 was 0.4 and 1.2 kg N $ha^{-1}y^{-1}$ respectively. No estimate was made of the contribution from NO_2, but measured annual average concentrations of around 4 ppb suggest dry deposition rates of around 5 kg N $ha^{-1}y^{-1}$, based on a deposition velocity of 2 mm s^{-1}. However, this deposition velocity is based on European data and may be too high, since uptake of NO_2 is primarily through stomata and only occurs when plants are active (i.e., not in winter). The estimated contributions to dry deposition of acidity in the report were 30, 80 and 30 g $ha^{-1}y^{-1}$ for HNO_3, NH_3 and NO_x respectively, making NH_3 the most important contributor. The deposition rates from Royal Park (Bates, 1996) suggest 0.7 and 2.1 kg N $ha^{-1}y^{-1}$ for HNO_3 and NH_3 respectively, but there do not appear to be data for NO_2. The median deposition velocities were similar for NH_3 and HNO_3 at both sites, although deposition velocities for SO_2 were approximately twice as high at Royal Park than at Beaverlodge. At Beaverlodge the molar ratio of NO_2:HNO_3 was around 36, about 3 times larger than across the UK, where the measurement networks indicate a fairly uniform ratio of around 12. It might be expected that the ratio in Alberta would be lower than in the UK, given the drier climate and higher sunshine levels, which would reduce removal rates of HNO_3 by wet deposition and increase HNO_3 formation rates. It could be that the site at Beaverlodge is influenced by local sources of NO_x that bias the ratio. Passive samplers from the Peace Airshed Zone suggest that annual average regional NO_2 concentrations are <2 ppb. More data are needed from other sites. Air concentrations of NH_3 were 0.4 – 1 μg m^{-3}, and of HNO_3 were 0.4 – 0.7 μg m^{-3} at these sites. Data from other NH_3 monitoring sites in Alberta (source: CASA Data Warehouse. www.casadata.org) suggest air concentrations (annual average) in the range 0.1 (Range Road) to 9 (Lethbridge, Station 401) μg NH_3 m^{-3}, with one site (Redwater) up to 18 μg m^{-3}. This last site concentration would give annual N dry deposition of 40 kg N $ha^{-1}y^{-1}$ if the deposition velocities measured at Beaverlodge and Royal Park were applied to that site.

In conclusion, there are few available data for most gases and particles, especially in areas where dry deposition may be important, or for gases such as NH_3 whose role in total N deposition is

poorly known. Gas concentrations of NH_3 and HNO_3 are poorly represented in the current monitoring networks, and even for gases such as SO_2 there are few data in remote rural areas.

The available data from the sites that are not obviously affected by proximity to highways, local industrial sources or urban areas have been used to identify regions of priority for the installation of new sampling sites, based on kriged interpolations using a simple linear model. The results are shown in Figures 11-14. Although the patterns are not as similar as the constituents of wet deposition, the same general areas of priority are apparent.

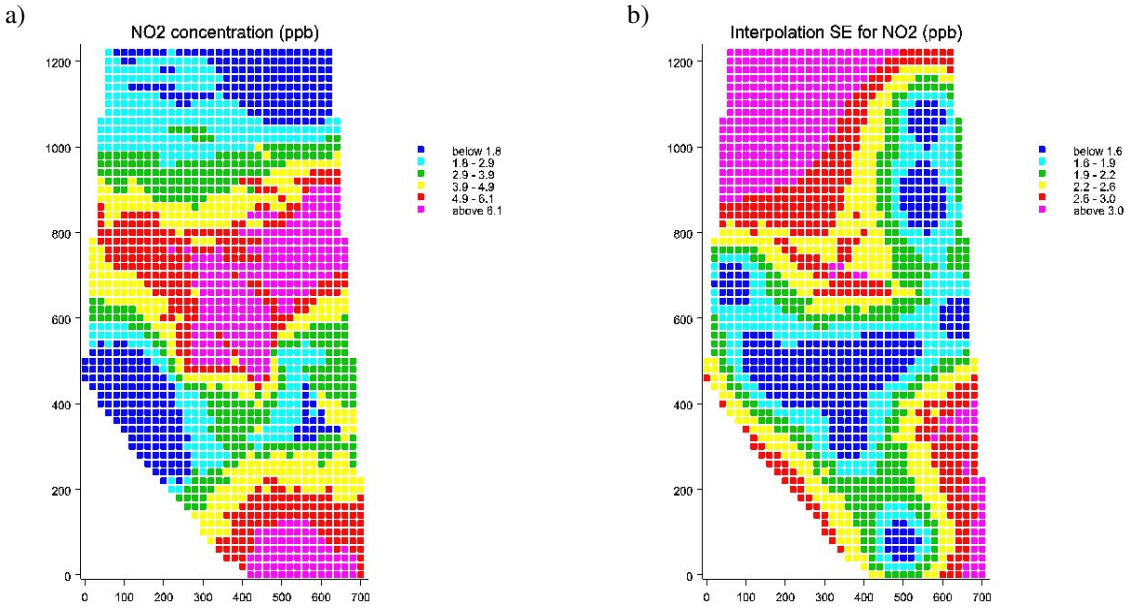

Figure 11 **a) NO_2 concentrations across Alberta based on rural monitoring data 2003-2006 (omitting sites influenced by highways, industrial sources or urban areas) b) Interpolation standard error, representing areas of highest priority for further measurements (product of concentration and uncertainty)**

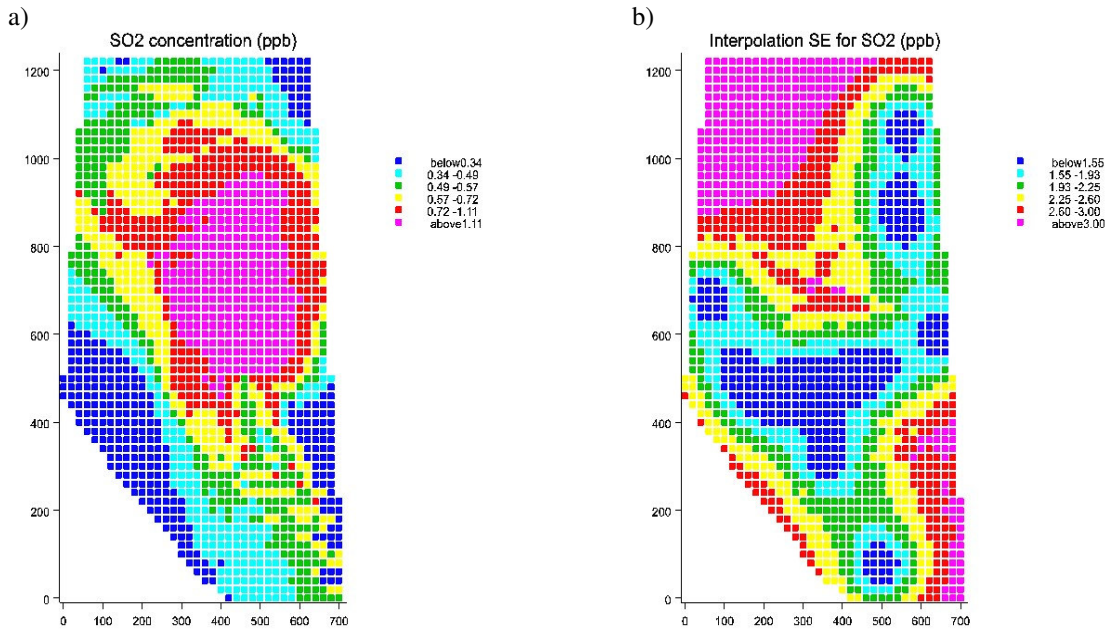

Figure 12 **a) SO_2 concentrations across Alberta based on rural monitoring data 2003-2006 (omitting sites influenced by highways, industrial sources or urban areas) b) Interpolation standard error, representing areas of highest priority for further measurements (product of concentration and uncertainty)**

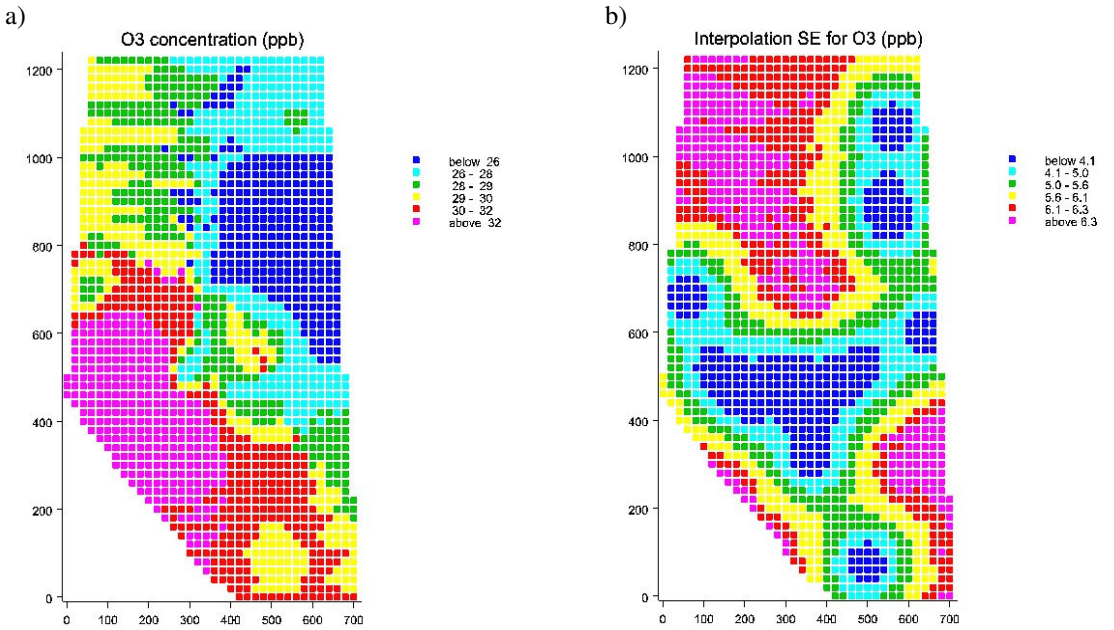

Figure 13 **a) O_3 concentrations across Alberta based on rural monitoring data 2003-2006 (omitting sites influenced by highways, industrial sources or urban areas) b) Interpolation standard error, representing areas of highest priority for further measurements (product of concentration and uncertainty)**

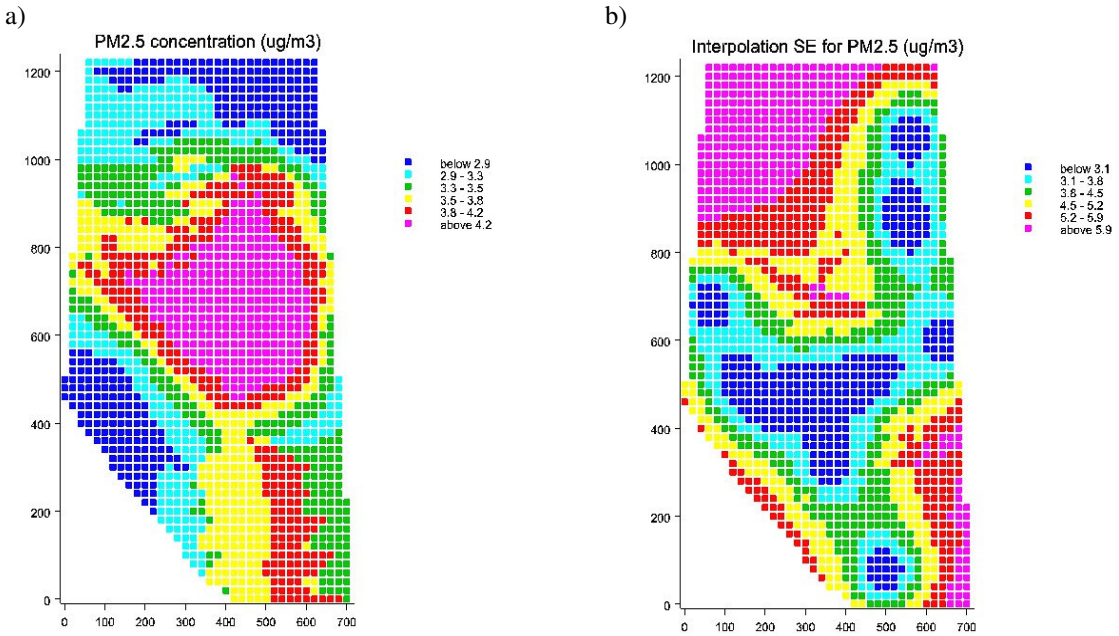

Figure 14 **a) $PM_{2.5}$ concentrations across Alberta based on rural monitoring data 2003-2006 (omitting sites influenced by highways, industrial sources or urban areas) b) Interpolation standard error, representing areas of highest priority for further measurements (product of concentration and uncertainty)**

2.6 Dry deposition - monitoring methods

Dry deposition can be estimated using a variety of methods, outlined below in order of increasing complexity and cost.

Simple inferential: average air concentrations of the pollutant concerned (g m^{-3}) are used in conjunction with average deposition velocities (m s^{-1}) to calculate the flux (g m^{-2} s^{-1}). Deposition velocities can be parameterised in terms of vegetation type (height) or surface roughness and average wind speeds, as a surrogate for turbulence, and can vary monthly to take account of seasonal patterns of wind speed and ground cover (seasonal vegetation changes or snow).

Inferential/meteorology: as above, but using actual measured wind speeds at the site rather than interpolated or regional measurements in order to convert concentrations to fluxes. A more complex (but more expensive) technique would use a sonic anemometer to measure turbulence characteristics directly, rather than simply wind speeds.

Integrating micrometeorological techniques: measurement of long-term average (week-month) vertical gradients in air concentrations controlled by a sonic anemometer so that only appropriate atmospheric conditions are sampled. This provides a direct measurement of material fluxes, rather than relying on parameterisations of deposition velocities. It is an established technique for short vegetation but untested over forests, and requires significant input in data analysis and interpretation.

Real-time micrometeorological techniques: these can involve continuous gradient measurements or eddy covariance, depending on the gas/aerosol of interest. These methods, while providing good data to underpin the understanding and modelling of deposition processes, as well as real-time deposition measurements, require specialist staff operating on-site, and complex evaluation of the data. At the moment this approach is more research-based than routine for monitoring purposes.

As an initial approach the simple inferential method (with appropriate parameterisations of deposition velocities for Albertan vegetation and/or climate) could be used, with perhaps some research using the more complex micrometeorological techniques.

2.7 Dry deposition – recommendations

We recommend:

1) That low-cost denuder/filter samplers be set up at each of the wet deposition network sites, which should already satisfy appropriate siting criteria. The CEH DELTA system or similar would be appropriate, to give air concentrations on a two-weekly/monthly basis for SO_2, HNO_3, NH_3, and particulate nitrate, ammonium and sulphate.
2) In addition, at these sites, passive diffusion monitors for NO_2 and O_3 should be installed.
3) If full denuder/filter systems are not installed, we recommend that as a minimum, passive diffusion samplers for NH_3 and HNO_3 be used instead. The network could comprise a mixture of active and passive samplers, with some co-location to provide cross-calibration of the techniques (cf. UK ammonia network)

4) A better but costlier alternative to passive sampling for O_3 would be a battery-powered UV ozone analyzer/data logger that could be supplied from a similar wind/solar-powered generator. This would provide data on peak concentrations measured during ozone 'episodes' which are likely to be important for direct effects on vegetation.
5) Temporary (3-5 year) installations at the E-W and N-S transect sites of the wet deposition network would also provide useful information on spatial patterns.
6) An annual study using passive samplers of the variation of O_3 concentrations with altitude in several regions of Alberta. Studies elsewhere have shown a strong relationship between altitude and average O_3 concentrations. If this also applied in Alberta, altitude could be used as a predictive variable for interpolative modelling of regional O_3 concentrations.

The active denuder systems would require electrical power (ca. 30 W) which can be supplied by a small wind turbine/solar cells if electricity is not available.

Such an installation does not include any measurement of PM, which in general requires higher power availability for active air sampling. However, the main risk from PM is to human (and animal) health, and these sites are in rural areas, away from human populations. Too little is known about the effects of PM on animal health to make monitoring useful at this stage. PM data in rural areas may become available from trans-boundary studies (see below).

Although not a direct influence on environmental or human health in rural areas, PM concentrations do affect visibility, and could influence tourism and recreational enjoyment of the countryside. There is a well-established network of visibility measurements in the USA (Malm et al., 1994), and it might be worth considering a similar investment. Alternatively, measurements of PM at existing or new monitoring sites where power is available would permit a better estimate to be made of regional PM concentrations, which in turn could be related to changes in visibility through empirical modelling.

3.0 NETWORKS RELEVANT TO HUMAN HEALTH

3.1 Background

The major concern over human health impacts is focussed on urban areas, although there may be occasions, for example during wild fires, when rural areas are also exposed to high concentrations of respirable particulates ($PM_{2.5}$). Regions downwind of major conurbations or industrial areas may also experience elevated PM concentrations, but given the human population distribution in Alberta, monitoring activity should be concentrated in areas with low air quality and high population density.

In urban areas the main air pollutants relevant to human health issues are particulate matter (especially the respirable fraction, $PM_{2.5}$), ozone (O_3) and nitrogen dioxide (NO_2), although there may also be local concern over heavy metals. The Air Quality Objectives for Alberta for these pollutants are shown in Table 1. Current patterns of exceedance of these criteria show that ozone and $PM_{2.5}$ are the main pollutants of concern. Although it should be noted that the Air Quality Objectives for NO_2 are less stringent than those applied in Europe to protect human health where limit values, to be achieved by 2010, are set at 40 μg m^{-3} (ca. 0.020 ppm) as an annual mean or 200 μg m^{-3} (ca. 0.10 ppm) as an hourly mean not to be exceeded more than 18 times per year. Although ozone concentrations in Albertan cities rarely exceeded the limits in 2006, the contribution of ozone to the overall Air Quality Index was greater than the contribution of $PM_{2.5}$ concentrations.

Alberta Air Quality Objectives for key urban pollutants relevant to human health.

Air pollutant	Annual average concentration	Daily average concentration	Hourly average concentration
$PM_{2.5}$		30 μg m^{-3}	80 μg m^{-3}
Ozone			0.082 ppm
Nitrogen dioxide	0.032 ppm	0.106 ppm	0.212 ppm

The potential risk to human health is measured in terms of exposure to air concentrations, as hourly, daily or annual averages. In the context of this review, the links between air concentrations and effects are not considered further, on the understanding that the Air Quality Objectives have been set in relation to the best available evidence from epidemiological studies. Therefore, the problem is to estimate how many sampling locations are required to define the air concentrations to which the population is exposed. Both temporal and spatial variability need to be addressed.

3.2 Particulate Matter (PM)

Particulate Matter, especially in the respirable fraction with diameter below 2.5 μm, has both long-range and local sources, and so concentrations are difficult to predict. Some of the PM is produced from resuspension of material on the ground (dust) and includes soil-derived and

vegetable matter, as well as heavy metals and organics that are deposited in and near highways from passing vehicles. However, much of the PM that is of relevance to human health is either produced directly from combustion processes (biomass burning, wood fires, incinerators, furnaces or motor vehicles) or is formed in the atmosphere by the oxidation of gaseous pollutants such as VOCs, SO_2 and NO_x, in combination with NH_3. The latter 'secondary' particulate is formed relatively slowly (tens of minutes to hours) so tends to have a regional pattern of distribution rather than being strongly influenced by local sources. The former, directly emitted, is much more variable in time and space, and air concentrations are greatly influenced by local topography and weather. In urban and built-up areas, it is the sum of all 3 sources (resuspended, secondary and primary) that constitutes the measured PM.

Many monitoring studies have compared measurements made within urban areas in terms of spatial and temporal homogeneity, and the results show no consistency across different cities. The available data on particulate matter were reviewed recently (Wilson et al., 2005), and included 33 published studies. Of these studies, 16 showed 'uniformity' (defined as variation across sites, within cities, of less than 20%) for $PM_{2.5}$, and 17 showed more heterogeneous distributions.

Several conclusions were drawn:

- Temporal correlations were often very good for $PM_{2.5}$ even though absolute concentrations may have varied more widely – such consistent temporal variation may be of use for time-series epidemiological studies, but is less useful where cohort studies need long-term average concentrations as measures of exposure.
- Absolute concentrations were less variable across cities for longer averaging times, and for different statistics. For example, mean or median concentrations were much more uniform than hourly maximum concentrations.
- Concentrations of PM_{10} were more variable than $PM_{2.5}$, attributed to greater spatial variability in the 'coarse' fraction (particles with diameters between 2.5 and 10 μm) derived from local sources.
- Variability tended to be greater in cities with high absolute PM concentrations
- Variability is linked to local topography, land use, location within a city and the siting criteria for monitoring equipment
- The local environment may be more important than the regional air mass for some locations.

A study in the United States of the variability in urban $PM_{2.5}$ concentrations across 27 urban areas (Pinto et al., 2004) showed that intra-urban variability in absolute concentrations was smaller for central and eastern cities than for cities in the west, and also noted that a high temporal correlation across sites within a city did not necessarily imply uniformity of concentrations. An earlier review, not confined to particulate matter (Monn, 2001), came to many of the same conclusions, and also drew attention to the much greater heterogeneity of ultrafine particles ($PM_{0.1}$) than $PM_{2.5}$, a feature confirmed in more recent European data (Puustinen et al., 2007). This review considered in some detail the relationship between human exposure and air concentration measurements, and discussed the interaction between temporal averaging scales and spatial variation, ranking air pollutants in terms of their (long-term) spatial variability, ranging from nitric oxide (most variable) to PM_{10} (least variable). $PM_{2.5}$

concentrations were not included in the analysis, but would be expected to be less variable even than PM_{10}. It concluded that the spatial distribution of $PM_{2.5}$ is 'relatively uniform', and that a central monitoring location may be used to characterise an urban area provided it is not strongly influenced by emissions from diesel exhausts. By contrast, much more care is needed in siting a central monitor for NO_2, especially for summer conditions, and the author recommended the use of passive samplers to assess urban spatial variability. The local variation in ozone concentrations in cities is determined by primary emissions of nitric oxide (NO) from vehicle exhausts and domestic heating, because of the rapid reaction between NO and O_3 to give NO_2, but as a result, ozone concentrations in cities are generally smaller than in the surrounding rural area.

Several conclusions may be drawn from the above concerning monitoring air pollutants in urban areas in order to assess human exposure:

- Local geography and topography play an important role in terms of pollutant dispersion. Greater spatial variability is to be expected in areas of complex terrain, with hills and coasts (Grivas et al., 2004; Wilson et al., 2006).
- Good temporal and spatial correlations, and uniformity of concentrations, are seen where weather conditions are similar across an urban area and where PM concentrations are dictated by long-range transport of secondary particulates (i.e., advected from outside the urban area)
- Ultrafine particles and coarse particles have greater spatial and temporal variability than $PM_{2.5}$.
- Site selection criteria are all important if choosing a central 'representative' urban background location for monitoring.

There are several methods in the literature for selecting appropriate 'urban background' locations for monitoring, to avoid local influences from vehicles or point sources. Recent published criteria are:

> More than twice height away from nearest building,
> > 20m away from trees,
> 50-250m away from building sources (e.g., vents),
> > 50m away from busy roads (Wilson, et al., 2006)
>
> Not in a street canyon (unless < 1000 vehicles day^{-1})
> > 5m away from any road,
> > 50m away from road with > 10000 vehicles day^{-1}
> > 100m away from road with >25000 vehicles day^{-1}
> > 200m away from road with >70000 vehicles day^{-1}
> > 100m away from small point/area sources (Puustinen, et al., 2007)

The latest European Directive on Air Quality received its second reading in the European Parliament on 11 December 2007. The text is available at:

http://www.europarl.europa.eu/sides/getDoc.do?pubRef=-//EP//TEXT+TA+P6-TA-2007-0596+0+DOC+XML+V0//EN. Relevant material has been extracted and is shown in Appendix 1. Criteria are provided for both macro-siting of samplers, and micro-siting.

The criteria for statutory numbers of samplers used in Europe and applied to the cities of Alberta would result in one sampler per urban area for each of the key gases (NO_2, SO_2 etc.), one $PM_{2.5}$, one PM_{10}, and two (Calgary and Edmonton) or one (elsewhere) for ozone. The European criteria for sample numbers are therefore already exceeded in Alberta. However, these are statutory minima; many member states of the EU have much greater sampling densities for sampling O_3, NO_2 and PM. For example, in the UK there are currently 21 O_3 sites, 33 NO_2 sites and 12 PM_{10} sites (2 of which also measure $PM_{2.5}$) with hourly sampling in the Greater London urban area (population ca. 7.5 million).

Concentrations of PM across an urban area, particularly in the suburbs where people live (and this is likely to be true of the lower urban densities of Albertan cities), are highly correlated as long-term (weekly/monthly) averages, although quantitatively there are differences which appear to be relatively predictable (e.g., the consistent gradient in concentrations across Edmonton). Consequently, long-term average data can be gained from measurements made at a few 'representative' sites across the city, where 'representative' means that the influence of major local sources (industry or major roads) is kept as small as possible. However, this does not capture the high temporal variability, nor the high spatial variability that exists close to sources or in dense urban centres, such as street canyons.

As noted above, measurement of PM requires active sampling, which effectively means access to electricity and a secure site. Rules of thumb for density of such measurements can be gained from the EU monitoring strategy (see earlier draft document). It would appear that the current site density in the two major cities is adequate to characterise PM concentrations across the urban area. In terms of people's perception of how urban monitoring operates, it is perhaps unlikely that the existing fixed monitoring sites in Calgary and Edmonton could be closed, even though to some extent the information they provide is redundant and resources might be better deployed in investigating spatial patterns and 'hot spots' through the cities.

In urban areas where there is little spatial variability in pollutant concentrations, one of the reasons is likely to be that the air concentrations are determined by long-range transport of material from outside the urban area. In order to estimate the influence of a city's emissions on air quality, and therefore the local potential for emission control, it is useful to measure air concentrations of secondary pollutants such as O_3 and PM in the region surrounding the city. This approach is almost impossible with the dense population of most of Europe, but could be applied in Alberta using a transect of monitoring sites along the direction of the prevailing wind. An upwind, city centre and downwind site would provide valuable information not only on the regional air quality (for impacts on vegetation) but also on the contribution of urban emissions both to the city itself and to the region immediately downwind.

Cities situated in fairly uniform terrain, and without major point sources of pollutants in the immediate upwind region, are likely to have fairly uniform air concentrations of $PM_{2.5}$ except in the immediate vicinity of local sources (roads and combustion sources). Consequently, careful

siting of air sampling equipment in a 'background' locale in the centre of the city may provide an adequate estimate of the exposure of the whole population to respirable particulate matter. In many cases, city centre 'background' data will tend to give higher concentrations than in suburban and residential areas, so will err on the side of safety as far as human exposure is concerned. For Alberta, there appears to be no significant difference in absolute $PM_{2.5}$ air concentrations across the urban monitoring sites in Edmonton, and high temporal correlation (at least on monthly averages); in Calgary, however, although the temporal correlation is still high, there is a systematic increase in average concentrations from north-west to east. Without a detailed analysis of the particular sites it is not possible to identify the causes of this spatial gradient, but a conservative estimate of human exposure would be provided by the Calgary East site. Even here, the monthly data over 4 years suggest that the Air Quality Objective is likely to be exceeded on only 2 or 3 days in a 4-year period (assuming that $PM_{2.5}$ concentrations are distributed log-normally with a geometric standard deviation of 2, which is typical for air pollutant concentrations).

In terms of strategies for controlling and improving air quality **we recommend**:

1) Installation of 'background' monitoring stations at about 100km from the two major cities upwind and downwind in the prevailing wind direction. These stations would provide information on the proportion of PM (largely secondary) that contributes to the urban PM, but over which the city authorities have no direct control. Secondly, the downwind site will provide data to evaluate the contribution of the urban area to regions downwind, superimposed on the 'background' regional PM concentrations. Care would be needed when siting these monitoring stations to ensure that they were not affected by local emission sources, and that they were at exposed sites (e.g., hilltop) where they would be sampling the well-mixed boundary layer for most of the time. Installation on a tall mast would be helpful, but increases the logistical difficulties.
2) Use of one or more mobile monitors that could be installed for relatively short periods of time (months) at strategic locations around the urban area, both downtown and in the suburbs, to gain a better idea of the quantitative and temporal correlations with the fixed monitors. This would allow the identification of potential 'hotspots' (perhaps influenced by industry) and would permit better spatial modelling of air quality based on the fixed monitoring locations. The aim would be to identify local sources of PM, so that more detailed (fixed) monitoring could be installed if concentrations gave cause for concern to human health.
3) Use of one or more mobile monitors installed for periods of months in other built-up areas (smaller towns and villages) or close to major sources where people may be exposed to high concentrations of PM outside the workplace. These could be targeted at sources of dust (mining operations), major combustion sources (smelters, electricity generating plants, steelworks), minor combustion sources with short stacks (incinerators, small factories, district heating, municipal heating) or area sources such as major highway intersections. Priority should be weighted by the numbers of people potentially exposed.

In both these situations, monitoring should be daily or hourly. Daily sampling using filters for gravimetric analysis also (if appropriate filters are chosen) provides the opportunity for subsequent chemical analysis of inorganic salts (sulphates, nitrates) and organic pollutants (e.g.,

PAHs or elemental carbon). For inorganic analytes the best filters are probably PTFE, or PTFE-coated silica fibres; for organic analysis, pre-fired quartz is the best material. Hourly sampling for PM can be achieved using TEOMs (Tapered Element Oscillating Microbalance). Black soot can be measured on similar time scales (or shorter) using an Aethalometer, which measures the reflectance of light from particles sampled onto a quartz fibre ribbon.

Sampling at high time resolution would permit estimates to be made of source apportionment. Several powerful statistical techniques have been developed over the past decade, which allow the quantitative contribution of different types of source (e.g., soil dust, vehicle emissions, specific industrial sources, combustion products) to be calculated for PM at a given site (Lee et al., 1999; Poirot et al., 2001; Polissar et al., 2001; Kim et al., 2003; Kim et al., 2005; Vallius et al., 2005). More detailed analysis of PM components (e.g., polycyclic aromatic hydrocarbons (PAHs)) would allow discrimination between different types of combustion source – diesel, petrol (gasoline), heavy fuel oil and coal (Khalili et al., 1995).

3.3 Nitrogen dioxide

Regional measurements of NO_2 in Alberta already show the influence of major roads or local industry in the monitoring data, both in passive sampling and active sampling. Many of the airshed zones have passive sampling to provide low temporal resolution data for spatial coverage within the zone. These provide adequate information for spatial interpolation and likely assessment of long-time exposures. The use of passive monitoring of NO_2 is recommended in order to identify potential 'hotspots' that arise either from local emission density or particular topographic conditions (e.g., mountain valleys). Such spatial networks should aim to characterise both 'background' conditions in open country, and typical human exposure in residential areas and commercial districts, which will often be influenced fairly continuously by vehicle emissions. Continuous monitoring of NO_2 using electrically-powered instruments with hourly reporting of data will probably only be needed to provide some measure of the extent, duration and magnitude of 'episodes' of high concentration, so that statistical relationships between weekly mean passive diffusion data and hourly peak values can be gained for a municipality or district. Continuous monitoring is particularly relevant when a site or urban area is affected by prolonged periods of stagnant air, leading to a build up of local emissions, or periodically exposed to plumes from a major point source or sources. For nitrogen dioxide, spatial variability is likely to be much greater because of reactions with ozone, and spatial patterns may need to be assessed using integrating passive samplers, so that automatic monitors can be installed if there are indications that Air Quality Objectives are likely to be exceeded at a particular site.

Passive diffusion samplers for NO_2 have been used extensively in the UK and Europe by local authorities to identify areas where air quality targets are exceeded, or likely to be exceeded. There are cautions on their use close to sources of NO_x (e.g., curbside) because of a tendency to show a positive bias, but in semi-rural conditions they work well. However, particular care should be taken over quality control of the whole process from sampler preparation through exposure to analysis, and the use of laboratory comparison studies across the Province is recommended if accurate data are to be obtained.

Geospatial statistical techniques have also been developed recently to combine 'campaigns' of intensive spatial monitoring with attributes such as distance to highways, distance to major point sources, wind direction etc. in order to model the spatial distribution of particulate matter and gases such as NO_2 within an urban area on spatial scales of tens of metres (Briggs et al., 2000; Ross et al., 2006; Sahsuvaroglu et al., 2006; Henderson et al., 2007). This type of exercise can provide very useful information on the location of areas with particularly high air concentrations that might warrant longer-term monitoring using either passive or active techniques.

We recommend that where passive monitoring of NO_2 in built-up areas shows significant increases in concentrations above the regional average (as determined from the network established for environmental monitoring in section 1) that short-term (one year) studies be established with a dense spatial network of passive diffusion monitors to identify the likely maximum areas of high exposure, so that long-term monitoring of the NO_2 risk to human health can be established. If the spatial passive monitoring indicates the likely sources of NO_x emissions, then consideration should be given to installing one or more continuous monitors to evaluate the temporal variation of NO_2 concentrations in relation to air quality standards. Passive monitoring should be used to provide spatial interpolation between continuous monitors – and should always be co-located with active monitors if used as part of an evaluation network. Geospatial statistical modelling should be developed as an interpolation tool for high-resolution modelling in urban areas.

3.4 Ozone

Exposure to ozone in urban areas is complicated by the reaction of ozone with NO (emitted from combustion) to give NO_2. Consequently, the sum of ($NO_2 + O_3$) concentrations (measured in ppm or ppb) may provide a better indicator of the overall oxidant level. Ozone concentrations, therefore, are usually higher in the surrounding countryside than in an urban area itself. However, health effects are usually stated in terms of the gases separately. Emissions of VOCs and NO_x within a city or industrialized area lead to the formation of ozone downwind in warm and sunny conditions. As for PM, a city perturbs the regional ozone pattern, which is normally fairly homogeneous spatially, and the pattern can be established from a regional network. However, ozone formation on a regional scale follows very strong weather-dependent temporal patterns which are not recorded by passive sampling. Sampling frequency of an hour or less is needed to monitor diurnal changes, and peak concentrations, which usually occur in mid-to-late afternoon. Outside a city these temporal patterns occur at roughly the same time across a wide region, being dependent on the scale of weather systems, and on the secondary nature of ozone as an air pollutant, which requires several hours of reaction before high concentrations are reached.

Although passive monitoring can establish the long-term patterns of exposure, continuous monitoring is necessary to establish the risk to human health. A few continuous monitors in rural areas may then be used to identify statistical relationships or even the temporal patterns across a region where long-term averages are fairly constant. In a built-up area, close to industrial or vehicle sources of NO_x, ozone concentrations will be less than in the rural area upwind.

Volatile organic compounds (VOCs) contribute to ozone formation in the atmosphere, even though they are not generally at concentrations that impact human or environmental health directly. However, both biogenic and anthropogenic VOCs participate (with NO_x) in ozone formation, a process which usually takes an hour or more. Consequently, local (and regional) patterns of ozone concentrations are determined by the mixture of precursors. The actual ozone formation rate is determined by the balance of VOCs to NO_x concentrations, and in general for Albertan conditions, the limiting constituent is NO_x (i.e., reductions in NO_x lead to proportionate reductions in O_3 formation). The role of major anthropogenic VOC sources such as cities (from vehicles and industrial activity) or major industrial sources (e.g., petrochemicals, oil extraction) should be investigated through direct measurement of VOCs. Such measurements are difficult and expensive, but passive systems are available, and active off-line sampling can be used for measurement campaigns of short duration. Continuous long-term hourly measurement is also available (as used in UK network, for example) but is costly to implement and operate. VOCs also lead to PM formation as secondary organic aerosol (SOA). Timescales for SOA formation vary greatly with weather conditions, but are another route by which PM concentrations can be influenced by industrial activity and vehicle use.

We recommend

1) that the long-term average ozone concentrations, and areas with highest average exposure, be identified from the regional rural measurements, using either passive or active sampling. Continuous monitors are now available at relatively low cost which can be battery powered.
2) the installation of continuous monitors upwind, downwind and in the residential areas of major towns and cities, to provide information relevant for human health. As for PM, this strategy provides good temporal information on the evolution of ozone 'episodes' that could be used for warning the population to avoid exposure, and also provides information on the contribution of urban emissions to the generation of ozone downwind, posing a threat to rural areas and agricultural production. Monitors could be co-located with the recommended PM monitoring sites (above).
3) campaign (week-month) measurements of VOC concentrations upwind and downwind of major urban areas and local point/area sources, as for PM and ozone, in order to understand the relative importance of anthropogenic and biogenic VOCs on ozone and SOA formation downwind of sources.

Ozone monitors in cities should be sited where people spend time outdoors, such as major recreational areas and parks. Ozone exposure indoors is usually much lower than outdoors. Monitors should also be sited well away from major sources of NO_x to avoid losses of ozone by (rapid) reaction with NO. They should be placed in well-ventilated regions, and ideally at several metres above ground, because ozone can be rapidly removed from the atmosphere in stable atmospheric conditions with low wind speeds, and this process is very variable spatially.

4.0 TRANS-BOUNDARY AIR POLLUTION TRANSPORT

Pollutants do not recognize provincial boundaries. Alberta both exports and imports air pollutants across its boundaries, and in order to estimate the net budget of emission and deposition within the province, the trans-boundary transport of pollutants by the atmosphere should be able to be calculated from reliable field measurements.

What are needed for estimating trans-boundary budgets are concentration data of the major pollutant species, which can be combined with measured or modelled wind fields to estimate the net flux through the boundary layer (BL). The estimation of the true average BL concentration is difficult because so many of the gases and particles are either emitted or deposited at the ground, leading to vertical concentration gradients. The best that can be done from the ground is to measure air concentrations as high above the surface (preferably a weakly absorbing surface such as dry grass or scrub), and under conditions when the BL is well mixed (i.e., when wind speeds are high). The regional network (section 1) will give data on the concentrations of all the gases and particles relevant to the transport of sulphur and nitrogen species, but concentrations may be biased at times of low wind speed, depending on whether the surroundings of the site act as sources or sinks. The best compromise would be to use a simple conditional sampling system that only activates the denuder/filter sampling pump when surface (or 5 m) wind speeds were above a pre-set threshold. This is to our knowledge an untested approach, so some experimental development may be required to establish an appropriate wind speed cut-off to use to maximise the possibility of sampling a well-mixed boundary layer. Some measure of BL depth would also be needed – this might be obtainable from meteorological data sites or modelling, and given the weekly integration time of the denuders, would only be an average value for conditions when the BL was well-mixed. It is likely that such a value could be estimated with reasonable precision (i.e., uncertainty on the order of 20%). A combination of air concentrations, vertical depth and mean horizontal wind speed would then provide an estimate of the trans-boundary fluxes.

We recommend the deployment of simple denuder/filter samplers and wind speed/direction monitors to control sampling of the well-mixed boundary layer at the boundaries of Alberta. For most purposes (unless there are primary emission sources close to the boundary) the major transported air pollutants will be in the particulate phase, so simple filter pack samplers (rather than denuder/filter combinations) may be adequate to characterise trans-boundary transport.

Calculation of transport to/from the east is more likely to be possible, across fairly uniform terrain, compared with transport to/from the west, over the Rockies, where local air flows along valleys and over passes may dictate flow patterns. An ideal sampling site would comprise 3 identical samplers – one operating continuously, to provide data of use for regional monitoring (section 1) but also as a check on the other samplers, which would operate when the BL was well mixed and air flow was either easterly or westerly, thereby capturing the average air concentrations of transported material in both directions. The duration of sampling and measurement of wind directions would then be used to estimate the proportion of time that air masses were moving east or west. Again, a well-exposed site, distant from local sources, would be required, ideally elevated above the terrain, such as a radio transmission mast, fire watch tower or similar. If the method were successfully developed, deployment of around 6 sites close

to the Saskatchewan border, and located so as to capture emissions from major source areas within Alberta (and Saskatchewan), should be adequate to quantify trans-boundary transport. A similar deployment but with fewer sites could be used to estimate transport of airborne material across the southern and northern borders of Alberta. Transport across the Rockies is more complex, and it may be possible to gauge the scale of such transport by installing measurement systems in major passes – this would depend on local knowledge of the extent to which emissions from major point sources are able to cross the mountains.

5.0 FUTURE PATTERNS

Knowledge of the current patterns of air pollution and deposition across Alberta, however good, does not provide any indication of future potential changes in patterns that might invalidate a simple statistical approach to monitoring network design. In the following, we have used a very simple technique to help forecast potential changes, based on the available projections of emissions, which are available by Census district (Cheminfo, 2007). We used the current interpolated measurements for the central 20x20 km grid squares in each Census district (Figures 5-7, 11-12) and scaled them by the projected ratio of emissions in 2015 to 2000 for that Census district, before interpolating across the whole province. This yields a smoother picture than for the original data, and is an indication of the crude nature of this projection. Given that the monitoring data used as a baseline was for the period 2003-2006, this may represent an overestimate of the likely changes. We assumed that any increase in emissions of primary pollutants (SO_2, NO_x) within a Census district would lead to a proportional increase in air concentrations, and in wet deposition. The former assumption is more reasonable than the latter, because of the longer time taken for primary emissions to react in the atmosphere and be returned to the earth's surface as wet deposition. We have not attempted to model the potential effect on ozone or PM concentrations – this would require a detailed model of climate patterns, VOC and NH_3 sources in addition to changes in NO_x emissions. The results are shown below as gridded maps across the Province. The original patterns (Figures 5-7, 11, 12) are reproduced alongside for comparison.

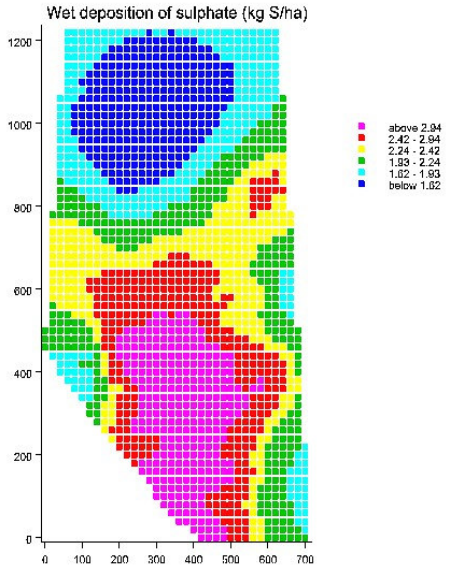

Figure 5 Interpolated wet deposition of sulphate across Alberta (based on precipitation data from 2003-2006)

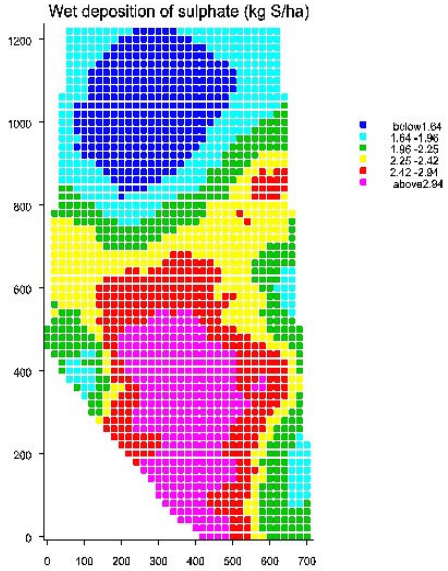

Figure 15 Interpolated wet deposition of sulphate over Alberta (2015 emissions)

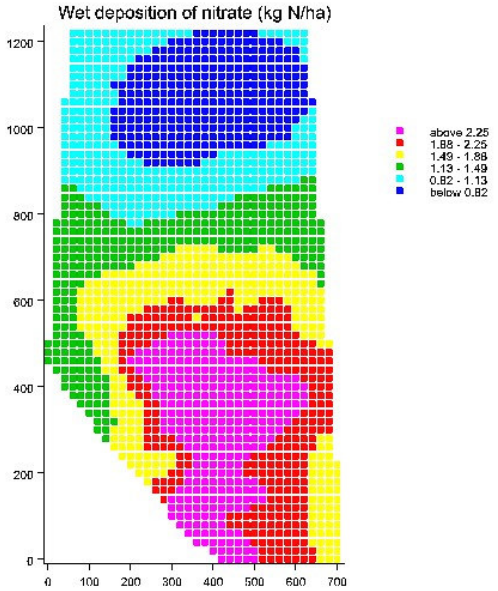

Figure 6 **Interpolated wet deposition of nitrate across Alberta (based on precipitation data from 2003-2006)**

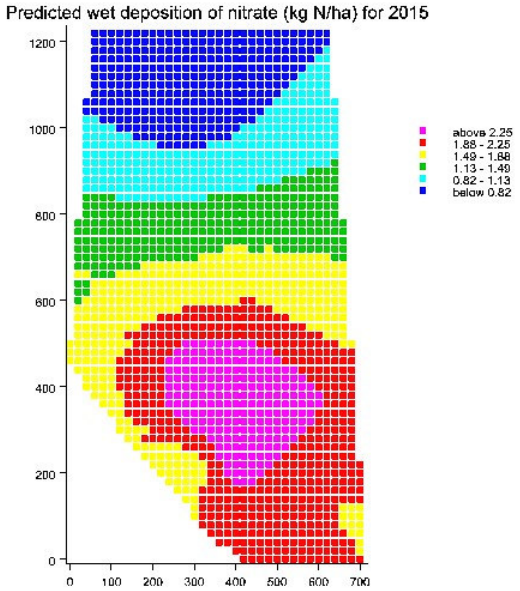

Figure 16 **Interpolated we deposition of nitrate over Alberta (2015 emissions)**

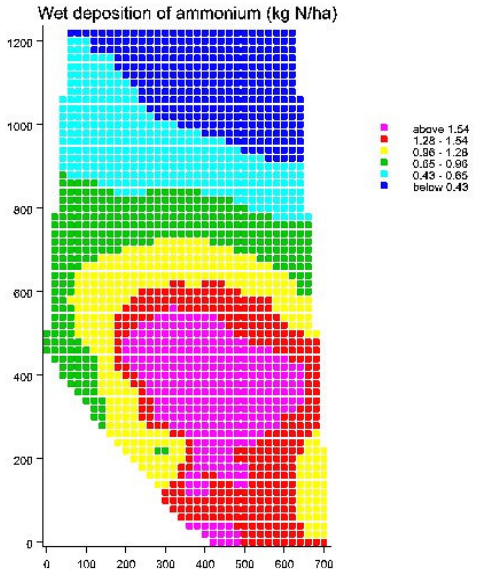

Figure 7 **Interpolated wet deposition of ammonium across Alberta (based on precipitation data from 2003-2006)**

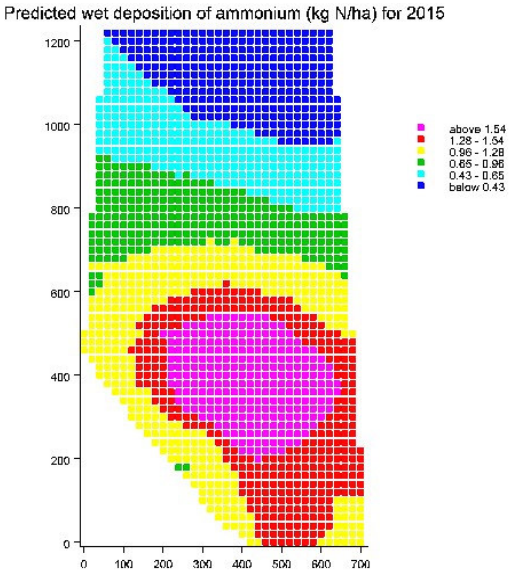

Figure 17 **Interpolated wet deposition of ammonium over Alberta (2015 emissions)**

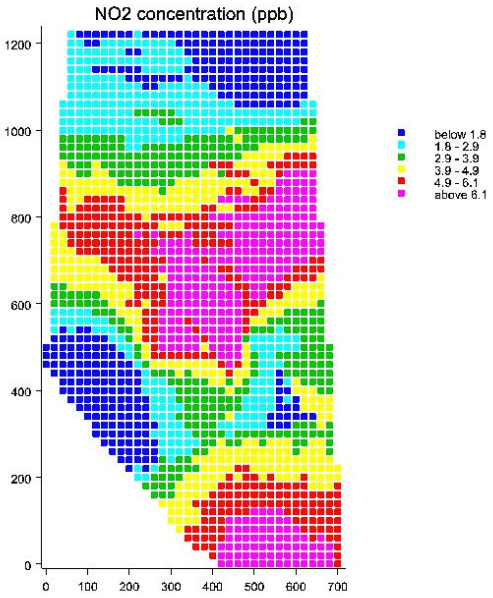

Figure 11 **NO_2 concentrations across Alberta based on rural monitoring data (2003-2006)**

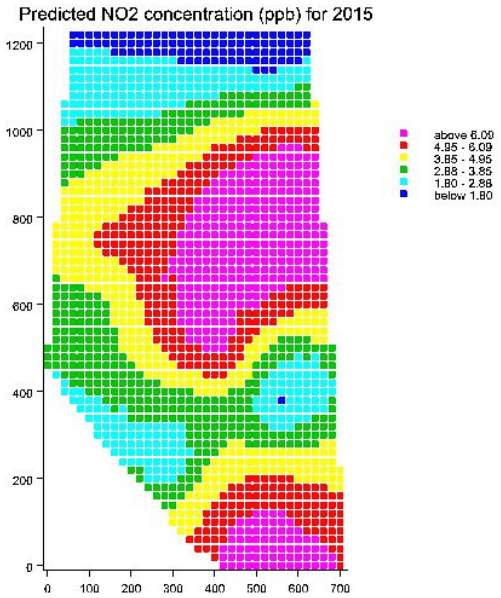

Figure 18 **NO_2 concentrations across Alberta projected for 2015 emissions**

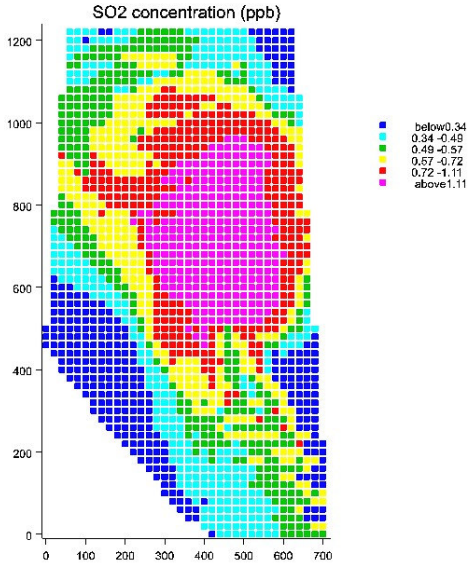

Figure 12 **SO_2 concentrations across Alberta based on rural monitoring data (2003-2006)**

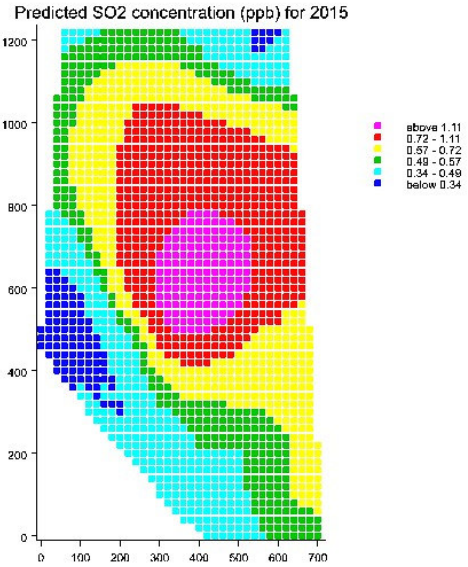

Figure 19 **SO_2 concentrations across Alberta projected for 2015 emissions**

The projections imply little change to the pattern of wet deposition across the province, but an increase in NO_2 concentrations in the south and west, and a decrease in SO_2 concentrations in the central Alberta with a small increase in the south and west.

6.0 DISCUSSION

Any monitoring network is a compromise between ideal spatial and temporal data capture and cost constraints. Although there are no *a priori* ways of optimising an initial network design, a pragmatic approach as used above identifies areas where uncertainty is greatest, weighted by the relevance of the measurements to either human or environmental health. Atmospheric chemistry/transport models may also be helpful in identifying regions where air concentrations or deposition are close to air quality limits. Once a network is in place, there are well established statistical techniques available for testing spatial redundancy. Temporal variability is more difficult to assess, because annual (or other long-term) average values tend to be dominated by the occurrence of infrequent 'episodes' of high intensity. Many studies have shown that air concentrations and deposition follow an approximately log-normal frequency distribution (Fowler and Cape, 1982), with the exception of ozone, which has a more complex distribution (Smith et al., 1989).

One cost-effective approach to establishing a network is to aim for a higher initial density of sites over 1-3 years followed by a statistical analysis of which sites are redundant in terms of their contribution to defining the Provincial spatial pattern. To some extent, such an approach already operates in Alberta, with higher spatial sampling in airshed zones that contain potential 'hot spots' of emissions and concentrations. In this respect, there is scope for a detailed analysis and synthesis of all the existing monitoring networks across the Province.

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