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INVESTIGATION OF ICE NUCLEI FROM THE INDUSTRIAL COMPLEX AT EXSHAW, ALBERTA

BY

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To my Parents

ABSTRACT

In an earlier study, ice nuclei were measured in during aerial sampling of the exhaust plume of a cement producing facility in southern Alberta. To investigate the possibility of inadvertent weather modification due to this effluent, two predictor schemes were developed using five weather stations to determine whether precipitation amounts or precipitation events were anomalous at a sixth station located near to but downwind of the facility. Despite negative departures from predicted values, no linear correlation could be confidently made between monthly mill production and precipitation anomalies at Calgary, the downwind station, during the ten year analysis period from 1981 to 1990.

To investigate the possibility that the source of the ice nuclei was incorrectly identified, a bulk ice nucleation investigation of kiln and stack particulates from industrial facilities in the region was undertaken. Using relative activation temperature as a ranking guide, it was determined that natural nuclei from a nearby lakebed and hydrated magnesium and calcium oxides from calcination operations have a nucleating potential superior to that of cement effluent. However, particle emission rates confirm that cement effluent contributes the greatest number of ice nuclei to the downwind environment.

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CHAPTER 1: INTRODUCTION

1.1 General concepts and hypotheses

Man's impact on his environment, including the atmosphere, has long been a source of conjecture and speculation. Plutarch (AD 46-120), the Greek biographer, first alluded to this impact with his observation that great battles were often followed by rain. He attributed this to either divine intervention or to some causal mechanism, perhaps troop movement or enhanced saturation of the air (Townsend, 1975). The uncertainty present in Plutarch's interpretation of his meagre statistics continues as a dominating force even today, despite refinements in measurement and analysis. The main difficulties in isolating the causal mechanism(s) in weather modification are that (1) cloud systems are complex and (2) obtaining adequate experimental controls by which to judge and understand the experimental results is often difficult or impossible (Braham, 1986a).

Every properly designed experiment has a hypothesis, or proposition or supposition made from known facts that is used as a basis for further reasoning or investigation. This thesis investigates two hypotheses, both of which rely on the fact that the introduction of ice nuclei (IN) into the atmosphere can induce changes in cloud processes (e.g. Dennis, 1980). These hypotheses, along with the null hypothesis that IN do not induce changes, are described below:

Hypothesis:

If an isolated industrial complex releases IN as an airborne waste product, and if such IN have the potential to alter cloud and therefore precipitation processes, then precipitation amounts and events downwind of the complex could be expected to differ from natural precipitation measured in the same area under non-downwind conditions.

Hypothesis:

As a corollary, if the difference between natural and "seeded" precipitation can be quantified, and if airborne emission rates are proportional to production rates within the complex, then a correlation between production and anomalous precipitation amounts and anomalous precipitation events may exist.

Null hypothesis:

If IN do not effect cloud and precipitation processes, then (1) precipitation downwind of the complex should not differ from precipitation that would occur naturally, ergo failure of the first hypothesis, and (2) a correlation between (IN) production and anomalous precipitation should not occur, ergo failure of the second hypothesis.

The two hypotheses are explored in Chapter 2, a version of which appeared in the Journal of Weather Modification (O'Dowd, 1994). The failure of both these hypotheses at statistically significant (t-test) levels led to exploration of the null hypothesis in Chapter 3, where the results of laboratory analysis of the ice nucleating potential of airborne and related particulates are presented. Both Chapters 2 and 3 are written in the format of free-standing scientific papers, including separate introductions, conclusions and references. Figures and tables are included at the end of each chapter.

1.2 Modification of natural precipitation processes

The formation of natural precipitation at temperate latitudes involves several well-defined stages, beginning with the formation of cloud and ending with the arrival of precipitation at ground level. Cloud drops form as a result of the initial condensation of water vapour on hygroscopic or at least partially soluble nuclei called cloud condensation nuclei (CCN). This process begins when air becomes saturated with water vapour, mainly through adiabatic cooling associated with a decrease in pressure with ascent. Clouds typically have 100 to 1000 cloud drops per ml, implying that active CCN concentrations must be comparable. These cloud drops typically have a narrow range of diameters, and vary between 10 μm and 30 μm. Cloud condensation nuclei are of varying composition and must include partially soluble acids or salts. Sulphates derived from dimethylsulphides from ocean areas are believed to account for much of the observed CCN concentration, with other gas precipitates, sea salt from ocean spray, windblown dust, industrial particulate emissions, and lesser unidentified sources making up the remainder (Sumner, 1988).

The size range of common CCN varies between diameters of 0.2 μm and 2.0 μm. Smaller and much more abundant particles (called Aitken nuclei) generally do not act as CCN, while larger particles (called giant aerosols), although active, are far less abundant. Typical CCN measure 0.2 μm in diameter and have an airborne concentration of between 10^5/litre over ocean surfaces and 10^6/litre over land surfaces.

Once condensation commences, differing terminal velocities of different sized cloud drops potentially result in drop collision and subsequent coalescence and growth. However, except in the presence of low CCN concentrations and to some degree the presence of unusually large individual CCN (a situation commonly found over oceans and in tropical latitudes) precipitation can not arise out of this "warm-rain" process. The efficiency of the collision and coalescence process depends heavily on a few cloud drops growing by condensation to a diameter of approximately 40 μm, at which size their collision efficiency with the more abundant 20 μm drops increases rapidly. Most mid-latitude clouds never achieve 40 μm drops, and the result is what cloud physicists refer to as stable liquid clouds.

Freezing is necessary for further drop growth to occur. Drops readily undergo supercooling although spontaneous freezing does not begin until temperatures of approximately -32°C or lower are reached. At warmer temperatures, freezing must be induced by the presence of primarily insoluble foreign particles called ice nuclei (IN), through a process called heterogeneous nucleation. Induced freezing has been shown to depend primarily on a similarity between the crystal properties (atomic unit cell geometry and size, in particular) of IN and natural ice. Properties similar to those of natural ice lowers the surface free energy at the ice-substrate interface (e.g. Fukuta, 1958; Thangaraj et al., 1988) and in turn increases the probability that ice growth will be triggered on the substrate material. In a typical, freshly-formed cloud composed of 500 supercooled 20 μm diameter cloud drops per ml, ice crystals occur in an abundance of 1/litre at -20°C, increasing or decreasing in abundance by an order of magnitude for each 4C° of cooling or warming respectively (Fletcher, 1962).

When introduced into a supercooled cloud environment, an ice crystal will grow readily by vapour deposition at the expense of nearby evaporating cloud drops, the saturation vapour pressure over the more abundant cloud drops being greater than that over the ice particles at the same temperature. These growing ice crystals can reach the mm size range in minutes and through the additional physical growth processes of (1) ice particle collision and subsequent aggregation, and (2) ice particle and cloud drop collision and subsequent riming, can reach sufficient size to overcome updrafts and fall from the cloud as precipitation. Once freezing commences, secondary natural ice fragments assist in the precipitation process, these fragments formed through splintering during ice particle collisions and expansion bursting of rapidly chilled accreting cloud drops. In warmer weather, the frozen particles will fall through the freezing level and undergo partial or complete melting. This process leading from cloud drops to rimed ice particles and finally to rain drops is known as the "cold-rain" process and is prevalent in temperate latitudes.

Ice nuclei, unlike CCN, are rare in the atmosphere, often measuring less than 1/litre, although a concentration of between 1/litre and 10/litre is generally considered necessary for efficient precipitation formation (Braham, 1986b). Silver iodide, perhaps the most widely used artificial nucleating agent, has unit crystal dimensions within 2 % of that of natural ice and begins to induce nucleation at -4.0°C. In contrast, many natural IN consisting of windblown dust (particularly clays), spores, bacteria and perhaps even meteoritic debris do not become active until temperatures of -15°C or lower. This difference in threshold activation temperature translates into an additional kilometre or more of vertical cloud height that can be tapped for precipitation through the use of a more effective nucleating agent, such as silver iodide. Activation temperature varies with the size of the nucleating agent, with smaller particles generally activating at lower temperatures (e.g. Fletcher, 1959; Vali, 1971). For silver iodide, Vonnegut (1947) found that activation occurred at -4.0°C for 1.0 μm diameter crystals and decreased to -8.0°C for 0.01 μm crystals. Most commercial seeding equipment produces silver iodide particles in this size range (Dennis, 1980), with only a few grams theoretically required to completely nucleate a typical cumuliform cloud (Mason, 1971).

Glaciogenic seeding, or cloud seeding using ice nuclei in a supercooled cloud environment has a scientific foundation that employs the aforementioned simple physical principles and two further postulates (Braham, 1986a):

1. That the precipitation efficiency of some clouds, particularly convective clouds, is limited by a shortage of natural nuclei effective at temperatures prevailing in the lowest portions of the cloud. Additional artificial nucleators, either of a deliberate or inadvertent nature, should improve the conversion of cloud drops to ice crystals and thereby increase precipitation on the ground. This postulated mechanism of weather modification is referred to as static-mode cloud seeding.

2. In the enhanced conversion of liquid water to an ice phase due to seeding, the consequent release of latent heat of fusion increases buoyancy and invigorates cloud updrafts. Since this results in higher and colder cloud tops, and since the number of effective ice nuclei carried aloft by updrafts increases with falling temperature, more cloud volume is effectively nucleated, with an attendant increase in precipitation on the ground. This postulated mechanism of weather modification is referred to as dynamic-mode seeding.

Despite early success of airborne field tests of both static- and dynamic-modes of cloud seeding (e.g. Schaefer, 1946; Kraus and Squires, 1947), quantification of rainfall increases, and hailfall decreases (where applicable) has remained difficult. There have been hundreds of weather modification projects world-wide, and yet very few have unequivocally provided hard evidence to support or even refute weather modification claims. Part of this problem stemmed from the commercial or operational nature of many of these projects, where bias in evaluation was inevitable. However, the greatest problems arose where agriculturally significant but none-the-less small changes in precipitation due to seeding had to be extracted from a natural precipitation record that varied both spatially and temporally.

Three projects with definite statistically significant seeding results are commonly cited in the literature to demonstrate the range of weather modification impacts. In Israel, randomized seeding projects running from 1961 to 1967 and from 1969 to 1975 demonstrated a 13 to 15 % increase in precipitation due to aerial seeding operations 30 km upwind of the target area (Gagin and Neumann, 1981). In Missouri, however, a similar randomized aerial seeding project running from 1960 to 1964 (Project Whitetop) demonstrated a significant decrease in both rainfall amounts and radar echoes due to seeding. This was later attributed to overseeding, particularly in light of unexpectedly high natural IN concentrations (Braham, 1979). In Switzerland, somewhat conflicting results were realized from the randomized hail suppression project Grossversuch III running from 1957 to 1963. Results of this project, which used an array of ground-based IN generators in the southern Alps, indicated that although a possible 33 % increase in rainfall occurred, the duration, intensity and aerial extent of hailfall remained unchanged as a result of seeding, and that the incidence of hail even increased on seeded days (Neyman and Scott, 1973).

1.3 Deliberate weather modification in Alberta

Following significant crop losses due to hail in the early 1950's, two weather modification programs were launched in Alberta: a ground-based operational hail suppression program and an independent research program. The suppression program operated from 1956 to 1968 and was organized and funded by farmers making up the Alberta Weather Modification Cooperative Ltd. (AWMC). The target area was an L-shaped corridor varying in size from 1400 km^2 to 11,655 km^2, and was situated midway between Calgary and Red Deer (Gray and Goyer, 1983). Irving P. Krick and Associates of Canada Ltd. supplied up to 190 ground generators of two designs - a silver iodide coke furnace and a high voltage silver iodide electrode arc generator. This ground-based seeding technique, referred to as broadcast seeding, was further supplemented by direct in-cloud aircraft seeding. In 1969, commercial seeding was suspended due to a legal reinterpretation of provincial legislation dealing with funding and plebiscites (Petersen, 1972).

In 1956, an independent research program also commenced, operated by the Alberta Research Council and McGill University, with support from the National Research Council, the Canadian Meteorological Service and the Alberta Government (Gray and Goyer, 1983). Actual in-field studies commenced in the summer of 1969, with operations situated at the military airbase at Penhold, Alberta (now the Red Deer Airport). Project Hailstop, as it was then called, first attempted to study the in-cloud trajectory of seeding material using tracer elements. From 1970 to 1972, cloud-top seeding was investigated in a 8800 km² target area situated near the original commercial seeding area. In 1973 the target area was expanded to 13,000 km² and the Alberta Agriculture funded Interim Weather Modification Board (IWMB), later known as the Alberta Weather Modification Board (AWMB), took over responsibility for managing the project.

In 1974, the AWMB initiated a five year program to assess the technological and economic feasibility of hail suppression in Alberta. A near-circular experimental area of approximately 48,000 km² was established, with Penhold, 20 km south of Red Deer, at its centre. Initially, operational seeding was carried out in the south half of the area and randomized seeding carried out in the north half. However, in 1977 randomization was abandoned and all storms within the experimental area were operationally seeded. Up to seven aircraft, provided by Intera Technologies Inc. of Calgary, were employed in updraft and cloud-top seeding using fixed and ejectable silver iodide flares and pressurized silver iodide/acetone burners. In 1979 the project was extended to 1981 (Gray and Goyer, 1983).

Soon after the AWMB embarked on its five year airborne program, and in response to the Advisory Committee on Weather Modification chaired by J. Christie, a prominent local farmer and outspoken advocate of cloud seeding, the AWMB contracted Irving P. Krick and Associates of Canada Ltd. to once again commence a ground-based seeding program. A target area of 2000 km² was established 30 km southeast of Calgary and made use of 17 ground generators (Gray and Goyer, 1983). The ground-based project was terminated at the end of the 1975 season and renewed in 1980.

In 1980, the Alberta Research Council assumed responsibility for all research and operations of the program, now called the Alberta Hail Project (ALHAP). The project goals were expanded considerably and in 1982 the northern half of the research area was re-designated as a storm experiment and discretionary seeding zone. New initiatives included rainfall and snowfall studies to determine the potential for drought alleviation, the evaluation of dry ice as a seeding material, and the evaluation of different seeding agent delivery systems, including ground generators (Humphries et al., 1987). The ground generator program was renewed, with an expanded target area of approximately 11,900 km^2 situated between Calgary and Lethbridge.

In 1986, funding for the project by Alberta Agriculture was frozen and all ground and air seeding operations were terminated. In 1993, the Insurance Bureau of Canada put forth a proposal for limited hail suppression over Calgary, due in part to claims exceeding $400 million following a severe hailstorm on September 7, 1991. However, the issue of reinsurance, particularly in light of a recent decision by Lloyd's of London permitting the underwriting of limited rather than unlimited liability by Names (individual Lloyd's investors), remains unresolved and at the time of this writing, the project is still at the proposal stage.

1.4 The aims of deliberate weather modification

Natural IN concentrations active at -15°C vary between 0.01/litre and 10/litre, the ideal concentration being approximately 1/litre. Each IN should be at least 0.1 μm in diameter, with a mass of approximately 10^{-15}g for 0.1 μm IN and 10^{-12}g for larger 1.0 μm IN, presuming an average density of 5 g/cm^3. In a cubic km (10^{12} litres) of ideally nucleated atmosphere, there are 10^{12} IN weighing a total of only 10^{-3} to 10^0 g. In a typical 1000 km^3 thunderstorm there are approximately 1 to 1000 g of active IN. On a regional scale, to optimally nucleate the lower 3 km of air over central Alberta covering an area of 300 km x 300 km with IN particles of a diameter of between 0.1 and 1.0 μm, 0.3 to 300 kg of IN would be required. An industry the emits ice nucleating particles in this size range would need only emit fairly low particle masses to sustain optimum seeding of tremendous atmospheric volumes. The Exshaw facilities emit thousands of kilograms of particles every day, and the potential for seeding or over-seeding would appear good.

1.5 Statistics

To determine the validity of the two hypotheses investigated in this thesis, the relationship between two precipitation population samples had to be statistically evaluated. For the first hypothesis, both the parametric Student's t-test and the non-parametric Mann-Whitney U-test were used to compare seeded and unseeded precipitation. The parametric technique addresses the common situation where the sample size is small and where total population parameters, particularly mean and standard deviation, must be estimated from the sample. The t-distribution, a symmetrical distribution very similar to a normal distribution, is used as a means of making this comparison. The null hypothesis tested is that the sample means and thus the total population means are not different. The significance of the difference is expressed as a significance level which then either supports or refutes the null hypothesis, according to a pre-established significance threshold. By convention, a significance level of 0.01 or 0.05 is considered necessary to reject the null hypothesis.

The non-parametric technique addresses the situation where the sampled population distribution may not be normally distributed or is completely unknown (Chao, 1974). It is presented as a supplement to the t-test and is commonly applied to similarly derived weather modification data. If the underlying population is truly normal, the non-parametric rank tests have an efficiency of between 86 and 100 % (Snedecor and Cochran, 1967). Non-parametric techniques rely on ranks or orders and consequently the null hypothesis investigated is that the rank distribution of the two samples is identical. Sample mean is not evaluated as in the t-test. The significance of the difference is expressed in significance levels, and again a 0.01 or 0.05 value is considered necessary to reject the null hypothesis.

The second hypothesis, one of correlation evaluation, considers the strength of the relationship of samples from two different populations - cement production and precipitation.

The correlation is evaluated in terms of "r", the coefficient of correlation, or "r^2" the coefficient of determination, with a value of unity representative of an ideal relationship. The relationship between samples does not necessarily have to be a linear one, but to be considered statistically significant, the correlation coefficient must be equal to or greater than a value specified significant at the 0.01 or 0.05 level (Snedecor and Cochran, 1967). For example, for five data pairs (three degrees of freedom) a correlation coefficient of at least .878 and .959 are necessary to be significant at the 0.05 level and 0.01 levels, respectively.

1.6 Site details

The isolated industrial complex under investigation is located at Exshaw, Alberta, on the eastern edge of the Front Range of the Rocky Mountains (Figures 1.1 and 1.2). Industry was originally established here in the mid 1880's to exploit both readily accessible, high-grade limestone deposits of Exshaw Mountain, and a new and expanding rail and road access into the growing Town of Calgary. The Exshaw complex today consists of three different facilities, each producing unique commercial and waste products. Calgary, the downwind climate impact site, is situated 80 km to the east, in the transition zone between rolling foothills and flat prairie grassland. Calgary has maintained a first order meteorological observing facility since 1884.

1.7 Investigation history

In 1985, in the course of assessing the nucleating ability of ground-based cloud seeding equipment, the Alberta Research Council detected unusually high IN concentrations over and downwind of the cement producing facility at Exshaw (Heimbach, 1986). The following year, the author undertook a series of site investigations, photographing and touring each facility and establishing a dialogue with the facility managers. Lafarge Canada Inc. (then known as Canada Cement

Lafarge Ltd.) was able to provide stack effluent data and monthly production details for a five year period.

Formal M.Sc. research commenced in 1991. Feedback from a public presentation of preliminary results and subsequent analysis later that year indicated a need for a larger production data set, and dialogue with the facility managers was re-established. Realistic environmental and trade concerns led to protracted negotiations for further data and kiln and stack samples. Data for an additional five year period was finally obtained from Lafarge Canada Inc. in March of 1993, and samples from all facilities were obtained in June and July of 1994. Climate data for Calgary and five other Alberta stations was provided by Environment Canada in 1992, but due to format processing delays, the data was not available for analysis until the spring of 1993.

Climate and production data were finally analyzed in the fall of 1993, and as indicated earlier, the results were published the following year. The nucleating potential of the Exshaw particulates, including local natural nucleators was investigated during August and September of 1994. Results and conclusions ranking the relative nucleating ability of the various samples were written in the form of a scientific paper. These results have not, however, been submitted for publication at this time.

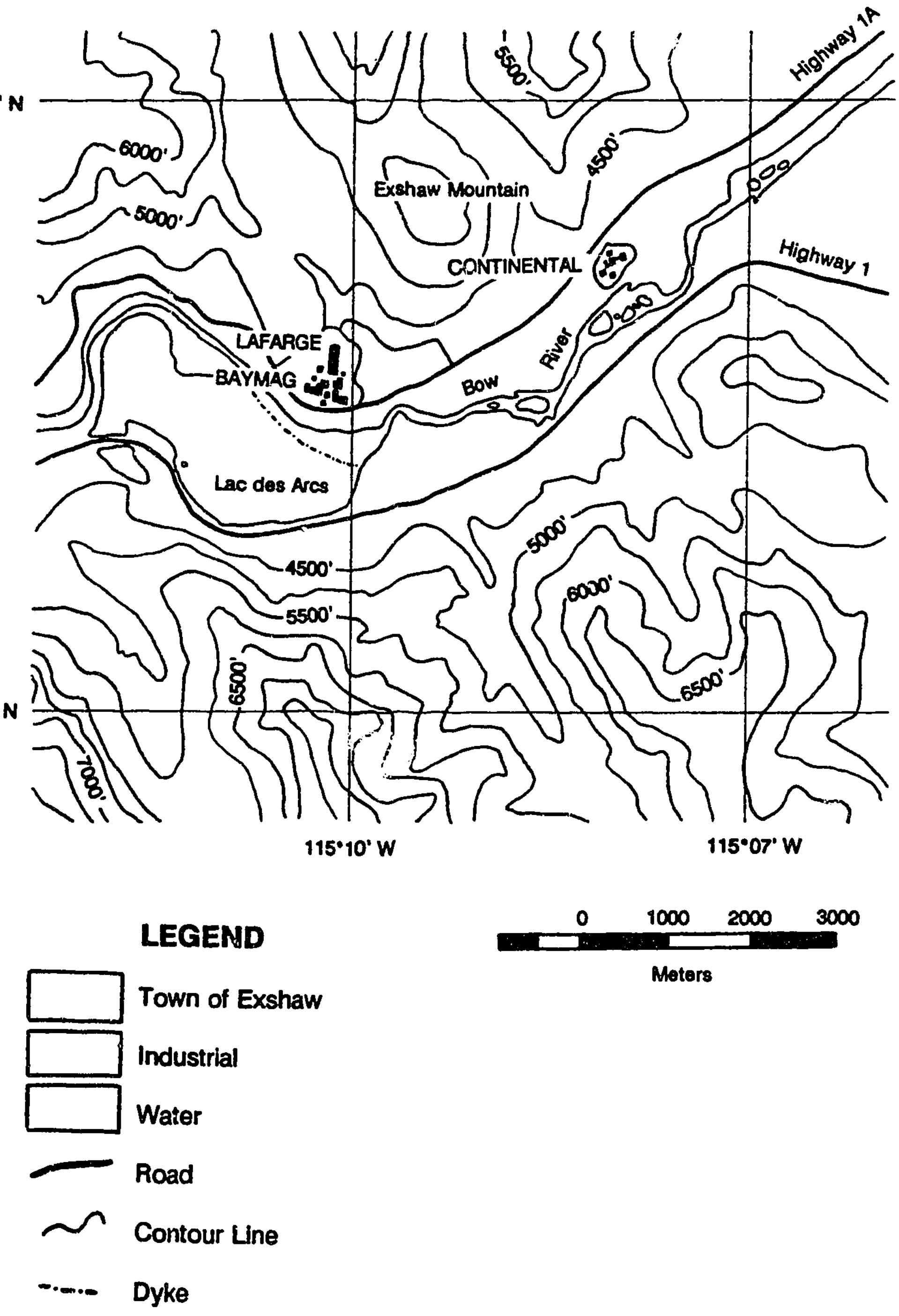

Figure 1.1: Map of Exshaw and surrounding area.

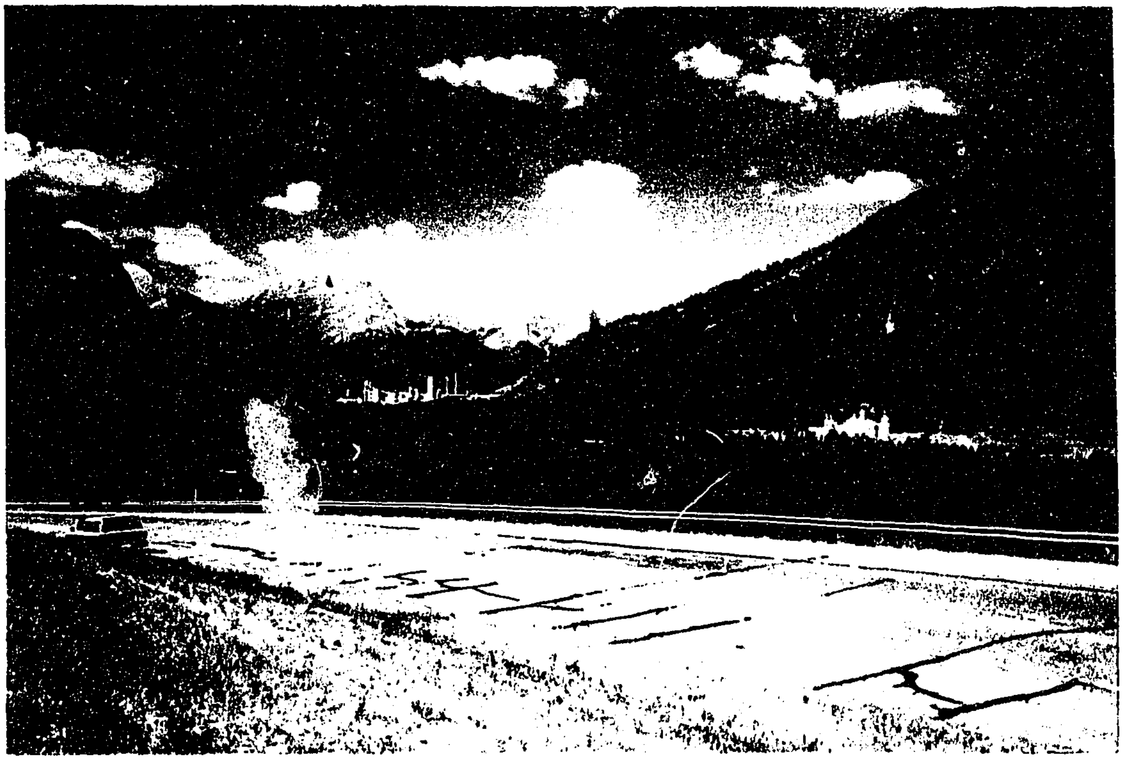

Figure 1.2: Oblique view of Exshaw, Alberta as viewed from the east. Baymag and Lafarge are on the left and Continental on the right.

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CHAPTER 2: INVESTIGATION OF THE EFFECT OF ICE NUCLEI FROM A CEMENT PLANT ON DOWNWIND PRECIPITATION IN SOUTHERN ALBERTA[1]

2.1 Introduction

In southern Alberta, on the eastern edge of the Rocky Mountains, there is situated a large, isolated industrial complex that has been in operation since the late 1800's. Located on the Bow River at Exshaw, three cement and calcination plants produce large quantities of waste heat, water vapour and airborne particulate matter. Located 80 km east of the facility (Figure 2.1) and situated in rolling prairie farmland, is the city of Calgary, a large urban centre with a population of 775,000. The hub of farming, ranching and oil and gas activity in western Canada and the site of the 1988 Winter Olympics, Calgary has a large regional recreational and agricultural economy that is particularly sensitive to precipitation amounts and events.

In June of 1985, ad hoc Alberta Research Council airborne particle sampling flights using a National Centre for Atmospheric Research (NCAR) ice nuclei (IN) counter were made over and downwind of the Exshaw site, the author in attendance. Nuclei concentrations from the single cement producing plant measured several km downwind were 5/litre at an altitude of 7,500 feet, with an NCAR chamber temperature of -20°C. In direct plume penetration, however, concentrations became comparable to those produced by commercial airborne cloud-seeding equipment (Heimbach, 1986). Over 3300 IN were measured in a single penetration pass of less than 1 minute, producing a measured IN concentration minimum of 320/litre. However, unlike a commercial seeding operation, this IN source is virtually a continuous one operating 24 hours a day, 365 days a year, barring equipment overhaul or breakdown (J. Brown, personal communication, 1986), and only two complete

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1 A version of this chapter has been published. O'Dowd 1994. Journal of Weather Modification. 26: 89-97.

shutdowns occurred in the ten year period from 1981 to 1990. The aim of this paper is to determine whether Calgary shows climatological evidence of anomalous precipitation and, if present, whether such precipitation can be unequivocally related to industrial output at the suspect Exshaw facility.

2.2 Weather modification principles

Modification of supercooled clouds using ice nucleating agents is possible because (1) many clouds have a deficit of natural ice nuclei, (2) most clouds consist mainly of liquid water drops, and (3) the saturation vapour pressure over ice is lower than over liquid water at the same temperature. This difference in vapour pressure, an important component of the Bergeron nucleation process (Dennis, 1980), causes ice crystals to grow by vapour deposition at the expense of nearby supercooled liquid water drops. As these ice crystals grow, collisions between other ice particles and supercooled water drops further enhance the growth process. In addition, increased buoyancy results from latent heat release during the phase change, augmenting cloud updrafts and enhancing the growth and nucleation process (Braham, 1986). When growing ice particles overcome updrafts and fall from the cloud, precipitation is the result.

The role of most seeding agents (natural and artificial) is to mimic the inter-molecular dimensions and hexagonal shape of a natural ice crystal and thus provide a substrate for ice deposition. Such seeding agents (1) improve the efficiency of precipitation processes by increasing the number of ice nucleating sites, potentially increasing rain and snowfall, and (2) through small ice particle competition for available water, potentially increasing the number of hailstones with an attendant decrease in hailstone size. Size is a major factor in agricultural and urban hail damage. Naturally occurring IN can include true ice crystals from the glaciation of strong vertical cumuliform growth as well as solid particles of dust swept aloft by wind, volcanic aerosols, meteoritic debris, gas precipitates, spores and bacteria (e.g. Pseudomonas Syringae).

While the introduction of IN improves precipitation processes to a point, overseeding of the same mentioned cloud processes has the potential of reducing and even preventing precipitation where natural IN concentrations are optimal (e.g. Project Whitetop; Braham, 1979). An excess of IN can result in smaller sized precipitation droplets or crystals, thus increasing the likelihood of complete evaporation prior to reaching the ground. Virga, consequently, is more likely to occur in overseeded situations. Incomplete or insufficient seeding of hail situations also has the potential of creating unexpected hail damage, increasing the number of hailstones formed but failing to sufficiently limit their growth. Indeed the attendant risks associated with deliberate weather modification programs has seen a number of States in the USA and Provinces in Canada enact legislation to regulate or at least monitor such operations (Miller, 1992).

2.3 Ice nuclei and accidental industrial weather modification

High concentrations of IN from industrial sources have rarely been directly observed in experiments to date. However, the release of such nuclei has often been hypothesised where climate data reveals anomalous precipitation or storm events. Some of the first observations of weather modification through industrial process were made in England by Ashworth (1929). He noted that rainfall amounts on Sunday, the day that factories were regularly shut down, were lower than during the rest of the week and hypothesized that "the fine flue dust ejected by the draught up the chimney may supply an abundance of nuclei which promote the formation of rain". Almost forty years later, an association between increased iron and steel production in Chicago, Illinois and increased precipitation and storm events downwind at La Porte, Indiana was evaluated and statistically defended as being plausible (Changnon, 1968). The conclusions drawn in METROMEX (Metropolitan Meteorological Experiment) similarly suggested that increased rainfall and storm activity observed over and downwind of St. Louis, Missouri were due to urban/industrial effects, with anthropogenic IN considered to be a contributing factor (Changnon, 1981). Mather (1991) draws similar conclusions on the basis of invigorated storm activity noticed in the vicinity of a South African Kraft paper mill.

In contrast, some instances have been noted where a suspect industrial complex does not show evidence of downwind weather modification, despite favourable indicators for the contrary. Although investigation by Telford (1960) revealed IN concentrations of 300/litre at -22°C in the effluent of steel plants in the Newcastle/Sydney (Australia) area, downwind impact was determined to be negligible (Ogden, 1969). The validity of some of Ogden's results, however, relied on non-statistical evaluations and were challenged in later discussion (Changnon, 1971). In an investigation of the downwind climatological impact of a single steel complex in Hungary, Lowry and Probald (1978) similarly found insufficient evidence to support the release of IN and consequent weather modification.

A hybrid situation arose in the results presented by Hobbs et al. (1970). In their investigation of airborne effluent from a variety of isolated industrial complexes in the State of Washington, using airborne IN detection equipment, they noted anomalously high cloud condensation nuclei (CCN) concentrations but low or absent IN concentrations. They sampled plumes from a copper smelter, a steel furnace, a ferroalloy plant, an aluminum smelter, a Kraft mill and a saw mill, with only the ferroalloy plant producing measurable IN at close to background levels. However, annual precipitation and stream flow amounts were found to increase in the vicinity of many of these operations, despite the low IN values. The excess CCN appeared to provide fertile ground for periodic injections of naturally occurring IN, triggering, through this two-step process, anomalously high precipitation amounts. It is considered to be a hybrid situation due to evidence for weather modification in the absence of increased IN concentrations.

None of the above mentioned industrial processes contains any reference to cement production. Furthermore, the literature is exceedingly sparse in discussions of the nucleating and hygroscopic effects of cement kiln effluent. Budilova et al. (1969) noted that a possible 5 % increase in precipitation fall could be realized during seeding of convective clouds with a halite and cement mixture, and Murty and Murty (1972) confirmed the nucleating properties of Portland cement through laboratory testing, but without implication that cement plant airborne waste effluent could be an IN source. They showed that the threshold nucleation temperature of Portland cement to be -4.6°C to -5.0°C, between that of silver iodide (-4.0°C) and lead iodide (-6.5°C), two materials with well established potential for use in weather modification experiments and operations.

2.4 Exshaw industry

Three separate mineral comminution and beneficiation processes take place at the industrial complex at Exshaw, each under the auspices of a separate company. These companies are Lafarge Canada Inc., Continental Lime Ltd. and Baymag, all three providing data and information on their operations for this study, as presented below.

Lafarge Canada Inc. (Lafarge), one of Canada's largest producers of cement, is believed to be the source of ice nuclei detected in aerial sampling tests reported by Heimbach (1986). In the manufacture of cement, raw materials are initially crushed, blended, ground together and then introduced into long, gently sloping rotating kilns. At 900°C, calcination takes place, and at final temperatures of 1450 - 1650°C, aluminum and calcium complexes form. The kiln product, referred to as clinker, is ground and with a small amount (5 %) of gypsum added to control setting, becomes Portland cement.

Lafarge currently uses two kilns, each kiln having a primary kiln stack and secondary cooler stack. The principal sources of heat, vapour and particulates are the kiln stacks, located at the upper end of the kiln complex. The exhaust gas temperatures average 146°C for kiln five and 336°C for kiln four. Kilns one and two were both decommissioned in 1976 and kiln three was transferred in October 1982 to Baymag (see below).

The cooler stacks, located at the lower end of the kiln complex, release gas at comparable velocities but at lower temperatures than the main stacks - kiln four at an average of 146°C and kiln five at an average 169°C. These stacks exhaust air used in cooling the resulting clinker to temperatures that can be handled elsewhere in the facility. Both kilns are fuelled by natural gas, using 400,000 cubic metres per day. Though not currently used, discarded automobile tires have recently been tested as a fuel supplement (Lafarge Canada Inc., 1994).

The raw materials used in the process include Upper Devonian limestone from the Palliser Formation of Exshaw Mountain, immediately behind the plant, Upper Cretaceous sandstone from the Belly River Formation, Upper Cretaceous shale from the Wapiabi Formation, industrial iron and fly ash. Ash and shale are recognized as common, naturally occurring ice nucleating agents (Dennis, 1980) although during the manufacturing process they become part of the complex cement phyllosilicate and tectosilicate structure, and their individual mineralogical structure is lost. On hydration, the cement complex becomes extensively cross-linked and hardens to form the construction material known as concrete.

Exhaust that exits each of the two kiln stacks is cleaned of 99.7 % of particulates by an electrostatic precipitator (ESP). The secondary cooler stack exhaust is cleaned by gravel bed filters of similar efficiency. The ESP, responsible for limiting average particulate outputs of each stack to less than 55 kg/hour, is periodically deactivated for a number of production and safety reasons. During these brief transient events, which are carefully logged and reported to Alberta Environment, the Provincial Government department responsible for air quality, particulate loading can theoretically increase by two to three orders of magnitude. This would be anticipated to result in a similar increase in the downwind IN concentration of the effluent from the observed 5/litre to greater than 500/litre, comparable in magnitude with those concentrations measured by Telford (1960) over steel mills in Australia.

Particles released are believed to include complex dicalcium and tricalcium silicates, tricalcium aluminate and tetracalcium aluminoferrite, all common cement constituents (Ramachandran, 1984), as well as calcium carbonate, silicon dioxide and various sulphates, metal oxides and other salts (Portland Cement Association, 1992). Chemical assays provided by Lafarge show highest concentrations by weight of calcium and silicon, with decreasing amounts of magnesium, potassium, sulphur, aluminum and iron. The greatest percentage of particles released are less than 0.3 μm in diameter, accounting for approximately 83 % (by weight) of the solids released, with 6 % between 0.3 and 10 μm, and 11 % larger than 10 μm. It was noted by Telford (1960) that effluent from Australian steel mills was inert, with high amounts of manganese and silicon, and that particles released were initially in the size range of 0.1 to 1.0 μm, with later coagulation to larger than 10 μm. Table 2-1 presents a comparison of particle size distributions for the three facilities.

The other two facilities located at Exshaw include Continental Lime Ltd. (Continental) and Baymag (Baymag). Both firms, like Lafarge, are mineral processors. Continental, located 5 km east of Lafarge, uses two rotating horizontal kilns for the calcination of limestone ($CaCO_3$) into quicklime (CaO), and a short kiln for drying crushed limestone. Limestone is from the Mount Head Formation of the Mississippian Rundle Group, and is quarried from a site 13 km away. Airborne particulate output is significantly lower than at Lafarge, averaging less than 5 kg/hr/kiln. Baymag, adjacent to Lafarge, uses the former Lafarge kiln 3 for the formation of magnesium oxide (MgO) through the calcination of magnesite and dolomite, obtained from the Middle Cambrian Cathedral Formation of Brussilof Mountain, 70 km away. Despite low production amounts, typically 180 tonnes/day, and the use of an ESP, exhaust stack particulate amounts are comparable to Lafarge kiln stacks, averaging almost 50 kg/hour.

2.5 Data

Lafarge, the suspected IN producer, has provided monthly production data for the 1981-1990 period. These production figures are believed to be proportional to stack effluent amounts, the electrostatic precipitation (ESP) equipment used in particulate capture being fairly uniform in efficiency regardless of the output rate (J. Brown, personal communication, 1988). In order to make the target-control separation, the production amount under downwind conditions had to be separated from the production amount under non-downwind conditions (see Section 2.6.2).

Particulate emission data was obtained from independent laboratory results provided by Lafarge and Continental, and by personal communication for Baymag (B. Walsh, personal communication, 1986).

Daily precipitation data was provided by the Atmospheric Environment Service, Canada's national weather forecasting and climate data service. As indicated, only first order meteorological stations in southern Alberta with precipitation and daily prevailing wind data were used. Prevailing wind was defined as the most commonly occurring two minute mean wind as measured every hour in a 24 hour period, and in this case covered azimuths of 250 to 290 degrees true, the direction that would carry Exshaw emissions towards Calgary. Precipitation was measured in millimetres, or the melted equivalent if the precipitation was snow or hail, and precipitation events were marked by any day in which measurable precipitation equalled or exceeded 0.2 mm.

2.6 Methodology

The evaluation of a potential seeding impact at Calgary due to anthropogenic ice nuclei (ANIN) was carried out in two parts. The first sought to determine whether the precipitation at Calgary (both amount and number of events) was anomalous by developing a scheme for predicting what the unseeded precipitation at Calgary should be and thereby produce residuals. The second part was dependent on the first, with an attempt to quantify the relationship between Lafarge production over the ten year period from 1981 to 1990 and both (1) calculated event and amount residuals and (2) the ratio of observed to predicted events and observed to predicted amounts (e.g. Thompson and Griffith, 1981).

2.6.1 Anomalous precipitation

In attempting to determine any anomalous nature in the precipitation at Calgary, methodologies frequently used by researchers, and in particular by weather modification operators, were considered. The most difficult problem posed here, and indeed in most weather modification evaluation schemes, was determining what would have happened had there been no seeding treatment. As it is not possible to observe what naturally happens and then retroactively apply a seeding agent, indirect schemes for predicting the background or natural state have been developed over the years. These include the target-only, target-control and crossover designs. All three, however, require that weather parameters (in this case precipitation amount and incidence) be measured during some period of non-seeding. This presents considerable difficulty in the present case because mill records prior to 1980 are vague and shutdown periods cannot be determined prior to this period. Furthermore, in the 120 month sample data set complete shutdown of both kilns occurred only on 4 months (January 1981, February 1981, November 1984, December 1984), insufficient to create a predictor useful for the entire 10 year period. Monthly Lafarge production is presented in Figure 2.2.

A solution to this problem was to use data from other Alberta meteorological stations in a modified target-control approach, and determine whether there was a relationship between precipitation and an independent variable that could be used for predicting what the "unseeded" precipitation at Calgary target station should be. Partial support for this approach was the good correlation observed by Longley (1974) between precipitation amounts at prairie stations with less than 400 km separations. Five first order Alberta stations were used as control stations, all latitudinally displaced from Calgary but in a band of roughly equivalent longitudinal displacement from the mountain barrier (Figure 2.1). The stations included Edmonton, Edson, Lethbridge, Medicine Hat and Red Deer.

Testing of various relationships between monthly precipitation (e.g. measurable precipitation amounts and events during westerly flow, total precipitation, precipitation during non-westerly flow, and ratios of the above) and time (e.g. days per month of westerly flow, days per month of westerly flow in which measurable precipitation fell, days of non-westerly flow, days of non-westerly flow with precipitation, and ratios of the above) were carried out. It was found that the strongest relationships were between the number of days in a given month that the prevailing surface wind was from the west (250 to 290 degrees) and (1) the amount of precipitation that fell during westerly flow (type A predictor), and (2) the number of precipitation events during the same westerly flow (type B predictor). By combining data from all five stations, the strength of a least squares linear correlation could be evaluated for each predictor on a month by month basis, 120 months in total. The coefficients of determination for each predictor and for each month of the ten year period are presented in Figures 2.3 and 2.4.

Of concern was spacial variability of precipitation due to geographic situation, particularly latitude, and rigorous filtering of the predictor months was initiated to eliminate suspect values. A threshold coefficient of determination of 0.90 was established as the minimum, corresponding to a significance level of approximately 0.01. Any predicted value from a month with an r^2 value below 0.90 was rejected.

As a check of the validity of the relationships as predictors, it was noted that for January 1981, February 1981, November 1984, and December 1984, the inclusion of Calgary data did not change the coefficient of determination by more than 0.04. While this supports the premise that Calgary precipitation should not be anomalous for those months in which there was no seeding taking place, it is by no means conclusive as the coefficient of determination in all four cases was below the 0.90 rejection threshold.

2.6.2 Cement production

The type A (precipitation amounts) and type B (precipitation events) residual data, extracted as above, as well as ratios of observed to predicted amounts and events were then compared through a least squares linear regression with weighted production amounts at the Lafarge facility. Raw Lafarge production data took the form of total monthly kiln production measured in tonnes, and the weighted production values took the form of daily estimated production (monthly tonnage divided by the number of days in the month) multiplied by the number of days for that month in which prevailing wind at Calgary was from the west. Type A results are presented in Table 2-2 and type B results are presented in Table 2-3.

Figure 2.5 illustrates the relationship between residual precipitation amounts (the difference between what was observed and what was predicted to have fallen had there been no seeding influence) and weighted production, the three positive values indicative of precipitation augmentation and the nine negative values indicative of precipitation suppression. The single zero value indicated no seeding influence. Figure 2.6 illustrates the same relationship for days with precipitation events, rather than precipitation amounts, with five instances of augmentation, eight instances of suppression and three instances of no impact.

Figures 2.7 and 2.8 illustrate the relationship between ratios of observed to predicted precipitation amounts (Figure 2.7) and precipitation events (Figure 2.8). Values in excess of unity suggest precipitation augmentation and values below unity suggest precipitation suppression. Values of unity indicate no seeding influence, and values of zero indicate a complete absence of a precipitation event where one was predicted. Figure 2.7 presents three instances of augmentation and nine of suppression, and Figure 2.8 presents four instances of augmentation, eight of suppression, and one of no impact. Data points in both figures were culled (one in Figure 2.7 and three in Figure 2.8) where the predicted precipitation amount or event value was zero, resulting in a zero in the ratio denominator and an undefined ratio value.

In all four figures the least squares linear regression coefficients of determination were low (0.04 for Figure 2.5, 0.23 for Figure 2.6, 0.02 for Figure 2.7 and 0.03 for Figure 2.8) and clearly not significant at a 0.05 confidence level. These results are discussed further in Section 2.7.

2.7 Results

An initial total of 13 type A and 16 type B residual and ratio values were produced after filtering. Paired t-test comparisons of the calculated precipitation amounts with the observed values (type A predictor) indicated significant differences at the 0.07 confidence level for precipitation amounts alone and 0.11 for ratios of observed to calculated precipitation amounts. Comparison of the calculated precipitation events with the observed events (type B predictor) had significance differences at the 0.15 confidence level for events alone and 0.89 for ratios of observed to calculated events. Non-parametric comparisons using Mann-Whitney U-tests revealed threshold confidence levels of 0.05 and 0.02 for the type A residuals and ratios, and 0.24 and 0.25 for the type B residuals and ratios, similar to t-test values. As noted by Griffith et al. (1991), these statistical tests are indicators of validity rather than proof, the randomness and independence requirements not being completely fulfilled.

At a significance level of 0.05, only the non-parametrically evaluated results of the Type A predictor proved to be statistically significant. For the others, the null hypothesis that measured and calculated precipitation were from the same population, and consequently not different, remained valid. Furthermore no linear correlation was evident between precipitation amounts or events and weighted Lafarge production for either set of predictor values. In all four cases (type A and B), the coefficient of determination was below 0.23 and not significant at the 0.05 confidence level.

However, the type A residual results did have a non-linear trend, suggestive of an amplitude-increasing sinusoidal or cubic function (Figure 2.5). For shorter periods or lower rates of seeding, as suggested by lower production amounts during westerly flow, the impact on precipitation is unclear. However, with increasing duration or intensity of seeding (11,000 to 29,000 tonnes weighted production), there first appears to be a precipitation deficit, which then becomes a precipitation excess at still higher seeding rates (over 29,000 tonnes weighted production). While tempting to attribute these fluctuations to overseeding or the impact of increased heat or water vapour (e.g. Hindman, 1977), it should be noted that variations in both intensity and duration of seeding are indistinguishable consequences of changes in weighted production amounts. As the physical implications of each are not necessarily the same, it may be misleading to draw conclusions solely based on these production figures alone.

2.8 Conclusion

Cement production at the Lafarge facility, on the basis of the tests carried out in this study, cannot be confidently linked to precipitation amount or event anomalies determined at Calgary. Despite the majority of points in Figures 2.5 to

2.8 lying in the precipitation suppression zones of these graphs, the trend described in the results section must be considered consequential rather than causal, with concrete evidence of cement plant effluent affecting Calgary's precipitation still lacking.

There are a number of reasons why the indicators are inconclusive. Anomalous precipitation at Calgary could be due to some situational feature not present at the other five stations used in producing the residual. Also, there may not be a completely linear relationship between kiln production and stack effluent amount (varying ESP efficiency). Furthermore, it is possible that there exists a sink that deactivates or scours IN from the air downwind of Exshaw. This may be manifest simply as deactivation through particulate coagulation, as noted in steel mill plumes in Australia (Telford, 1960) and in cement effluent in the former Soviet Union (Vdovin et al., 1974), or as aggravated particulate settling due to mesoscale phenomena (e.g. subsidence over Ghost Lake, located 20 km east of Exshaw).

It is also possible that the source of IN was incorrectly identified during the original sampling flights, and that Continental or Baymag may also contribute to the release. Murty and Murty (1974) noted that quicklime (CaO) also acted as a nucleating agent in laboratory tests, although they also noted that the nucleating effect decayed rapidly on wetting due to solution effects.

Planned further study includes (1) the analysis of ESP dust samples for their nucleating ability and mineralogical content, and (2) the collection of rain samples in Calgary in order to carry out an analysis for cement plant effluent. Such effluent has a distinctive mineralogical signature (Arslan and Boybay, 1990) and downwind samples should be distinguishable from natural dust on the basis of the mineralogical "fingerprint" determined from ESP dust samples provided by Lafarge.

TABLE 2-1. Average size distribution of stack effluent particles based on particulate weight. Reported size refers to particle diameter.

Facility	< 0.3 μm	0.3 - 10 μm	> 10 μm
Lafarge	83 %	6 %	11 %
Continental	2 %	64 %	34 %
Baymag	1 %	34 %	65 %

TABLE 2-2. Type A observed, predicted and residual precipitation amounts as used in Figures 2.5 and 2.7. Weighted production amounts and coefficients of determination are also shown.

Month Number	Obs. Pcpn (mm)	Cal. Pcpn (mm)	Res. Pcpn (mm)	Pcpn Ratio[1]	r^2 value	Wt'd Prod.[2]
3: Mar 81	0.8	0.28	+ 0.5	2.9	0.902	1163
5: May 81	10.4	7.53	+ 2.9	1.4	0.952	7624
8: Aug 81	0.0	0.0	0.0	n/a[3]	0.948	0
14: Feb 82	0.0	0.36	- 0.4	0.0	0.926	2365
15: Mar 82	2.0	2.77	- 0.8	0.7	0.992	11953
33: Sep 83	0.4	8.00	- 7.6	0.1	0.923	13562
45: Sep 84	0.0	1.63	- 1.6	0.0	0.938	2472
59: Nov 85	0.0	0.52	- 0.5	0.0	0.916	5433
71: Nov 86	0.0	3.82	- 3.8	0.0	0.995	12908
92: Aug 88	0.4	4.48	- 4.0	0.1	0.944	13307
107: Nov 89	6.2	4.57	+ 1.6	1.4	0.915	31051
109: Jan 90	0	3.32	- 3.3	0.0	0.954	24791
120: Dec 90	1.0	3.80	- 2.8	0.3	0.976	16491

[1] observed/calculated precipitation amount
[2] tonnes
[3] undefined value

TABLE 2-3. Type B observed, predicted and residual precipitation events as used in Figures 2.6 and 2.8. Weighted production amounts and coefficients of determination are also shown.

Month Number	Obs. Pcpn Event	Cal. Pcpn Event	Res. Pcpn Event	Ratio[1]	r^2 value	Wt'd Prod.[2]
3: Mar 81	1	0.18	+ 0.8	5.6	0.957	1163
7: Jul 81	1	2.68	- 1.7	0.4	0.954	12847
8: Aug 81	0	0.00	0.0	n/a[3]	0.991	0
14: Feb 82	0	0.44	- 0.4	0.0	0.908	2365
18: Jun 82	1	0.00	+ 1.0	n/a[3]	0.942	1687
25: Jan 83	1	0.49	+ 0.5	2.0	0.988	7878
28: Apr 83	0	0.10	- 0.1	0.0	0.948	2168
56: Aug 85	1	0.58	+ 0.4	1.7	0.918	8729
57: Sep 85	2	3.00	- 1.0	0.7	0.953	13588
63: Mar 86	2	1.28	+ 0.7	1.6	0.915	34689
80: Aug 87	0	0.00	0.0	n/a[3]	0.998	0
96: Dec 88	0	1.39	- 1.4	0.0	0.907	6283
101: May 89	0	2.23	- 2.2	0.0	0.984	10376
113: May 90	1	0.99	0.0	1.0	0.968	3012
118: Oct 90	0	3.42	- 3.4	0.0	0.902	39766
120: Dec 90	2	2.58	- 0.6	0.8	0.941	16491

1 observed/calculated precipitation events
2 tonnes
3 undefined value

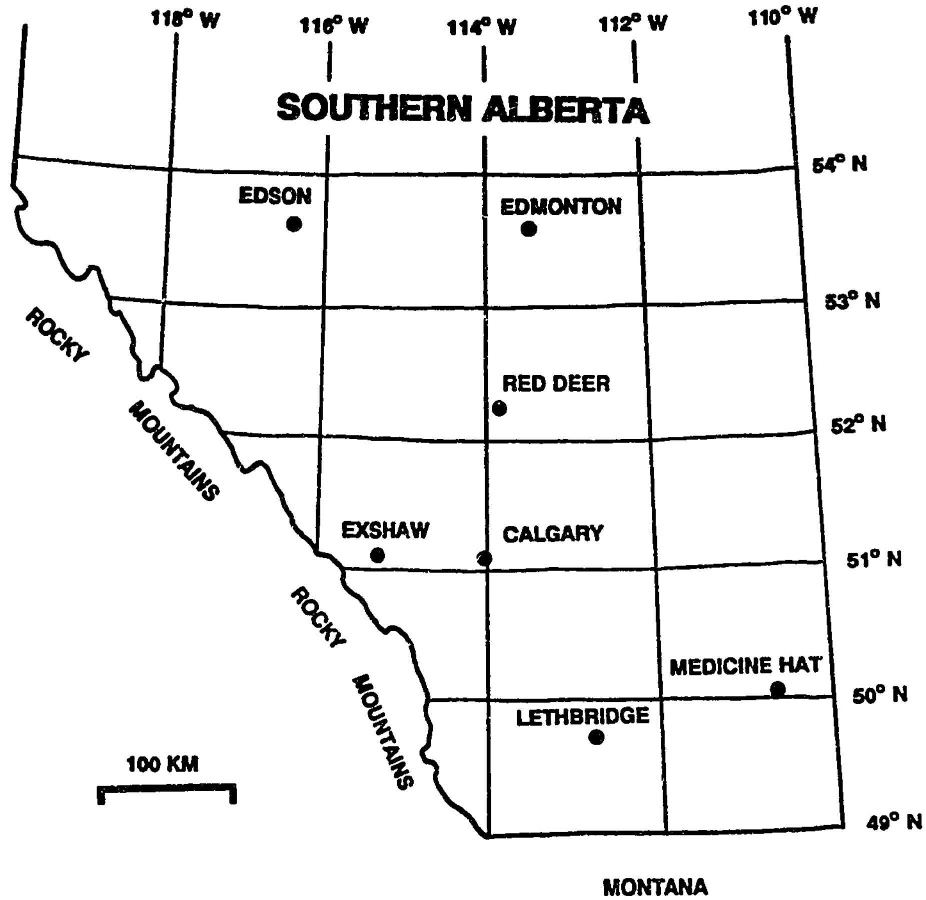

Figure 2.1: Map of southern Alberta. The five predictor control stations are shown (Edson, Edmonton, Red Deer, Lethbridge and Medicine Hat) as well as the ice nuclei source (Exshaw) and the target station (Calgary).

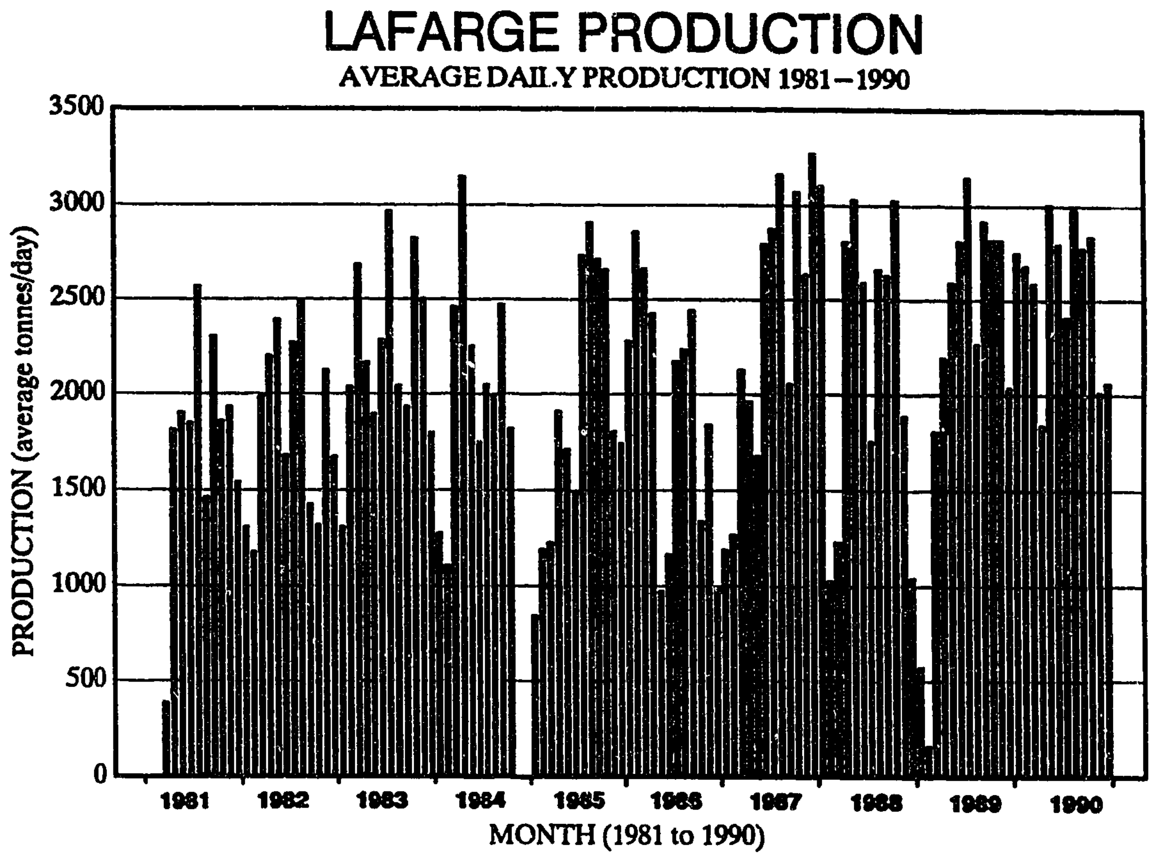

Figure 2.2: Average daily cement production at Lafarge. Production fell to zero during four maintenance months (January 1981, February 1981, November 1984, December 1984).

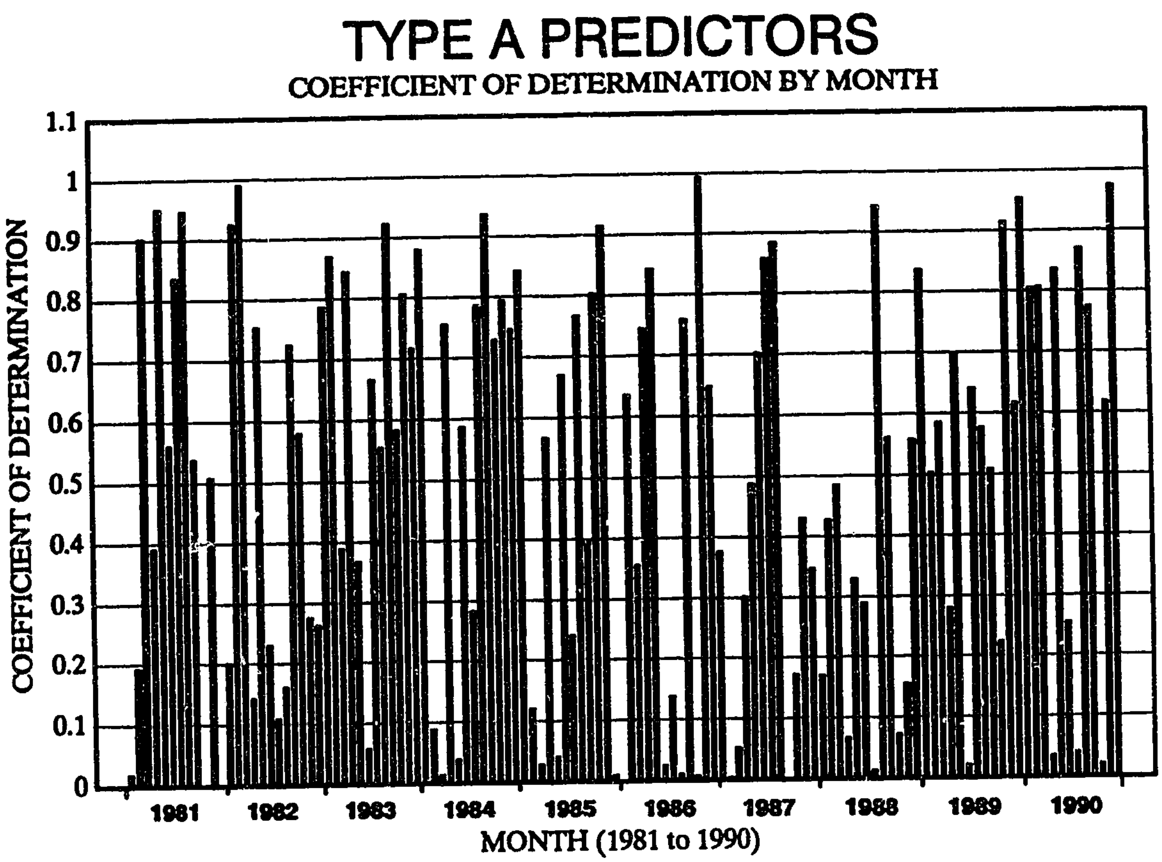

Figure 2.3: Coefficients of determination (r^2) for the type A predictor. Type A used a correlation between the amount of monthly precipitation that occurred during westerly flow and the number of days of westerly flow.

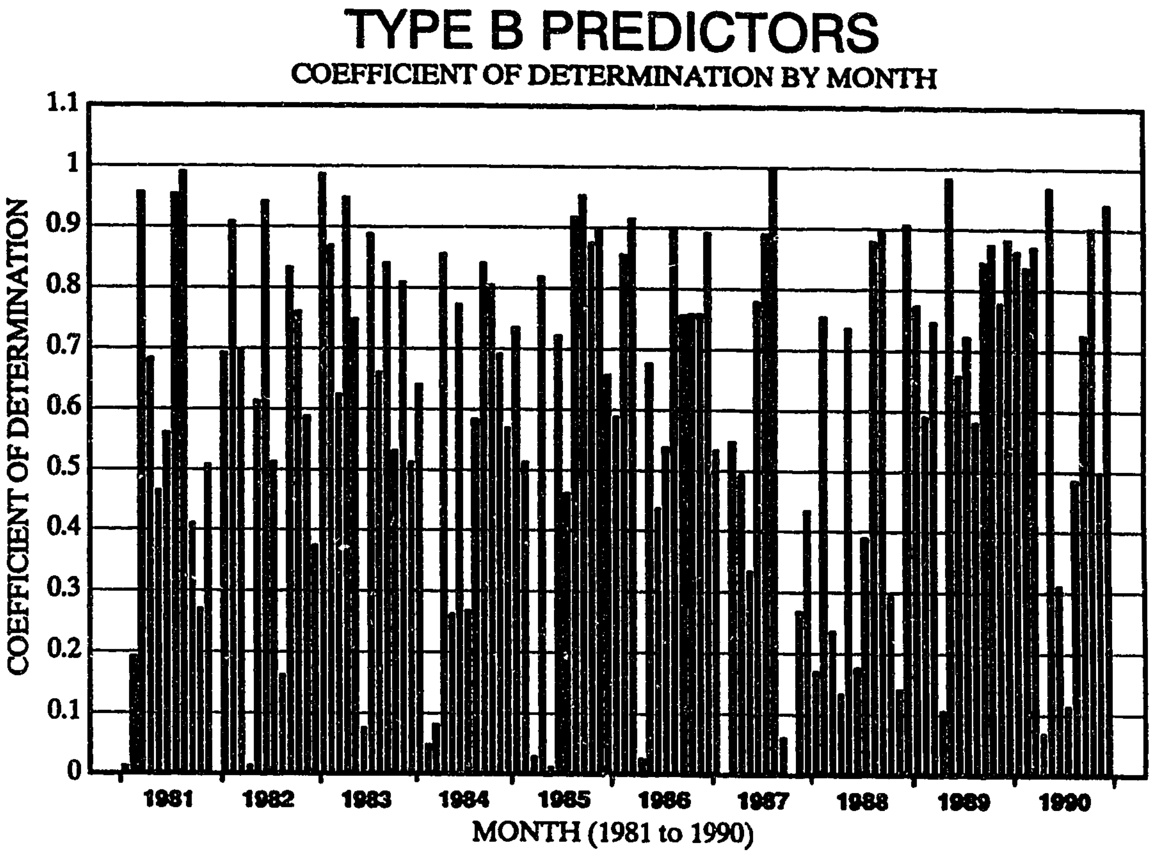

Figure 2.4: Coefficients of determination (r^2) for the type B predictor. Type B used a correlation between the number of monthly precipitation events that occurred during westerly flow and the number of days of westerly flow.

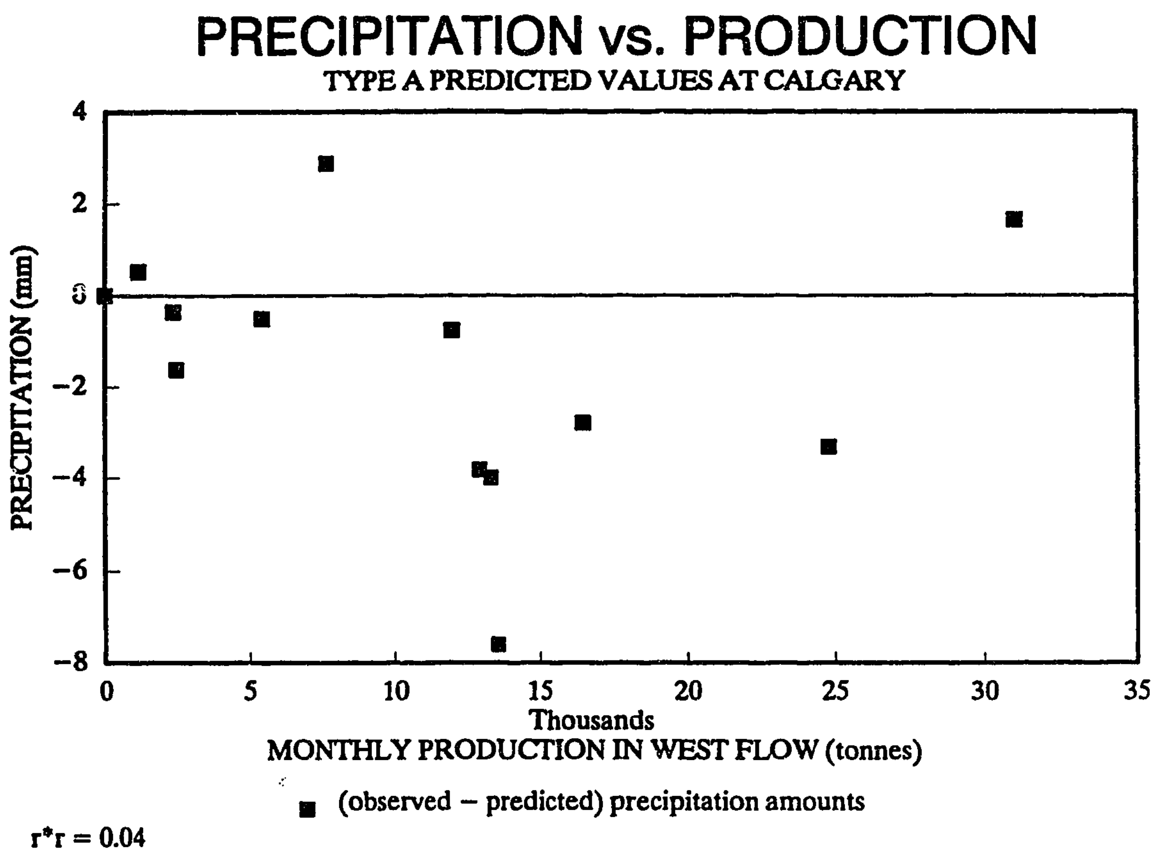

Figure 2.5: Relationship between type A residual precipitation amounts (determined when the predictor coefficient of determination was in excess of 0.90) and production amounts during westerly flow.

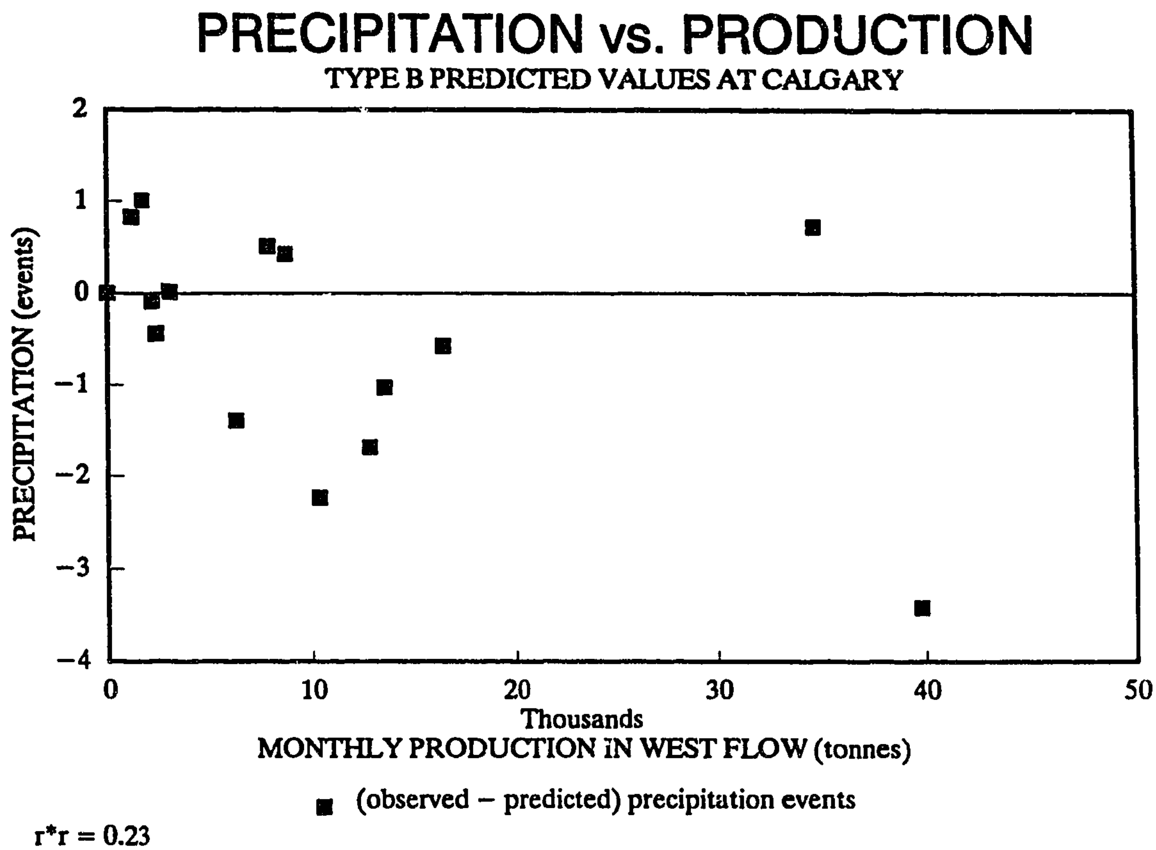

Figure 2.6: Relationship between type B residual precipitation events (determined when the predictor coefficient of determination was in excess of 0.90) and production amounts during westerly flow.

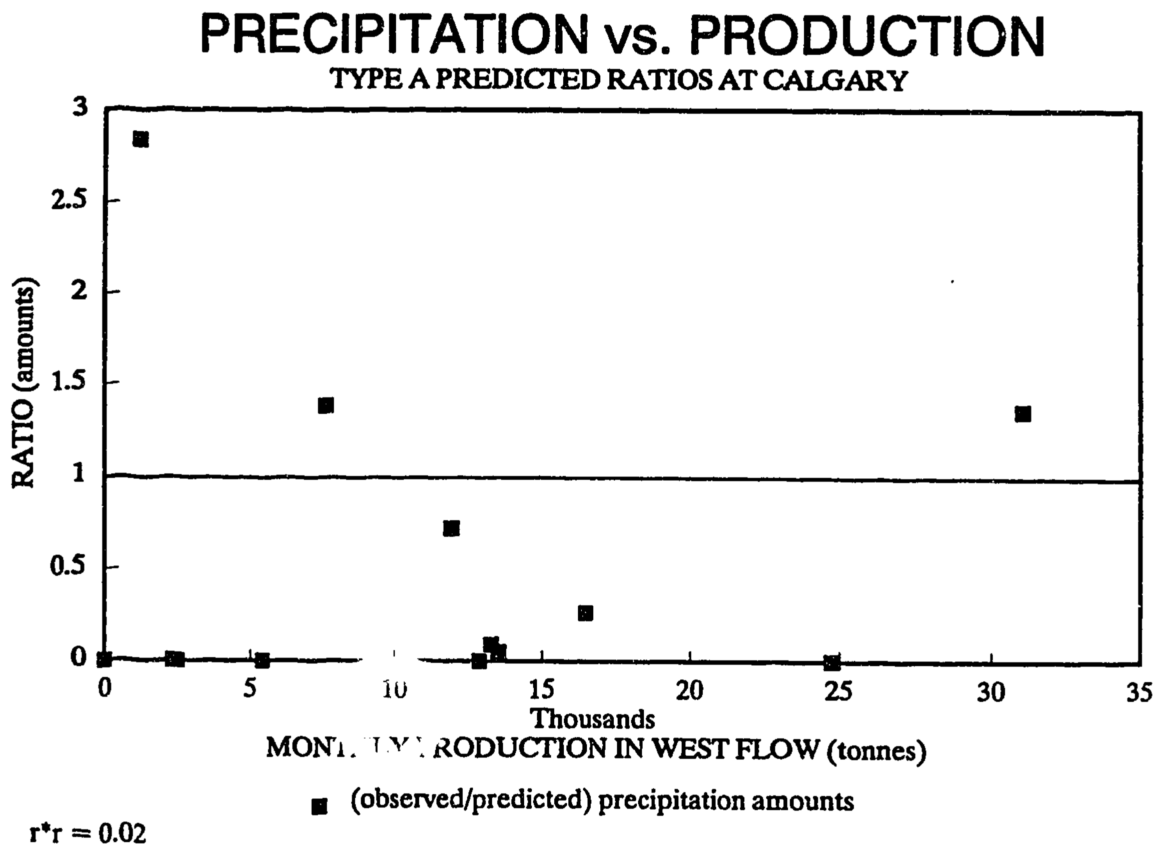

Figure 2.7: Relationship between the ratio of observed and type A predicted precipitation amounts (determined when the predictor coefficient of determination was in excess of 0.90) and production amounts during westerly flow.

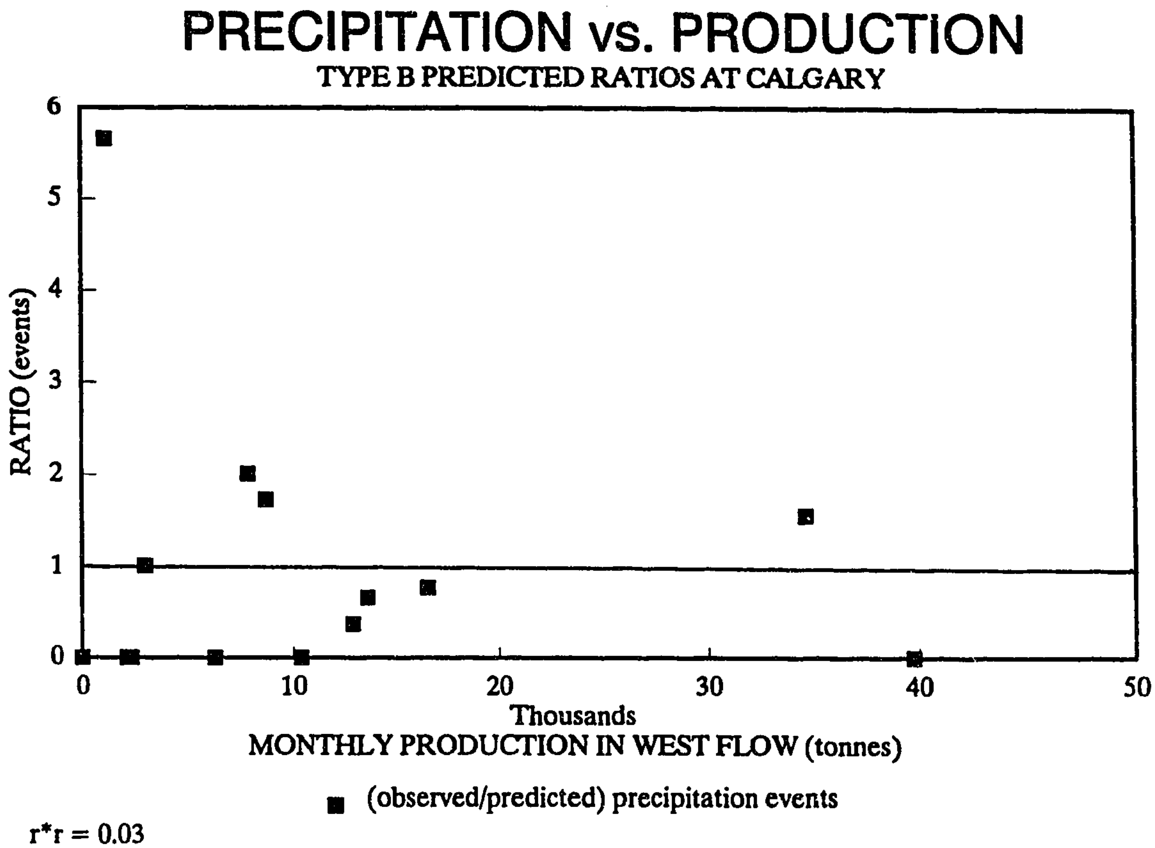

Figure 2.8: Relationship between the ratio of observed and type B predicted precipitation events (determined when the predictor coefficient of determination was in excess of 0.90) and production amounts during westerly flow.

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CHAPTER 3: INVESTIGATION OF THE ICE NUCLEATING PROPERTIES OF INDUSTRIAL PARTICULATES

3.1 Introduction and background

Situated at Exshaw, Alberta, 80 km west of Calgary and only minutes from the eastern entrance to Banff National Park, is a large mineral processing complex. In operation since the late 1800's and pre-dating the park, the complex contains three separate industries that produce cement, quicklime and magnesium oxide from local mineral deposits. These industries also emit large quantities of waste heat, water vapour and airborne particulate matter, including ice nuclei. Ice nuclei are fundamental to natural precipitation processes, and in commercial weather modification operations they are injected into clouds to stimulate rainfall or decrease hailfall. The discovery of ice nuclei in the vicinity and downwind of the cement plant was made during ad hoc Alberta Research Council airborne particle sampling flights in 1985, the author in attendance. In a subsequent climatological impact study (O'Dowd, 1994) it was postulated that such nuclei may modify the weather downwind at Calgary. Cement stack emissions, based on monthly production data, were compared to anomalous precipitation amounts, based on regional precipitation trends. Results were inconclusive as to the role of ice nuclei from the cement plant. Furthermore the statistical significance of differences between measured and predicted precipitation amounts at Calgary varied according to the testing technique, t-test results indicative of no difference at a 0.05 significance level, unlike Mann-Whitney U-test results which were supportive of a difference at the same significance level.

Explored in this chapter is the null hypothesis that anthropogenic ice nuclei from the industries located at Exshaw may have failed to induce changes in cloud processes due to some defect in particulate nucleation ability. Also explored is the corollary that poor production-precipitation correlation results could be the consequence of additional sources of ice nuclei that were not identified during the original 1985 airborne investigations.

In an attempt to rank the nucleating effectiveness of the various airborne and kiln products, and to further establish whether a causal link exists between effluent from any or all of the Exshaw facilities and downwind precipitation at Calgary, a simple laboratory experiment was designed. This experiment made use of factory supplied kiln and stack effluent samples obtained in June and July of 1994, and followed the procedures used by Murty and Murty (1972,1974) in establishing the effectiveness of Portland cement and quick lime as ice nucleants.

Four different processes permit the activation of natural or anthropogenic ice nuclei and induce freezing (Dennis, 1980). They are:

1. deposition, in which water vapour directly precipitates onto the nucleus substrate as ice. Latent heat release limits the effectiveness of this process at near-freezing temperatures,

2. condensation-freezing, in which a partially soluble particle first acts as a cloud-condensation nucleus, picking up a partial or complete liquid water sheath, and then prior to collision and coalescence, undergoes freezing,

3. contact nucleation, in which Brownian motion as well as thermophoresis and gravitational capture results in a chance collision between a supercooled cloud drop and a nucleus, and

4. bulk freezing, in which the nucleus is totally immersed in a water drop and freezes when supercooled temperatures are ideal. In the case of water soluble ice nuclei, protracted residence times may result in dissolution and partial deactivation.

The highest or warmest temperature at which a particle acts as an ice nucleator is considered to be its activation temperature. This threshold value is commonly used in comparing the effectiveness of various suspected nucleators. Much of the classical work in this field explores contact nucleation, and uses some form of cloud chamber (e.g. Mason and Hallett, 1956; Fukuta, 1958; Langer and Weickmann, 1971; Mason, 1971). To a lesser extent, bulk freezing has also been explored, using continuously cooled drops (e.g. Price and Gornick, 1967; Vali, 1971).

The advantages of bulk freezing experiments are twofold: the experimental equipment required can be fairly unsophisticated and robust, and where only activation temperatures are determined, experiments can be quickly run and repeated easily. The primary disadvantage of such experiments is that it is often difficult to produce drops of identical size, particularly where the surface tension of the drop is effected by differing water soluble nucleating agents. A second disadvantage is that bulk freezing of larger drops (e.g. 2 mm diameter) is not representative of actual cloud nucleation situations, where the largest cloud drop rarely exceeds 0.2 mm in diameter, and where most are closer to 0.02 mm (Dennis, 1980).

The water drops used by Murty and Murty (1972,1974) had a diameter of 2.2 mm, and a calculated spherical volume of 5.6 mm^3. These authors do not specify whether this was a mean, median, or mode value, or how they produced these drops. The drops used in the current experiment, produced using a glass Pasteur pipette, had a mean equivalent diameter of 2.4 mm, and a calculated spherical volume of 7.2 mm^3, approximately 29 % larger than the Murty and Murty drops. Equipment limitations prevented smaller drops of equivalent size and volume from being considered.

3.2 Tested materials

Three separate mineral processes take place at the industrial complex at Exshaw, each under the auspices of a separate company. Lafarge Canada Inc. (Lafarge), one of Canada's largest cement producing organizations, has the largest single facility at Exshaw. Baymag (Baymag), located adjacent to Lafarge, has been in operation at Exshaw since 1982 and uses the former Lafarge kiln 3 to produce magnesium oxide. Continental Lime Ltd. (Continental) is located 5 km east of the Lafarge-Baymag complex, and produces quicklime and crushed limestone.

For the purpose of inadvertent weather modification investigation, only stack samples were considered important, although both kiln and stack samples were tested. Stack samples consisted of particulates trapped by factory emission control equipment, and were not samples directly taken from the exhaust plume being vented to the atmosphere. Fugitive dust of kiln composition, rarely released and then only during loading and shipping operations, was evaluated as an ice nucleating agent for comparison with the results for Portland cement and quick lime (CaO) obtained by Murty and Murty (1972,1974). A physical description of the samples is presented in Table 3-1.

As indicated, all three industries provided the author with both raw kiln product and captured stack effluent. Lafarge and Baymag stack effluent was dry capture from an electrostatic precipitator (ESP). Lafarge provided samples from two different ESP circuits. Continental effluent was wet capture from a scrubber (effectively a fine water spray through which the stack exhaust stream passes prior to atmospheric release). All kiln products were unground and without additives, although commercial Portland cement contains up to 5 % gypsum to control setting times. Gypsum, a hydrated calcium sulphate, is a natural ice nucleating material with an activation temperature of -16°C (Mason, 1971).

In addition to industrial products and by-products, three other materials were tested: silver iodide, pure water and lake sediments. Commercially available purified silver iodide

(AgI) was used as a warm temperature control, having a high activation temperature. For bulk freezing, Murty and Murty (1972,1974) found this to be -4.2°C, and it was anticipated that none of the tested materials would induce freezing at temperatures above this. For a cold temperature control, distilled, de-ionized water was used. Pure water, lacking nucleation sources, can be strongly supercooled, and for small cloud drops (e.g. smaller than 10 μm) can reach temperatures as low as -40°C before homogenous nucleation occurs (Mossop, 1955). Murty and Murty (1972) found that 2.2 mm diameter double distilled drops would not freeze at temperatures as low as -9.8°C and Mason (1971) noted that 2.0 mm drops could be supercooled to as low as -35°C.

The final material tested was near-shore lake bottom sediment taken from Lac des Arcs, a shallow water body of approximately 250 ha (2.5 km^2) located immediately south of Exshaw and connected to the Bow River. Due to significant lake level fluctuations prior to 1991, large portions of the lakebed acted as a dust source, a local problem considerably exacerbated by prevalent strong and gusty winds. Since 1991, there has been an attempt to ameliorate this problem with the construction of a dyke across the lake. It is designed to both limit further sedimentation by keeping water in the main river channel that would have previously entered the lake, and can be closed, cutting off the lake from stream flow completely. During the 1985 sampling flights, very little lakebed was observed to be exposed, and therefore lakebed dust was believed to be at a minimum.

The lakebed dust is believed to be primarily of natural origin, containing organic matter and quartz, plagioclase, feldspars and various phyllosilicates - minerals characteristic of weathering of upstream sedimentary, metamorphic and igneous Cordilleran source rocks. No unfiltered liquid effluent from the Exshaw facilities is currently released into the lake or adjoining stream, although from 1939 to 1976 the predecessor of Lafarge used a different, water intensive process for cement production. It is unclear whether any anthropogenic sediments were released into the adjoining watercourses during this period. Of possibly related interest are the results of ad hoc geotechnical investigations of shore sediments in 1986, which revealed metastable thixotropic conditions. Thixotropy is a condition in which a solid/liquid system, effectively solid when at rest, will liquify and flow when subjected to shearing stresses (Whitten and Brooks, 1972). Fine arenaceous and argillaceous beach samples were found to be able to bear significant loads, but would spontaneously liquify when the load was rapidly removed or the surface was 'shocked' in some manner. A similar phenomenon has been observed in Champlain Sea (Leda) clays in eastern Ontario and western Quebec (e.g. Mitchell and Wong, 1973; Mitchell and Markell, 1974; Lefebvre and La Rochelle, 1974). These clays were deposited in a Pleistocene saline environment and were later rendered meta-stable through de-ionization of phyllosilicate lattices as a result of fresh water leaching, and through the dissolution of calcareous and amorphous cement bonds under low pH groundwater conditions (Bentley and Smalley, 1979). Unfortunately, no salinity or pH tests were made during the 1986 investigation, and with the disruption of the lake bottom with the construction of the dyke, this thixotropic activity has not been since observed.

3.3 Equipment and procedure

Twenty drops of 2.4 mm diameter, produced from a freshly prepared aqueous suspension of 2 grams of oven dried sample in 200 ml of distilled, de-ionized water, were placed on an ordinary glass (50 x 75 mm) slide. A single drop of ethylene glycol and water, chilled to approximately 0°C to counter sensor lag, was placed in the centre of the slide to ensure representative contact between the slide and the temperature measuring thermistor. The slide was transferred to the Styrofoam and Plexiglas insulated stage of a commercial Peltier-effect cold plate, and the thermistor lowered into contact with the plate and the glycol mixture. The drops were continuously observed through crossed polarizing filters, and the temperature (calculated from thermistor resistance) and time of both the first and last freezing events were noted.

Unfrozen drops would appear dark, whereas frozen drops, due to birefringence, would appear bright and coloured. The experiment was repeated at least five times, and the drops were under observation for up to ten minutes, lesser observation times being appropriate where total nucleation occurred and all drops froze. The aqueous suspension was then stored for one full day, and the experiments repeated to test the effect of "aging" (hydration or dissolution or chemical recombination). All glassware was triple rinsed in distilled, de-ionized water before use, and the accuracy of the thermistor was checked daily by using a well mixed ice-water temperature control. Fluctuations in stage temperature, acute during the positioning of the slide and thermistor, were partially dampened by the use of a 6 mm thick brass plate on the stage. The stage was allowed to come into thermal equilibrium before each experiment, and it was subsequently found that a measured slide temperature of -7.7°C was the cooling limit for the apparatus. Below this limit, the measured temperature would oscillate unpredictably, and sustained cooling was no longer guaranteed. A schematic diagram of the equipment is presented in Figure 3.1.

A ten minute test period was established as optimum for two reasons. The first related to minimizing the possibility of accidental nucleation. Vonnegut (1948) noted that in cold plate experiments the proportion of frozen to unfrozen drops increased with time, and concluded that nucleation was time dependent. Mason (1971) noted that this could also be due to an increasing probability of contact with an unrelated nucleating trigger (airborne contaminants or substrate). This was observed by the present author during preliminary trials of long duration (30 minutes), when the sublimation of atmospheric moisture onto the slide as hoar frost occurred. The frost grew dendritically, triggering nucleation in the supercooled drops on contact. A ten minute period was selected to minimize the chance of hoar initiation. The second reason for this test period related to equipment limitations. The measured slide temperature reached a steady minimum value only after the cold plate had been in operation for at least six minutes and in some cases as long as 20 minutes. Ten minutes was selected as a compromise between table temperature stability and the possibility of accidental nucleation.

The stack samples provided by the various industrial sources contained uniformly clay-sized particles. The kiln samples had a broader size distribution, containing clay to pebble sized particles. In the case of the kiln products of Lafarge and Baymag, additional manual grinding was necessary to provide a sufficient quantity of fine clay sized material for testing. As these unhydrated kiln materials were considered crystalline with perfect cleavage, grinding was believed to reduce the crystal size rather than change the morphology. Conchoidal fracturing was conceded to be present, but because it also could be expected in the natural mill environment, was deemed to be acceptable. A geological classification of particulate size is presented in Table 3-2.

3.4 Sample chemistry

Chemical and crystallographic properties play a significant role in ice nucleating ability (e.g. Vonnegut, 1947; Thangaraj et al., 1988), and are useful in comparing different potential nucleators. Summarized in Tables 3-3a and 3-3b are relevant crystal parameters of common dry and hydrated stable forms of the tested materials. References for these tables are numerous, and include Palache et al. (1944,1951), Donnay (1963), Pounder (1965), Deer et al. (1967), Ramachandran (1984) and Weast (1989). In cases of conflicting crystal data, the most recent data has been cited. Kaolinite, an alteration product of feldspars and other aluminum bearing minerals (Mottana et al., 1978), has been included as it is a common, naturally occurring nucleator (Mason, 1971) that may be present in lakebed sediments. Many cement hydration products are not presented as they are either xerogels with ill-defined crystallography or form too slowly to be of interest. Readers interested in a full list of cement and cement hydration products are referred to Table 1.2 (pp. 9-10) of Ramachandran (1984).

Crystal size and shape, particularly those similarities with hexagonal natural ice crystals, are discussed in view of nucleation results in Section 3.6. Readers unfamiliar with inorganic chemistry may wish to consult additional references on mineralogy and crystallography. The introductory pages of Mottana et al. (1978) provide a particularly concise description of crystal symmetry and unit cells.

3.5 Results

The results of the activation temperature experiments are presented in Table 3-4. This table also includes data on the final temperature at which all drops nucleated/froze. Where initial or final freezing was incomplete, the percentage of successful test runs is indicated. A test run was rated incomplete if liquid drops remained after ten minutes at a measured stage temperature of less than -7.7°C. As mentioned previously, although the cold plate was capable of lower temperatures than this, further cooling was unstable and erratic. The table also provides similar data for aged samples that remained in solution for a full day.

3.5.1 Airborne particulate results

Of the five potential airborne samples, the freshly mixed lake bottom sediments from Lake des Arcs had the highest average activation temperature (-4.2°C) and the widest activation temperature spread, ranging from -1.1 to -5.8°C. The Continental scrubber (stack) samples followed at -4.9°C, and showed a better overall nucleating capacity, with all drops activated at an average temperature of -5.7°C, compared to -6.7°C for the lake samples. The Baymag ESP samples, ranked third, saw initial activation in 100 % of test runs at an average temperature of -6.1°C. Total activation occurred in 50 % of the test runs at an average final temperature of -7.3°C. The Lafarge ESP A samples, ranked fourth, had an average activation temperature of -6.1°C, but only 20 % of test runs saw total activation after 10 minutes of cooling. The Lafarge

ESP B samples, ranked last, showed both the lowest percentages of initial and total nucleation runs, as well as the lowest average temperatures for these runs. Only 50 % underwent initial activation at an average temperature of -6.7°C, and only 17 % underwent total nucleation at an average final temperature of -6.9°C. The remaining 83 % of test runs remained liquid to below -7.7°C. The range of observed activation temperatures was also the narrowest for these lowest ranked Lafarge nucleators.

The Lafarge results are consistent with the observation that smaller particles nucleate at lower temperatures (e.g. Vonnegut, 1947; Fletcher, 1959). Lafarge airborne effluent contains a weight percentage of smaller particles well in excess of that of either Continental or Baymag, with 83 % of particles measuring less than 0.3 µm in diameter.

The overall ranking and average activation temperatures for fresh airborne samples are as follows:

1.	lake sediments	-4.2°C	
2.	Continental scrubber	-4.9°C	
3.	Baymag ESP	-6.1°C	
4.	Lafarge ESP A	-6.1°C	
5.	Lafarge ESP B	-6.7°C	50% incomplete

With aging, the ranking of the airborne particulates changed. Baymag ESP samples showed noticeable improvement on hydration, with an average initial activation temperature of -4.7°C and an average total nucleation temperature of -6.5°C. The Continental scrubber samples showed a 0.5°C decrease in the average activation temperature to -5.4°C, but no change in the average total nucleation temperature (-5.7°C). Although this decrease in initial activation temperature is consistent with the results of Murty and Murty (1974) for pure CaO for the same time period, their nucleation temperatures underwent a larger change, falling a minimum of 5.6°C. This suggests that Continental scrubber particles may be of a different chemistry or morphology, containing clay and sulphide undesirables naturally present in the host rock and not present in the final kiln product. The hydrated lake sediments, now ranked as third, showed a 1.2°C drop in average initial activation temperature, decreasing to -5.4°C, with a 20 % drop in successful total nucleation test runs. Although the Continental scrubber and lake sediments have the same average initial activation temperature, the former is considered the superior nucleator on the basis of its warmer average complete activation temperature (-5.7°C). Ranking was based on average initial nucleation temperature, with identical values further ranked on the basis of their average complete nucleation temperature. The Lafarge ESP samples showed lower activation temperatures and a higher incidence of incomplete initial and total nucleation. ESP A showed only 40 % of test runs underwent initial nucleation at an average temperature of -6.3°C. ESP B showed the same incomplete initial nucleation rate, with successful test runs averaging -7.0°C. However, the latter showed an improvement in complete nucleation test runs, up from 17 % to 40 %.

The variability of initial nucleation temperatures for the aged samples appears to be similar to that for the fresh samples, with a narrow range of values for Lafarge and Baymag ESP samples, and a broader range for lake and scrubber samples. However, as both the Lafarge ESP A and B samples exhibited high incidence of incomplete nucleation at an experiment closing temperature of -7.7°C, their true range of initial activation temperatures may be wider than suggested here.

The overall ranking and average activation temperatures for aged airborne samples are as follows:

1.	Baymag ESP	-4.7°C	
2.	Continental scrubber	-5.4°C	
3.	lake sediments	-5.4°C	
4.	Lafarge ESP A	-6.3°C	60% incomplete
5.	Lafarge ESP B	-7.0°C	60% incomplete

3.5.2 Kiln particulate results

Of the three kiln samples, the Lafarge cement product was the best nucleator, activating at an average temperature of -6.4°C, with complete nucleation occurring at an average of -6.7°C in all test runs. Despite the highly heterogeneous composition of cement (Ramachandran, 1984), the Lafarge samples also exhibited the narrowest range of initial activation temperatures (-6.3 to -6.5°C), suggesting the presence of a single nucleator. The Baymag MgO kiln product activated at -7.3°C, but only 20 % of experiments reached complete nucleation. The Continental quick lime (CaO) kiln product had an initial activation temperature of -7.5°C, but only 40 % of experiments underwent initial activation and reached complete nucleation. This CaO activation temperature is at variance with the Murty and Murty (1974) results, where CaO was found to have a comparable activation temperature to that of silver iodide.

The overall ranking and average activation temperatures for fresh kiln samples are as follows:

1.	Lafarge cement	-6.4°C	
2.	Baymag MgO	-7.3°C	
3.	Continental CaO	-7.5°C	60% incomplete

With aging, the kiln products, like the airborne samples, showed a change in overall ranking, with two cases showing a definite improvement in nucleating ability. Again the Baymag product showed improvement, with the average temperature of activation increasing from -7.3°C to -4.3°C, and the number of experimental runs undergoing complete nucleation increasing from 20 % to 50 %. The Lafarge samples also showed an increase in the average activation and total nucleation temperatures (-5.1°C and -5.9°C) but a decrease in the number of complete nucleation runs. The Continental kiln product, again ranked as the poorest potential ice nucleator, showed no initial nucleation in any experiment. The range of initial activation temperatures for Baymag and Lafarge increased significantly over that of their non-hydrated counterparts, a possible consequence of the evolution of new nucleators of varying size.

The overall ranking and average activation temperatures for aged kiln samples are as follows:

1.	Baymag MgO	-4.3°C	33% incomplete
2.	Lafarge cement	-5.1°C	20% incomplete
3.	Continental CaO	< -7.7°C	100% incomplete

3.5.3 Other particulate results

The results for pure water (distilled, de-ionized) were consistent with those of Murty and Murty (1972), with no initial nucleation observed in the course of maximum drop cooling. However, in an earlier series of preliminary test runs using pure water drawn from an open beaker, an average activation temperature of -3.9°C was observed. This value may be attributable to either accidental mechanical nucleation due to hoar frost or scratches on the cooling surface, or to contamination by atmospheric dust particles. Vonnegut (1947) speculated that airborne silver particles caused by sparks at silver or silver-bearing copper electrical contacts may be naturally present in laboratory air.

The results for silver iodide (AgI), one of the most commonly used commercial cloud seeding agents, were initially puzzling. Average initial activation temperatures in all test runs were above 0°C, a situation clearly impossible under conditions of normal atmospheric pressure. Clearly, equipment response lag was being indicated, with the thermistor initially cooling at a slower rate than the stage cooling surface. Figure 3.2 shows a typical cooling curve for the experiment.

Application of a correction factor based on silver iodide was considered, but rejected for two reasons. The first was that although Murty and Murty (1972, 1974) found the average activation temperature for bulk freezing of AgI to be -4.2°C, their published experimental data was unclear as to the size of the AgI particles used. Fletcher (1959) computed the theoretical size of AgI particles required for successful activation over a range of 0 to -20°C, and noted that larger particles activate at warmer temperatures. Similarly, Gerber et al. (1970) noted that the minimum AgI diameter necessary for activation at -20°C (0.020 μm) was smaller than that for -15°C (0.025 μm). Furthermore, other experimenters have found differing values for activation, with a high value of -2.6°C observed by Fukuta (1958) in contact nucleation experiments. The size distribution of AgI particles that contributed to nucleation in the present experiment was not determined and consequently a correction factor would be as uncertain as the distribution.

The second reason for rejecting a correction curve was that in the first 60 seconds of the experiment, where temperature change, and presumably the thermistor lag, was the greatest, only AgI was found to undergo initial activation. This suggests that while AgI results are in error, the remainder of the results are, at worst, correct in a relative sense, and at best, absolutely correct. Since one of the prime objectives of this experiment was to rank the nucleating ability of the various Exshaw facilities to help establish whether the Lafarge facility may have been misidentified as the ice nucleating source during 1985 aerial sampling missions, further work was deemed superfluous.

Silver iodide was also tested at 24 and 48 hour aging periods. A small decrease in both initial and complete nucleation temperatures was noted, and was possibly attributable to ultraviolet photodeactivation (e.g. Inn, 1951; Reynolds et al., 1951). It is this reaction to photons, though primarily at visible and near-infrared energy levels, that causes silver halides in photographic film emulsions to become elemental silver, producing a negative image. Partial dissolution of miersite, the weakly soluble cubic form of AgI, may also have contributed to the observed degradation of nucleating ability.

The overall ranking for fresh samples based on average activation temperatures are as follows:

1.	AgI	+1.8°C	
2.	lake sediments	-4.2°C	
3.	Continental scrubber	-4.9°C	
4.	Baymag ESP	-6.1°C	
5.	Lafarge ESP A	-6.1°C	
6.	Lafarge kiln	-6.4°C	
7.	Lafarge ESP B	-6.7°C	50% incomplete
8.	Baymag kiln	-7.3°C	
9.	Continental kiln	-7.5°C	60% incomplete
10.	pure water	< -7.7°C	100% incomplete

The overall ranking for aged samples again based on average activation temperature are as follows:

1.	AgI	+1.3°C	
2.	Baymag kiln	-4.3°C	33% incomplete
3.	Baymag ESP	-4.7°C	
4.	Lafarge kiln	-5.1°C	20% incomplete
5.	Continental scrubber	-5.4°C	
6.	lake sediments	-5.4°C	
7.	Lafarge ESP A	-6.3°C	60% incomplete
8.	Lafarge ESP B	-7.0°C	60% incomplete
9.	Continental kiln	< -7.7°C	100% incomplete
10.	pure water	< -7.7°C	100% incomplete

3.6 Discussion

The ability of any of the Exshaw particles to induce freezing is a function of a number of particle properties. These properties, summarized by Thangaraj et al. (1988), include (1) lattice match and crystal morphology, (2) solubility, (3) particle size, (4) polarizability, (5) hydrophobicity and hydrophilicity, (6) surface charge, and (7) number and strength of surface sites capable of adsorbing water molecules.

In the classic work carried out by Vonnegut (1947), lattice match was investigated, with silver and lead iodides (AgI and PbI_2) determined to be similar to ice and consequently have nucleating potential. When water freezes, it forms a hexagonal crystal, with an a-axis length of 4.523 Å, a c-axis length of 7.367 Å, and a a:c axis ratio of 1:1.629 (Pounder, 1965). AgI occurs in three forms at standard temperature and pressure (STP) - hexagonal iodyrite, hexagonal silver iodide and cubic miersite, the latter weakly soluble in water (Weast, 1989). The a:c axis ratios for the hexagonal forms are 1:1.635 and 1:1.633 respectively, and both have a unit crystal size approximating that of ice. Table 3-3a contains similar crystal lattice data for the other particles evaluated in the course of this investigation. These are discussed below on a source-by-source basis.

3.6.1 Continental discussion

The isometric Periclase group crystal lime (CaO), formed during the calcination of limestone ($CaCO_3$), is believed to be the primary mineralogy in Continental kiln and stack samples. CaO is a non-ideal ice nucleator. Its size and symmetry differs from that of ice and its activation temperature is low. On hydration, the nucleating potential of CaO decreases even further and may be attributable to a reaction with dissolved carbon dioxide (CO_2) in which some of the CaO reverts back to a hydrated parent calcite ($CaCO_3 * nH_2O$) form. A recent study of fugitive dust in the Bow Valley partially supports this conclusion (H. Bertram, personal communication, 1994). Although the $CaCO_3$ substrate is hexagonal and a potential nucleator at -7°C (Mason, 1971), it appears that the sheath of water molecules increases the crystal size and changes the axis ratio sufficiently to impair its nucleating ability. Had the CaO simply hydrated to the intermediate mineral portlandite ($Ca(OH)_2$), a slight improvement in nucleation might have been anticipated. Portlandite is a hexagonal layered mineral of the Brucite group, and forms flat hexagonal platelets (Bye, 1983) resemblant of snow flakes. However, portlandite crystals are smaller than ice crystals and have a different a:c axis ratio, factors that may offset some of the nucleating advantage due to symmetry. Lesser amounts of limestone, dolomite and sedimentary impurities, including phyllosilicates, inferred to be present in stack particulates, may account for the warmer nucleation temperatures observed for these stack samples. Limestone and dolomite are both hexagonal with an a-axis length close to that of ice.

3.6.2 Baymag discussion

The isometric crystal periclase (MgO) is believed to be the primary mineralogy of Baymag kiln and stack samples. Formed through the calcination of magnesite ($MgCO_3$), MgO crystals are smaller than ice crystals, and like CaO are non-ideal ice nucleators. On hydration, however, their nucleating ability improves significantly. This change is most likely attributable to the formation of the intermediate hydration product brucite ($Mg(OH)_2$). Brucite, the magnesium parallel of portlandite, is hexagonal and forms clusters of thin platelets. Base crystals are smaller than ice, but have a similar a:c axis ratio. In time, however, brucite will react with periclase and dissolved carbon dioxide to form the end hydration product hydromagnesite (e.g. Deer et al. 1967). Hydromagnesite occurs in several orthorhombic and monoclinic forms according to the number of bound water molecules, and in all cases the base crystal is larger than that of ice and has a dissimilar morphology. These final hydration forms are considered to be non-ideal nucleators. Based on the improvement in nucleating ability observed, it would appear that brucite remains relatively unchanged after a 24 hour hydration period.

3.6.3 Lafarge discussion

Unlike Continental and Baymag, the kiln and stack samples of Lafarge are highly heterogeneous in terms of chemistry and morphology. The nucleation improvement on hydration observed for the kiln product, near-Portland cement, and the decay in nucleation observed for both types of Lafarge stack sample also suggests a compositional difference between these two particulate streams.

Unhydrated Portland cement has four main constituents (Bye, 1983):

1) tricalcium silicate Ca_3SiO_5
2) dicalcium silicate Ca_2SiO_4
3) tricalcium aluminate Ca_3AlO_3
4) tetracalcium aluminoferrite Ca_4AlFeO_3

Both tri- and dicalcium silicates are orthosilicates consisting of discrete SiO_4^{-4} tetrahedra in a variety morphologies. Together they account for between 75-80% of Portland cement (Ramachandran, 1984). Their symmetry increases with temperature of formation and two stable hexagonal forms exist, although other hexagonal, orthorhombic and monoclinic forms can exist in an unstable state (Donnay, 1963). The tricalcium form has a crystal a:c axis ratio of 1:3.523 and an a-axis length of 7.080 Å, significantly different from that of ice. The dicalcium form, also with a larger a-axis length than ice, has a axis ratio of 1:1.238 similar to that of portlandite (1:1.332), which is a suspected nucleator. Tricalcium aluminate and tetracalcium aluminoferrite are potentially poorer nucleating structures, being cubic and orthorhombic respectively (Bye, 1983). The ice nucleation results of Murty and Murty (1972) for Portland cement suggest that activation occurs near -5°C which is probably attributable to a significant dicalcium silicate content with a particle size distribution wide enough to ensure an optimum-sized particle will activate. It is unclear whether there was a significant gypsum or admixture content in their tested samples, or whether the samples were heated to eliminate atmospheric moisture, which could have triggered the hydration and setting process creating new silicate products.

On cement hydration, or, more properly, hydrolysis (Bye, 1983), the tricalcium and dicalcium silicates form calcium hydroxide (portlandite) and several poorly crystalline calcium silicate xerogel hydrates. As discussed earlier, portlandite has some potential as an ice nucleator. However, the hydration process here is a slow and steady one, taking up to 28 days for tricalcium silicate and up to a year for dicalcium silicate (Eglinton, 1987), and is unlikely to be the main cause of improved nucleation.

Tricalcium aluminate, on hydration, forms strongly crystalline hydration products (Bye, 1983) and these are postulated to be the main reason for improved nucleation. These crystals are platelets of hexagonal symmetry, resemblant of portlandite, and form very rapidly during flash hydration (Eglinton, 1987). Significant heat is evolved and the process is often measured in hours. However, these forms are thermodynamically unstable, and will ultimately convert to a more stable cubic form (Ramachandran, 1984) that would likely be a poorer ice nucleator. Ettringite or woodfordite ($Ca_6Al_2(SO_4)_3(OH)_{12} * 26H_2O$) is also produced when gypsum is present, and though hexagonal in crystal structure, forms acicular crystals with an a:c axis ratio of 1:1.9084 (Palache et al., 1951), dissimilar to ice. These crystals are also very large, with an a-axis length of 11.240 Å, approximately 2.5 times larger than that of ice (4.523 Å). Ettringite crystals retard growth of tricalcium aluminate hydration products and thereby control the setting time of the concrete mix.

The hydration of tetracalcium aluminoferrite, the fourth main cement constituent, is slower than that of the tricalcium aluminate. Both iron-substituted hexagonal hydrates and cubic hydrogarnets are produced, particularly if CaO is present (Bye, 1983). While these hexagonal hydrates, like those from the hydration of tricalcium aluminate, could act as ice nucleators, the longer setting time suggests that the two hydration products do not co-exist, at least in the time frame used for the aging experiments.

3.6.4 Lakebed discussion

Phyllosilicates, including kaolinite, are believed to be the primary nucleating agents present in lakebed samples taken from Lake des Arcs. Although generally monoclinic or triclinic, these layer-lattice minerals often exhibit a pseudo-hexagonal habit (Mottana et al., 1978) that may account for their observed nucleation properties (e.g. Mason, 1971; Houghton, 1985). During hydration, water molecules are bound along the negatively polarized crystal perimeter (Deer et al., 1962) changing the size and shape of the crystal and presumably its nucleating ability. On hydration, the lakebed samples were observed to nucleate at a lower average temperature, consistent with sheathing of substrate morphology by bound water molecules. For kaolinite, hydration results in a tubular structure similar to that of halloysite, although the latter forms in a different environment (Hurst and Kunkle, 1985) and incorporates hydroxyl molecules directly within its layered structure (Deer et al., 1962). The range of initial nucleation temperatures measured for lakebed samples was very wide, suggestive of a wide variety of mineralogies present. Mason (1971) notes a broad nucleating range for phyllosilicates, consistent with this premise.

3.7 Commercial applications

It has long been recognized that insoluble particles are the best commercial nucleating agents (e.g. Fukuta, 1958; Dennis, 1980). Unlike soluble particles, they theoretically remain isochemical and isomorphic in a cloud environment, and react in a predictable manner. However, the results of this study suggests that kiln and stack waste products from some of the Exshaw operations, despite being polychemical, polymorphic and in some cases, exothermically reactive, could be employed as low cost alternative cloud-seeding agents.

The apparent commercial usefulness of any of the Exshaw industrial particulates, kiln and stack alike, is evident from the ranking below, based on average activation temperature where all test runs exhibited some initial nucleation:

1.	Baymag ESP (hydrated)	-4.7°C (-3.7°C)
2.	Continental scrubber (dry)	-4.9°C (-3.1°C)
3.	Continental scrubber (hydrated)	-5.4°C (-4.1°C)
4.	Lafarge ESP A (dry)	-6.1°C (-4.8°C)
	Baymag ESP (dry)	-6.1°C (-5.6°C)
5.	Lafarge kiln (dry)	-6.4°C (-6.3°C)
6.	Baymag kiln (dry)	-7.3°C (-6.1°C)

In support of this ranking system, it was noted that an alternative ranking based on the highest (rather than the average) initial nucleation temperature produced virtually the same results, with only minor switching at the scale extremes. When applied to the data in Section 3.5, only minor changes in the intermediate rankings were observed. The highest initial nucleation temperatures are presented above in brackets.

As indicated earlier, while the measured activation temperatures allow for relative ranking of the various particulate sources, they are not necessarily useful in absolute ranking against well documented insoluble agents, such as AgI, PbI_2 or the organic nucleator Pseudomonas Syringae. It is likely that the absolute activation temperatures of the Exshaw particulates are as much as two degrees lower than indicated above. Even so, these activation abilities would be considered good, with the more chemically and morphologically predictable Baymag and Continental kiln and stack products being the best commercial choices. The low cost of these products and the virtual ubiquity of calcining operations around the world makes these products an attractive cloud-seeding option.

Unlike commercial distribution systems for silver iodide that vaporize the seeding medium and allow it to cool and precipitate, a purely mechanical distribution system would be needed for the Exshaw products. Like Pseudomonas Syringae, the Exshaw products are in their final form and simply need to be dispersed as a fine aerosol. Though likely to be impractical for direct or updraft target commercial cloud seeding due to their low density and tendency to coagulate, such aerosols may be an option for wide area ground-based broadcast seeding, such as is done in France (Dessens, 1986) and in Spain (Sanchez et al., 1988). Through injection into existing high temperature or high velocity gas emission streams situated upwind of a target area, these particles would possibly permit seeding under conditions often impractical or hazardous for airborne platforms. A number of industrial processes, including many in the petrochemical industry, have airborne exhaust streams that are suitable candidates for SPINSEED (solid particle injection seeding).

3.8 Conclusion

The objective of these nucleation experiments was to rank the nucleating abilities of natural and anthropogenic Exshaw particulates, and to further determine the likelihood that airborne effluent from the Lafarge kilns was the exclusive source of ice nuclei detected in the 1985 aerial sampling flights (Heimbach, 1986). Despite the equipment response lag and the lack of absolute activation temperatures, results suggest that lake bottom sediments may be a significant source of natural ice nuclei when lake levels are low. Additionally, the unhydrated output from the Continental stacks could also be considered a strong possible ice nuclei source. However, while this airborne effluent appears to be superior in nucleating ability to effluent from Lafarge or Baymag, when ice nuclei production rates and downwind concentrations are considered, the ranking potentially changes. Lafarge produces far more particles and therefore potential nucleators than either Baymag or Continental (Table 3-5), with the downwind ice nuclei concentration at Calgary estimated to be approximately 2600/litre. This is more than two orders of magnitude greater than necessary for optimum precipitation production (1/litre to 10/litre; Braham, 1986). If, however, particle coagulation occurs, as was reported by Vdovin et al. (1974), then the downwind concentration of Lafarge produced ice nuclei could fall to values comparable to those for Baymag and Continental, two to three orders of magnitude below optimum, and within background levels measured between Exshaw and Calgary (Heimbach, 1986).

Cement plant nucleation is a complicated issue. While the Lafarge ESP particulates from Exshaw have potential as ice nucleators, the efficacy of such airborne effluent is unquestionably a function of source rock geology and fuel type, and is further complicated by preferential ESP capture, exothermic hydration and particulate size. The highly heterogenous nature of the kiln raw materials, particularly additives of shale and fly ash (Gnosh, 1983), play a significant role in the composition of stack effluent. The introduction of chemical wastes into the kilns for destruction (not currently carried out at Exshaw) and the use of automobile tires as a fuel supplement (evaluated by Lafarge in May of 1993 and operationally used by Inland Cement in Edmonton, Alberta) also modifies the composition of both kiln and stack particulates, and undoubtably has an effect on their nucleating ability.

In addition, there is evidence that during cement production vaporized alkali chlorides and sulphates that precipitate on kiln particles are preferentially captured by ESP equipment (Portland Cement Association, 1992), and that escaping particles may be lacking these soluble salts. Thangaraj et al. (1988) observed that purified silver iodide was a poor nucleator until doped with copper and bromine impurities that acted as hydrophilic centres on the insoluble substrate, and such kiln volatiles may act in a similar capacity. The Lafarge ESP B capture, being from the first fields of the ESP and being part of a closed circuit that returns this dust to the kiln, is probably more representative of true stack effluent. The ESP A capture from the last ESP fields are finer and enriched in alkali chlorides and sulphates, and were shown to be superior to ESP B nucleators. Due to lower kiln temperatures and fewer additives, particulate capture from the Baymag ESP would also be lacking such salts. As a further complication in the nucleation process, it is likely that heat evolved during flash hydration of tricalcium aluminate limits the efficiency and effectiveness of these nucleators, much like the release of latent heat impairs the effectiveness of deposition activation. Altogether, these factors render ESP dust a unique and site specific product.

The relevance of hydrated (aged) results to downwind weather modification is unclear. The applicability of 24 hour hydrated residence times may not be reasonable for straight line air transport, as an average wind speed of 3.3 km/hr would be needed for particles to arrive over Calgary, 80 km away. The twenty-five year (1955-1980) normal average wind speed for westerly flow is 26.0 km/hr, for west-southwesterly flow it is 18.4 km/hr, and for west-northwesterly flow it is 21.1 km/hr (Environment Canada, 1982). While the hydrated results may appear, on this basis, to be of academic interest alone, there are additional reasons for their inclusion. First, it should be noted that all of the Exshaw facilities liberate considerable water vapour and that particulate temperatures are significantly elevated. This combination could be expected to accelerate the hydration process. In addition, the hydration process is an on-going one, and significant hydration may occur in advance of 24 hours. Murty and Murty (1974) noted that CaO, after only 4 hours in solution, would no longer act as a nucleator at temperatures above -9.8°C. Furthermore, there has been reported in the literature (e.g. Bowen, 1966; Bigg and Turton, 1986) cases of unusually long periods of persistence of cloud-seeding materials, well beyond the expected natural ventilation period. It therefore seems possible that these hydration products play some role in weather modification, particularly those produced by Baymag and, to a lesser extent, those produced by Continental.

In conclusion, based on both the nucleation results of this study and ice nuclei production rates estimated from factory supplied emission data, Lafarge appears to be the single most significant source of ice nuclei with potential to effect precipitation at Calgary. However, if coagulation of Lafarge airborne particulates occurs, then estimated Exshaw-produced anthropogenic ice nuclei concentrations downwind at Calgary could be below that required for effective cloud seeding. Although both Baymag and Continental produce more effective ice nuclei, production rates are lower, and these nuclei may only influence cloud processes in the vicinity of Exshaw. If the mineralogical composition of kiln source material has remained constant over the years, then it is likely that both Baymag and Continental contributed to the 1985 measured ice nuclei signatures. This may account, in part, for the lack of a pronounced trend in the comparison of weighted Lafarge production amounts and anomalous precipitation at Calgary (O'Dowd, 1994).

TABLE 3-1. Sample descriptions.

Number	Sample	Description
1	Water	distilled, de-ionized, clear
2	Silver iodide	purified, uniform yellow grey colour with a fine crystalline form, generally silt sized particles that form a bright yellow suspension that quickly settles
3	Baymag stack electrostatic precipitator (ESP)	fine white clay-sized powder, even texture, uniform sized, settles and solidifies on hydration with no colour change, but easily disturbed and re-suspended
4	Baymag kiln	yellow-brown silty powder with some larger grains to 1 cm, darkens slightly on hydration
5	Continental stack scrubber	fine white clay-sized powder, even texture, uniform sized, easily suspended in water with no colour change
6	Continental kiln	dark-grey brown non-uniformly sized mixture of friable coarse and fine grains, cements on hydration with a yellow grey appearance
7	Lafarge electrostatic precipitator "A" (ESP A)	very light grey dust, even chalky texture, uniformly clay sized, hydrates into a milky suspension, does not solidify
8	Lafarge electrostatic precipitator "B" (ESP B)	grey dust, even texture, uniformly clay sized, hydrates into dark grey suspension, does not solidify
9	Lafarge kiln	coarse silt to gravel sized dark grey-black grains, settles rapidly and solidifies on hydration, with no colour change, can be agitated after setting to form fine colloidal suspension of floccuals
10	Lake bottom	light grey-brown sediments, generally arenaceous though some rudaceous clasts present, some organic matter, darkens on hydration

TABLE 3-2. Particle size terminology. From Whitten and Brooks, 1972.

Size range	Particle classification
> 256 mm	boulder
64-256 mm	cobble
4-64 mm	pebble
2-4 mm	gravel
1/16-2 mm	sand
1/256-1/16 mm	silt
< 1/256 mm	clay

TABLE 3-3a. Chemical and crystallographic data.

chemistry	type[1]	a axis (Å)	b axis (Å)	c axis (Å)	a:c axis ratio[3]
AgI	h h i[2]	4.583 4.586 5.044	-- -- --	7.516 7.490 --	1:1.635 1:1.633 1:1.000
$Al_2Si_2O_5(OH)_4$	t[2] m[2]	7.250 14 337	8.890 8.882	5.130 5.145	-- --
$Al_2Si_2O_5(OH)_4$ * $2H_2O$	m[2]	10.250	8.920	5.200	--
CaO	i	4.812	--	--	1:1.000
$CaCO_3$	h	4.983	--	17.020	1:3.416
$Ca(OH)_2$	h	3.640 3.584 3.582	-- -- --	4.850 4.896 4.904	1:1.332 1:1.366 1:1.369
$CaCO_3$ * nH_2O	h	10.62 6.150 6.150	-- -- --	7.540 4.955 30.470	1:0.710 1:0.806 1:4.954
Ca_2SiO_4	h o[2]	5.460 6.750	-- 11.150	6.760 5.040	1:1.238 --
Ca_3SiO_5	h	7.080	--	24.940	1:3.523
Ca_3AlO_3	i[2]	7.639	--	--	1:1.000
Ca_4AlFeO_3	o	5.520	14.440	5.340	--
$Ca_6Al_2(SO_4)_3(OH)_{12}$ * $26H_2O$	h	11.240	--	21.450	1:1.908
H_2O	h	4.523	--	7.367	1:1.629
MgO	i[2]	4.211	--	--	1:1.000
$MgCO_3$	h	4.579	--	14.845	1:3.242
$Mg(OH)_2$	h	3.114	--	4.735	1:1.521
$Mg_5(OH)_2(CO_3)_4$ * $4H_2O$ $MgCO_3$ * $3H_2O$ $MgCO_3$ * $5H_2O$	o[2] m o[2] m	8.920 12.000 7.680 12.480	9.320 5.390 12.000 7.550	8.420 7.680 5.390 7.340	-- -- -- --

[1] crystal symmetries: h=hexagonal, i=isometric, m=monoclinic, o=orthorhombic, t=triclinic.
[2] other crystal dimensions also occur.
[3] axis ratios for isometric and hexagonal crystals.

TABLE 3-3b. Chemical nomenclature.

chemistry	primary source[1]	common name
AgI	n/a	silver iodide iodyrite miersite
$Al_2Si_2O_5(OH)_4$	N	kaolinite metahalloysite
$Al_2Si_2O_5(OH)_4 * 2H_2O$	N	halloysite
CaO	C	lime
$CaCO_3$	C	calcite
$Ca(OH)_2$	C	portlandite
$CaCO_3 * nH_2O$	C	hydrocalcite
Ca_2SiO_4	L	dicalcium silicate
Ca_3SiO_5	L	tricalcium silicate
Ca_3AlO_3	L	tricalcium aluminate
Ca_4AlFeO_3	L	tetracalcium aluminoferrite (brownmillerite)
$Ca_6Al_2(SO_4)_3(OH)_{12} * 26H_2O$	L	ettringite
H_2O	N	ice
MgO	B	periclase
$MgCO_3$	B	magnesite or giobertite
$Mg(OH)_2$	B	brucite
$Mg_5(OH)_2(CO_3)_4 * 4H_2O$ $MgCO_3 * 3H_2O$ $MgCO_3 * 5H_2O$	B B B	hydromagnesite nesquehonite lansforite

1 B=Baymag, C=Continental, L=Lafarge, N=natural.

TABLE 3-4. Nucleation results.

Type	Age	Initial Nucleation				Total Nucleation			
		%[1]	T_{MIN} (°C)	T_{MAX} (°C)	T_{AVE} (°C)	%[2]	T_{MIN} (°C)	T_{MAX} (°C)	T_{AVE} (°C)
Water	0 hrs	100	-6.3	-1.8	-3.9	100	-7.1	-2.8	-4.2
Water	0 hrs	0	<-7.7	<-7.7	<-7.7	0	<-7.7	<-7.7	<-7.7
Water	24 hrs	0	<-7.7	<-7.7	<-7.7	0	<-7.7	<-7.7	<-7.7
AgI	0 hrs	100	+0.4	+3.9	+1.8	100	-5.5	+0.3	-2.0
AgI	24 hrs	100	+0.6	+2.0	+1.3	100	-3.0	-1.9	-2.3
AgI	48 hrs	100	-0.2	+1.1	+0.5	100	-3.2	-1.8	-2.5
Baymg ESP	0 hrs	100	-7.1	-5.6	-6.1	50	<-7.7	-7.1	-7.3
Baymg ESP	24 hrs	100	-5.4	-3.7	-4.7	100	-7.3	-5.9	-6.5
Baymg Kiln	0 hrs	100	-7.7	-6.1	-7.3	20	<-7.7	-6.2	-6.2
Baymg Kiln	24 hrs	67	<-7.7	-3.7	-4.3	50	<-7.7	-4.4	-4.9
Cnt'l Stack	0 hrs	100	-6.6	-3.1	-4.9	100	-6.9	-4.2	-5.7
Cnt'l Stack	24 hrs	100	-6.4	-4.1	-5.4	100	-6.7	-4.4	-5.7
Cnt'l Kiln	0 hrs	40	<-7.7	-7.4	-7.5	40	<-7.7	-7.6	-7.5
Cnt'l Kiln	24 hrs	0	<-7.7	<-7.7	<-7.7	0	<-7.7	<-7.7	<-7.7
Lafrg ESP A	0 hrs	100	-7.5	-4.8	-6.1	20	<-7.7	-6.7	-6.7
Lafrg ESP A	24 hrs	40	<-7.7	-6.1	-6.3	20	<-7.7	-6.6	-6.6

Type	Age	Initial Nucleation				Total Nucleation			
		%[1]	T_{MIN} (°C)	T_{MAX} (°C)	T_{AVE} (°C)	%[2]	T_{MIN} (°C)	T_{MAX} (°C)	T_{AVE} (°C)
Lafrg ESP B	0 hrs	50	<-7.7	-6.4	-6.7	17	<-7.7	-6.9	-6.9
Lafrg ESP B	24 hrs	40	<-7.7	-6.8	-7.0	40	<-7.7	-7.0	-7.2
Lafrg Kiln	0 hrs	100	-6.5	-6.3	-6.4	100	-7.3	-6.4	-6.7
Lafrg Kiln	24 hrs	80	<-7.7	-3.5	-5.1	80	<-7.7	-4.8	-5.9
Lake	0 hrs	100	-5.8	-1.1	-4.2	100	-7.4	-6.2	-6.7
Lake	24 hrs	100	-6.9	-3.2	-5.4	80	<-7.7	-7.0	-7.1

1 percentage of test runs in which at least one drop underwent initial freezing.

2 percentage of test runs in which all drops underwent final freezing.

TABLE 3-5. Airborne particulate emission data for Exshaw facilities.

Facility	Lafarge	Lafarge	Baymag	Cnt'l
Estimated particle radius (μm)	0.1	5.0 presume particles coagulate	5.0	2.5
Estimated particle density (g/cm^3)	2.71	2.71	2.98	2.71
Mass per IN (g)	1.135×10^{-14}	1.419×10^{-9}	1.560×10^{-9}	1.774×10^{-10}
Solid emission rates[4] (kg/hr) (g/s)	99.0[1] 27.5	99.0[1] 27.5	48.6[2] 13.5	8.9[3] 2.5
IN/s	2.423×10^{15}	1.938×10^{10}	8.652×10^{9}	1.394×10^{10}
IN/m^3 downwind[5]	2.608×10^{6}	20.932	9.314	15.010
IN/litre downwind[5]	2608	2.093×10^{-2}	9.314×10^{-3}	1.501×10^{-2}

1 data source: independent laboratory tests, 1986-1990.
2 data source: facility supplied data, 1986.
3 data source: independent laboratory tests, 1984-1986.
4 where more than one kiln is in operation, rate is average combined output.
5 concentration at Calgary, presuming 80 km travel, 30° plume dispersion and 3 km vertical mixing depth, representative of daytime convective conditions.

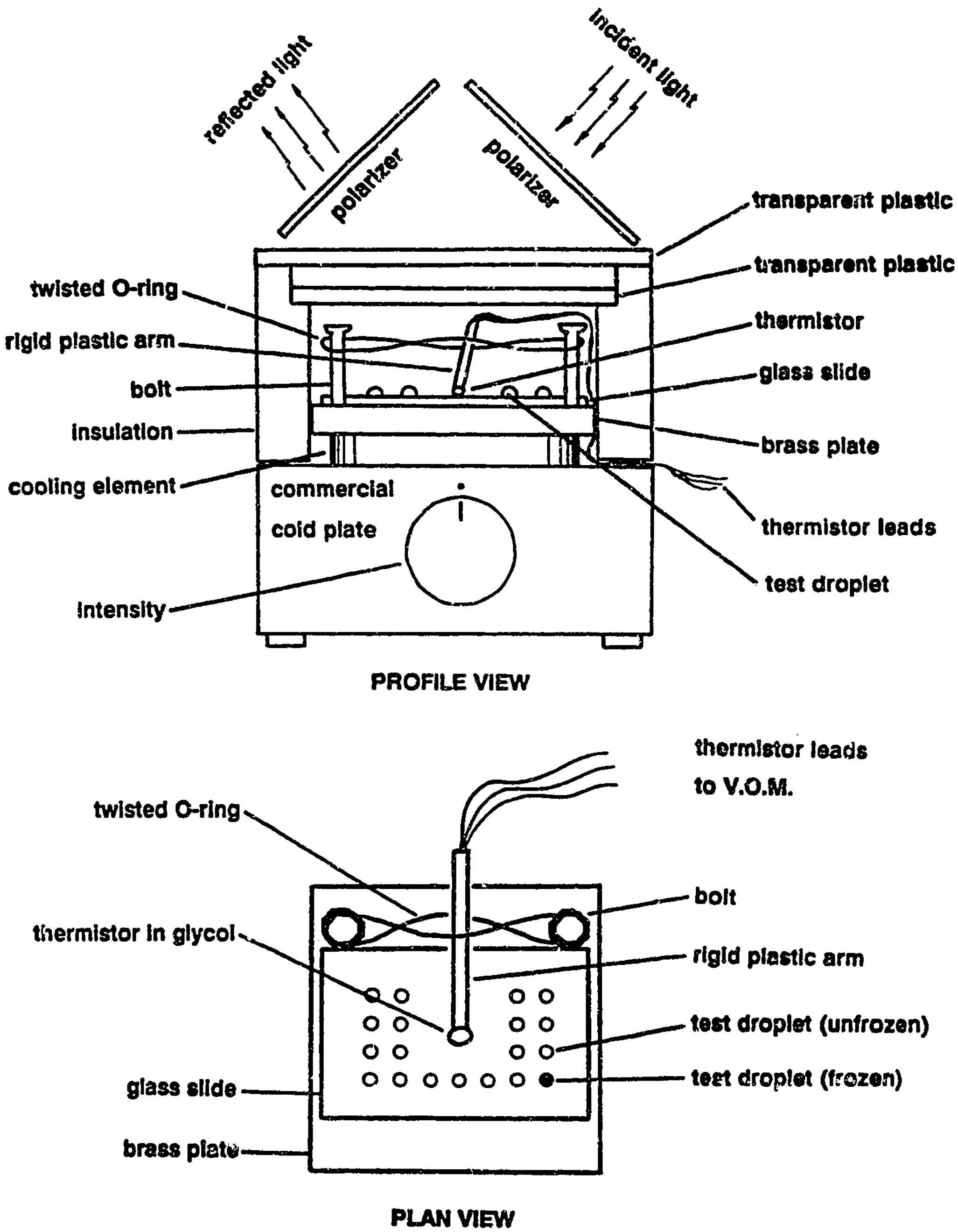

Figure 3.1: Schematic of equipment used in bulk nucleation experiments.

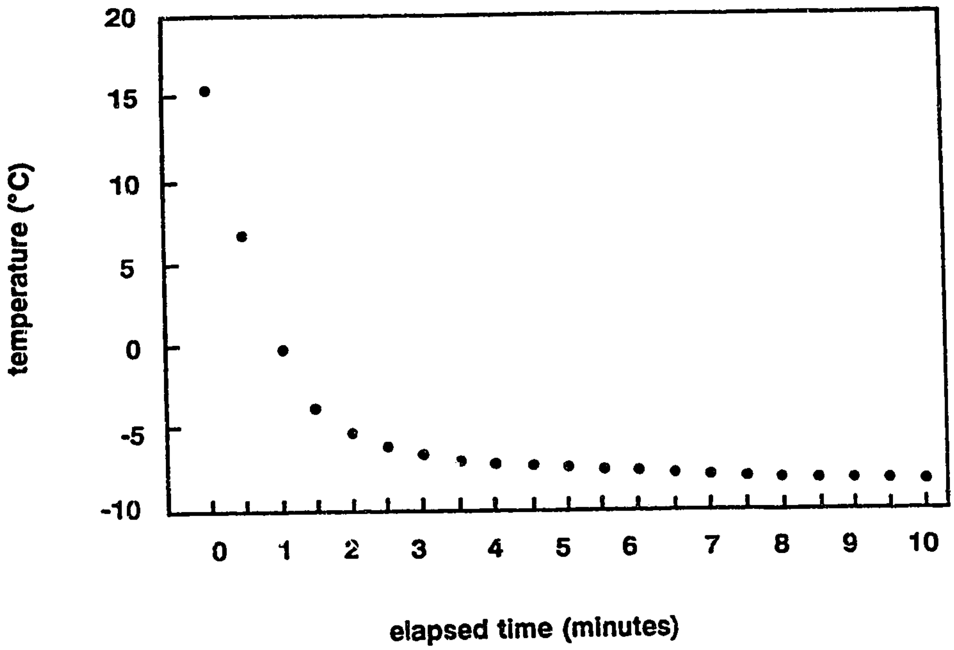

Figure 3.2: Cooling curve for the bulk nucleation apparatus diagrammed in Figure 3.1.

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CHAPTER 4: CONCLUSION

4.1 Summary

Investigation of the ice nucleating potential of airborne particles from the Exshaw industrial complex and their impact on downwind precipitation revealed a number of hereto unknown or unsuspected results. These, and general observations for the investigation, are summarized below:

1. Precipitation amounts and precipitation events at Calgary, during periods of surface wind flow that place Calgary downwind of the Exshaw complex, are generally lower than would be normally predicted on the basis of other stations similarly situated.

2. The release of cement plant airborne effluent, based on kiln production rates, is not correlated with anomalous precipitation at Calgary.

3. Stack particulates, in general, are superior nucleators to kiln particulates of the same process. Stack particulates may contain a significant quantity of impurities that are removed from the kiln product during sintering and/or calcination, or have a broader size distribution, increasing the likelihood of activation.

4. The nucleating potential of all Exshaw particulates, whether of kiln, stack or natural origin, changes on hydration. Particulates with a magnesium oxide (MgO) content appear to improve significantly on hydration, while most others show a slight decay.

5. All Exshaw particulates tested were inferior to the nucleating ability of silver iodide.

6. Cement plant airborne effluent is t the most efficacious industrial nucleating agent tested in laboratory studies. Stack effluent from calcination plants, in general, have higher activation temperatures.

4.2 Mitigating factors

A number of outside factors, not extensively addressed in Chapters 2 and 3, are listed below. These factors may play some role in the climatological and laboratory results obtained, although no attempt to isolate them has been made. These factors include:

1. Contact nucleation (e.g. Rogers and Vali, 1987). Is moist air crossing the Front Range upwind of Calgary being naturally nucleated by contact with snow-covered mountain surfaces, and is the ice nuclei concentration at mountain crest level, particularly during the winter, higher than background levels ?

2. Aircraft produced ice nuclei (e.g. Kelly and Gabor, 1991; Woodley et al., 1991). Do turbine aircraft using a major flight corridor west of Calgary trigger homogeneous nucleation ?

3. Plume dispersion (e.g. Irwin, 1983). Does the concentration of ice nuclei decrease significantly downwind of the Exshaw complex, and would the use of winds aloft rather than surface winds be a more representative in determining downwind precipitation episodes at Calgary ?

4. Particulate coagulation (e.g. Telford, 1960). Do solid exhaust particulates undergo coagulation, changing their downwind nucleating potential ?

5. Particulate concentration and subsidence sinks (e.g. Stout et al., 1993). Are solid exhaust particles concentrated downwind under certain combinations of airflow and terrain orientation, and does mesoscale subsidence over open waterbodies enhance the settling and deposition of such concentrated particles ?

6. Nucleation as a function of drop volume (e.g. Vali, 1971). Do small variations in test drop size account for differences in observed activation temperatures for the same sample ?

7. Transient events (e.g. Davis et al., 1981). Is anomalous precipitation at Calgary the result of unusual natural or accidental nucleating events, including large clouds of splintered rock material ejected during blasting operations or failures of stack emission control equipment ?

4.3 Further research

Overall, the nucleating potential of airborne stack particulates has been demonstrated in a laboratory setting to be good. Combined with virtually continuous and steady stack emissions, these particulates would seem to have a good potential to modify downwind precipitation. This, however, is speculative. While there is evidence to suggest that precipitation is suppressed at Calgary, and while there is also evidence that supports the heterogeneous nucleation potential of Exshaw airborne particulates, there is no causal link between the two. This is a risk inherent in correlations in general. While analysis of rain samples, as proposed in Chapter 2, would confirm that such effluent reaches Calgary, uncertainty would exist as to whether the particulates arrived as activated nucleating agents, were swept out of the air by pre-nucleated raindrops or simply were deposited as a dry dustfall. To make the necessary connection, cloud physics and cloud dynamics need to be evaluated for nucleated (seeded) and unseeded clouds. This could be accomplished through visual or radar measurements (e.g. Mather, 1991), modelling of various heat, moisture or ice nuclei inputs (e.g. Guan and Reuter, 1994) or plume tracing (e.g. Johnson, 1983).

Many of the crystallographic conclusions drawn were based on ideal particulate chemistry. However, as demonstrated, stack and kiln nucleation temperatures for the same facility often differed significantly. X-ray diffraction (XRD) analysis or scanning electron microscope (SEM) images of the tested particulates would allow for fewer inferential conclusions to be drawn to account for these differences.

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