HAT CREEK PROJECT

Environmental Research and Technology Inc. - <u>Air Quality and</u> <u>Climatic Effects of the Proposed Hat Creek Project - Appendix I</u> <u>Long Range Transport and Implications of Acid Precipitation</u> -November 1980

ENVIRONMENTAL IMPACT STATEMENT REFERENCE NUMBER: 24

ABSTRACT

Environmental Research & Technology, Inc. (ERT) was commissioned by the British Columbia Hydro and Power Authority to evaluate the potential for and effects of precipitation acidification due to air contaminant emissions from the Hat Creek Project, a proposed thermal generating station. Results of ERT's study indicate that deposition of airborne materials from the Hat Creek Project will produce no significant direct or indirect environmental effects in the aquatic systems and their biological communities as a result of project emissions.

APPENDIX I

EXECUTIVE SUMMARY

Environmental Research & Technology, Inc. (ERT) was commissioned by the British Columbia Hydro and Power Authority to evaluate the potential for and effects of precipitation acidification due to air contaminant emissions from the Hat Creek Project. The major objective of the study was the estimation of incremental hydrogen ion (H^+ion) deposition and its distribution over aquatic ecosystems surrounding the project area. Several potentially critical water bodies, and the expected biological communities within them were reviewed with respect to probable consequences of predicted acidity changes resulting from operation of the proposed thermal generating station. Results of ERT's study indicate that deposition of airborne materials from the Hat Creek Project will produce no significant direct or indirect environmental effects in the aquatic systems and their biological communities as a result of the project emissions.

These results apply mainly to the assumed use of a 366-m (1200-ft) stack with uncontrolled emissions. Full load power generation (maximum stack emission rate) for a one-year period was also assumed. This scenario was selected over other possible emission configurations (e.g., see Appendix C, Alternate Methods of Ambient Sulfur Dioxide Control) because it represents the case with maximum potential impacts on important water bodies out to 200 or so kilometers from the proposed Hat Creek site. Calculations of pH change associated with the use of scrubbers for removal of SO₂ are also presented. No quantitative estimates of pH change due to plant operations with other possible stack heights were made. Following is a qualitative assessment of changes in the predicted acidity effects with other emission configurations.

First, implementation of a meteorological control system (MCS) would have little effect on the results reported here. Such a program is mainly aimed at controlling intermittent, relatively rare potential violations of ambient air quality regulations, and by its nature does not greatly reduce total annual emissions. Thus, predicted annual

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effects for uncontrolled emissions would be essentially unchanged for MCS operation. Furthermore, the short-term episode cases analyzed in this study represent storm conditions which are not generally associated with poor dispersion and reduced emissions. Consequently, the results reported in this volume may be taken to apply equally well to plant operation with MCS and a 366-m (1200-ft) stack. 1

Introduction of constant emission controls, i.e., scrubbers, would have a significant effect on the study results. The scrubber system described in Appendix C is designed to reduce sulfur oxide emissions by approximately half. It has been assumed here that the scrubber will not change particulate and nitrogen oxide emissions, although it probably will reduce both to some extent. Thus, the SO₂ emissions that give rise to the formation of sulfate, a principal factor in acid precipitation, are reduced by flue gas desulfurization, while formation of the other main constituent, nitrate, is largely unaffected. The decrease in stack gas temperature resulting from scrubber operation will reduce plume rise and result in closer plume approach to elevated terrain elements. Overall, however, continuous control at the source may be expected to reduce impacts on precipitation and water quality more than other types of controls.

Reduction of the physical height without altering other power plant emission characteristics would result in a spatial redistribution in the predicted patterns of hydrogen ion deposition and resulting pH change. Because of the nonlinear nature of terrain effects on plume behavior, it is not possible (without additional modeling) to define a precise relationship between the peak deposition rates that would occur for different stack heights. However, on the basis of results obtained in modeling ambient concentrations due to the Hat Creek plant with 366 m (1200 ft) and 244 m (800 ft) stack heights, some semiquantitative estimates can be made regarding the effects on this study's conclusions that would be expected to result from a decrease to 244 m.

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In general, a stack height reduction would increase the magnitude of H^T deposition rates near the plant site and decrease the rates further downwind. The peak annual average deposition rate may increase by as much as 25% in the near field (within 25 km) where substantial soil and water body buffering capacity exist to neutralize such effects. However, a reduction in impacts in the poorly buffered areas in the far field, e.g., in Wells Gray Park, would also result since more plume material would be deposited before reaching such distances. Based on a nominal pH of 7. a 25% increase (decrease) in H⁺ deposition would lower (raise) the pH by about 0.1 units. Thus, the change in water body pH associated with a reduction in stack height from 366 m to 244 m will be well within the range of uncertainty of the calculations presented in this volume. Since considerable effort has been expended in this study to ensure that effects will be conservatively predicted, it is likely that the computed pH changes reported here are also reasonably representative for the shorter stack height.

This study is necessarily a multidisciplinary undertaking. The following paragraphs summarize the approaches adopted in addressing air quality, water quality and biological processes relevant to the analysis objectives.

Air Quality

The basic air quality modeling techniques used to assess regional air quality effects due to the proposed Hat Creek power plant are described in detail in Appendix B of the ERT report, "Air Quality and Climatic Effects of the Proposed Hat Creek Project." Power plant stack contaminants are the only project emissions capable of regional distribution through the atmosphere. The model described in Appendix B was modified for this study to include consideration of plume contaminant removal by precipitation and the effects of nitrogen compounds on precipitation acidity.

During long-range atmospheric transport (downwind distances greater than 50 km), a significant fraction of the nitrogen and sulfur oxides emitted by the power plant will be transformed to secondary products. The rate of such conversions depends on meteorological conditions and the other

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chemical constituents present in the plume. Natural removal of primary and secondary contaminants in the power plant plume will also occur by two other processes, wet and dry deposition, both of which decrease in efficiency as the contaminants are dispersed by atmospheric turbulence. The extent of dry deposition (contact and sticking) at the surface is governed by the wind speed, chemical composition of the contaminant and the surface characteristics, e.g. vegetation cover. Two types of natural wet removal are rainout (absorption of contaminants during cloud formation) and washout from the atmosphere by falling precipitation. ERT developed the Hat Creek Source Depletion Model (HCSDM) to include consideration of these removal processes.

ERT used another model, the PHOKIN (PHOtochemical KINetics) smog chamber simulation model to infer an effective transformation rate for the conversion of nitric oxide to nitrate in the Hat Creek power plant plume. The PHOKIN model simultaneously solves the equations governing entrainment of ambient air into the plume and the complex series of chemical reactions resulting in the atmospheric conversion of primary emissions to nitrate.

Precipitation data were available for 34 stations in southern British Columbia.* Annual and seasonal precipitation intensity and frequency statistics were also derived for each area of interest to allow a realistic simulation of wet deposition over long and short time periods. Based on the calculation of plume rise from the proposed 366-m (1200-ft) stack, a representative plume height was determined. Wind speed and direction data for the study area were also collected and used in the analysis. 7

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Water Quality

Several criteria were considered important in selecting the water bodies for detailed analysis of potential effects due to acidity change.

^{*}In the final stages of this study, a substantially larger precipitation data set was obtained. Addendum A to this Appendix contains revised analyses of the relevant precipitation statistics based on the new data, and provides comparisons between the original and expanded data sets.

Prevailing meteorological conditions, commercial and recreational importance, biological sensitivity and soil and water buffering capacities were the major considerations in this selection process. Since the predominant wind directions would usually transport Hat Creek Project emissions toward the sector northeast of the project site, most of the receiving water bodies studied in detail were chosen in this quadrant.

Aquatic ecosystems, especially lakes and streams with low alkalinities, respond more rapidly to inputs of hydrogen ions than do terrestrial systems. The buffering capacity of watersheds is the most important mitigating factor. Water bodies near the proposed Hat Creek Project site are moderately or well-buffered while waters farther away are poorly buffered. In addition, soils with high buffering capacity can aid in neutralizing the effects of acid precipitation on water body chemistry. The available measurements indicate that soil-water systems with substantial total buffering capacity are typical of the Hat Creek area.

Evaluation of effects at specific receiving water bodies involved utilization of the water quality data generally available. No attempt was made, however, to verify the reliability and validity of the water quality information. The model-computed proton H^+ deposition rates were used to calculate total deposition inputs over the total drainage areas of individual water bodies. The fraction of the total deposition reaching a water body unneutralized by soil buffering agents was estimated, and the water body discharge rates were used as an approximation of the water volume available for dilution of deposited H^+ ions. The net proton inputs to the water bodies were thus estimated. These were modified to reflect the buffering capacity of the aquatic systems at the pH range measured for each system. Finally, a pH change for each system was calculated assuming equilibrium between atmospheric and dissolved carbon dioxide.

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Not only were the proton donor additions predicted in this study very small, but the pH changes resulting from these additions were found to be small for both short-term events and long-term averages. The literature indicates that pH values between 6.0-9.0 are necessary for the survival of economically important species of fish. The pH values of water bodies in the Hat Creek area are currently within this range and are projected to remain so over the short and long term with or without the deposition of the air emissions from the proposed Hat Creek Project.

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Biological Effects

A literature search was conducted to review the current state of knowledge regarding effects of changes in water chemistry to residing biological communities. Anticipated pH changes in the water bodies of the Hat Creek area will be small enough to preclude measurable biological effects due to proton donor deposition from the Hat Creek power plant stack emissions. No effects should be evidenced in adult, juvenile or spawning fish populations. In addition, the predicted pH changes will have no appreciable effect on the potential dissolution of heavy metals, including mercury, of either natural origin or those added by the Hat Creek Project within 200 km from the plant site. Biogeochemical cycling will be maintained at the present natural rates, and only small increases in biologically-active, heavy-metal compounds will be transported through the ecosystem.

Conclusions

This study represents the first (to ERT's knowledge) attempt to calculate pH change in actual water bodies due to a proposed future source. This being the case, it is not possible to estimate accurately the degree of uncertainty inherent in the reported conclusions. For this reason, it was deemed necessary to select analysis methods and input parameters that would compensate for the uncertainty by leading to conservative (overestimated) predictions of the Project's effects on aquatic ecosystems. In view of the economic and recreational importance of the interior waterways of the Province, such care was considered mandatory.

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The results of this study indicate that the pH changes expected from the Hat Creek Project air emissions will have no adverse environmental effects on the aquatic ecosystems of the area over the lifetime of the project. This conclusion applies to annual and seasonal average conditions and to individual precipitation events within the zone of impact of the project facilities.

The results of these studies can be summarized in the following conclusions:

- Proton donor deposition will occur primarily in the northeast quadrant from the Hat Creek Project area.
- Maximum deposition rates will be within a 50-km (30-mi) radius of the proposed poer plant site.
- Some deposition of project emissions will occur beyond 200 km from the power plant location but will be of very small magnitude.
- Model calculations indicate that average pH values in precipitation will be reduced to values no lower than 4.95 to 5.55 (assuming the only buffering to be due to the dissolution of atmospheric CO_2).
- Although small annual and episodic pH changes in the water bodies of concern are predicted, these changes will be of a magnitude similar to natural variations without the Hat Creek Project.
- The techniques used to predict cumulative effects of the Hat Creek Project on water quality tend to overestimate such effects. However, after the expected 35-year lifetime of this project, the calculated pH for specific water bodies all remain in the range required to sustain economically important aquatic populations.
- Estimated pH changes will have no effect on the maintenance of economically important fishery populations, including reproduction, growth and survival of sensitive species.

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- No adverse effects in the soils and vegetation of the area are expected to occur as a result of wet and dry deposition of Hat Creek emissions.
- No observable biological effects due to the predicted pH changes are expected for the eggs, larvae, juvenile, and ichthyoplankton segments of the animal populations.
- Net productivity and species composition of the phytoplankton, zooplankton, benthic, and aquatic macrophyte communities will be unaffected by the expected pH changes.
- Biological effects of trace metals, including mercury, will not be appreciably altered by any form of acid deposition due to Hat Creek Project emissions. Synergistic effects of acid and heavy metals will not change significantly from those which may be presently occurring in the aquatic systems of the area.

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APPENDIX I

I1.0 INTRODUCTION

II.1 PURPOSE

Environmental Research & Technology, Inc. (ERT) has been requested by British Columbia Hydro and Power Authority (B.C. Hydro) to expand upon an earlier analysis of deposition of atmospheric contaminants released by the proposed Hat Creek Project. The report "Air Quality and Climatic Effects of the Proposed Hat Creek Project" to which this document is Appendix I, includes a subsection 5.2(c)(v) on acidity changes in precipitation. Probable changes of precipitation pH due to Hat Creek Project emissions are projected. Appendix B, Modeling Methodology (Section 36.2) also addresses the calculation of pH change and presents additional background information. The purpose of Appendix I is to present the results of a more sophisticated modeling analysis to investigate the deposition of air contaminant emissions from the proposed power plant and their secondary products over the regions of interest, including an evaluation of impacts at specific aquatic bodies.

Terms of Reference were devised for this additional study, which expands upon investigations documented by the previous appendices with the following specific tasks:

- Expand the modeling methodology (Appendix B) to include both sulfur and nitrogen chemistry, depletion of air contaminants by wet and dry deposition, and incorporate additional regional meteorological data.
- Model air contaminant emissions to predict deposition distributions of relevant contaminants over a range of 200 km or more downwind of the Hat Creek Project.
- Discuss the current understanding of atmospheric and precipitation chemistry and calculate patterns of hydrogen ion deposition on an episodic, seasonal and annual basis.

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- Review the available data on soil and water chemistry in the vicinity of the Project. Estimate effects of the deposition of proton donors on water chemistry for selected receiving waters on episodic, annual and Project lifetime scales.
- Assess the biological implications of the predicted pH changes in water bodies in the Hat Creek area.

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I1.2 SCOPE

The acidity of precipitation over industrialized regions of the world is currently receiving considerable attention. Reports by various committees and agencies cite mimerous investigations of precipitation changes throughout the world.^{1,2,22} The "acid" precipitation phenomenon is most often related in the literature to industrial emissions of sulfur and nitrogen oxides. Once released in the atmosphere, these "primary" contaminants can undergo chemical transformations leading to the production of acidic compounds which are dissolved in precipitation. There is concern that the resultant input of acidity to the earth can affect many components of the environment, including soils, waters, vegetation and wildlife. The magnitude and geographical distribution of such environmental effects in a given area are believed to depend on the interaction of numerous factors, including emission strengths of sulfur and nitrogen oxides, atmospheric diffusion characteristics, atmospheric oxidation kinetics, topography and climatology as well as certain soil and water chemistry and biological characteristics.

Contaminants in a dispersing plume or in a mass of air containing several source emissions are eventually removed by two processes--dry and wet deposition. Dry deposition refers to any mechanism that results in depletion of contaminants by direct, contact with any feature of the earth's surface. Gravitational settling (perhaps aided by agglomeration or chemical reactions) and turbulent transport are the principal mechanisms. Contaminants not deposited in this manner close to the source can be transported over long ranges until they are removed by precipitation (wet deposition).

Wet deposition includes both direct involvement of the contaminants with droplet formation in clouds ("rainout") or entrainment of the pollutant

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by absorption in or collision with falling precipitation ("washout"). Rain, free of any ions other than those contributed by the dissociation of water (H^{+}, OH^{-}) and the dissolution of atmospheric carbon dioxide $(HCO_{z}^{\pi}, CO_{z}^{\pi})$, would have a pH of approximately 5.6 at 25°C. However, "natural" rain is not distilled water, but may contain sea salt, soil dust, organic acids, etc. Nevertheless, precipitation is usually classified as "acid" when pH levels are below about 5.6, although rain collected at nonpolluted locations throughout the world often has a pH less than 5.0. For example, in the Amazon Basin, a single storm pH of 3.6 has been measured^{8a} and in Pago Pago, American Samoa, the average pH of precipitation for the month of October 1976 was 4.74.^{8b} Rain with pH values as low as 2.8 and 2.1 have been observed in Europe and the eastern United States, respectively.³ Short rainfall events usually have higher average concentrations of scavenged contaminants than rainfall events of longer duration.⁴ It is also known that precipitation occurring early in a large rainstorm contains higher concentrations of air contaminants than precipitation occurring later in the same storm. These higher concentrations may result in either an increase or decrease in pH depending on the ratio of alkaline to acidic ion concentrations which is influenced by climatological. and geographic factors. Snowfall also removes contaminants from the atmosphere, but much less efficiently than rain.³

Increasing acidity of precipitation (lowering of pH) has been observed in Europe since 1950, and has been related to the increased use of fossil fuels and the corresponding increase in emissions of sulfur and nitrogen oxides.⁶ By the 1960s, investigations by Scandinavian scientists indicated that rivers in Sweden and Norway were experiencing a trend of increasing acidity.⁶ The significance of similar occurrences in North America began to receive attention in the 1970s.³ Investigators have reported detrimental effects associated with acid precipitation in ecosystems of the Adirondack Mountains in upstate New York, U.S.A.⁷ and in Ontario, Canada⁸, although the cause effect relationship of acidic precipitation and the observed water quality in the areas studied remains controversial and uncertain.

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In western Canada, concentrations of acidic compounds in precipitation are low, except directly downwind from Vancouver and the natural gas processing facilities in Alberta.⁵ However, proposed construction of the Hat Creek coal-fired power plant in central British Columbia raises concerns regarding the potential for changing the pH of precipitation downwind from the plant. Maximum deposition of acidic compounds in the Hat Creek plume will generally occur within 50 km downwind of the plant. The region in the northeast quadrant 100 to 250 km from the proposed plant site includes mountainous terrain that receives abundant snowfall. Accumulation of acidic compounds in the snowback during winter, and their subsequent release to surface waters during spring snowmelt is considered a possibility in this area. Although soils and water bodies in the near vicinity of the proposed plant have moderateto high-buffering capacities, soils and water bodies in the mountainous regions located 150 to 200 km north and east from the proposed plant site have lower buffering capacities. Evidently, environmental systems in the latter areas may be susceptible to acid precipitation. On the basis of an investigation of 205 water bodies in the area that could be affected by emissions from the proposed plant, 43 are considered vulnerable to acidification.⁹ Included among the sensitive waters are streams in the watersheds of the North and South Thompson Rivers which serve as major migratory pathways and spawning grounds for salmon.

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In view of the expected magnitude of sulfur and nitrogen oxides emissions from the proposed power plant, the potential susceptibility of waters downwind from the plant, and the regional importance of salmon fisheries, detailed studies of long-range transport and implications of precipitation chemistry from the proposed Hat Creek Project are warranted.

Following the Terms of Reference outlined in the previous section, ERT has estimated the effects of Hat Creek emissions on the pH of precipitation and receiving water bodies. Sections 2.0 (Methodology), 3.0 (Diffusion Modeling) and 4.0 (Critical Water Receptor Areas) review the development of the study, the modeling and computational methods adopted, and the

II-4

rationale involved in choosing regions for detailed analysis. Results of the deposition modeling and the assessment of effects are presented in sections 5.0 through 8.0, (Modeling Results, Water Quality Effects, Biological Effects and Conclusions, respectively).

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12.0 METHODOLOGY

The proposed Hat Creek power plant will emit atmospheric contaminants which, upon reaching the earth's surface, may affect the acidity of the area's soils and water bodies. To accomplish the tasks listed in the Terms of Reference, namely to assess the implications of long-range transport and acid precipitation, ERT established a comprehensive and multidisciplinary study plan. An understanding of the component study elements, the types and quality of available input information and the analysis procedures adopted is necessary for proper evaluation of the results and the applicability and uncertainties in the conclusions.

The emissions and stack gas characteristics assumed in the modeling analyses correspond to continuous, full-load power plant generation during the entire year. Emission rates were calculated for a case without pollution control equipment (such as scrubbers). A 366-m (1200-ft.) stack height was specified in the dispersion/deposition model. This emission scenario was chosen to allow examination of potential effects of precipitation acidification for the case in which the expected geographical extent of such effects would be most widespread. Other scenarios with shorter stacks, scrubbers, and meteorological controls have been considered for the proposed thermal plant (e.g., see Appendix C, Alternate Methods of Sulfur Dioxide Control). However, the quantity of airborne contaminants arriving at the earth's surface far downwind of the Hat Creek site for any of these configurations would be less than for the one assumed here. Thus, the selection of the uncontrolled case with the tallest stack is consistent with other efforts to portray worst-case impacts at the receptor areas where adverse effects are potentially most critical. Table 12-1 shows the emission rates for the various scrubber cases examined within this document.

I2.1 STUDY DESIGN

A flow chart has been prepared (Figure 12-1) for graphical display of the interrelationships between important study elements. The chart indicates the flow of data, the component analyses, and the relationships between analyses in the interdisciplinary effort. The methodology

TABLE I2-1

EMISSION RATES EXAMINED IN THIS STUDY

		Emission Ra	ce (kg/day)
Case	<u>50</u> 2	NOx	TSP
No controls	324,768	207, 248	40,000
48% SO ₂ removal	170,000	207, 248	40,000
54% SO ₂ removal	150,216	207, 248	40,000
86% SO ₂ removal	44,000	207, 248	∘40,000
90% SO ₂ removal	32,477	207, 248	40,000

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Figure 12-1. Long Range Transport and Implications of Acid Precipitation Air Quality and Climatic Effects of the Proposed Hat Creek Project Study Flow Chart.



shown in the chart applies to both the long-term average and episodic cases chosen for analysis, in compliance with the Terms of Reference. All important parts of the study are shown as inputs, outputs, study procedures, study elements or results. -

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The four study procedures (shown as centerline rectangular boxes on the chart) represent the key analysis steps in the study. First, the transport and dispersion of emitted contaminants are simulated by means of a mathematical model. Expected ground-level ambient concentrations are computed for all important plume contaminants that may contribute to soil or surface water acidity. Initial concentrations of the various species are established. Wet and dry deposition of selected compounds are calculated separately in the model and the removal of plume constituents by these processes is reflected in the computed ambient concentrations.

The calculated concentrations and deposition rates are input to the second study procedure, the analysis of atmospheric chemistry. Those chemical processes not readily incorporated in the diffusion model are considered, and the sensitivity of the analyses to key assumptions and estimated parameterizations are evaluated. Patterns of wet and dry deposition over the entire study area are computed for the major acidic species emitted either directly from the power plant or formed in the plume by atmospheric reactions.

The third study procedure, the assessment of water chemistry effects, involves analyses of the mechanisms and pathways for transfer of deposited contaminants to water bodies in the study area. Wet and dry deposition on the soils, vegetation, snow pack, and water of the study area must all be considered. Input data requirements for this study phase include estimates of deposition rates from the second study procedure as well as information regarding the nature of the soils in the impacted areas, vegetation cover, lake and stream chemistry, water body sizes, flow rates and drainage areas, and precipitation statistics. A sensitivity analysis is an important part of the results. Predicted changes in the pH of selected water bodies and in the precipitation itself are computed.

Determining the importance of water chemistry effects on specific aquatic ecosystems constitutes the fourth study procedure, the biological effects assessment. The principal conclusions in this regard are drawn from an analysis of predicted water quality effects in terms of the available literature. The potential importance of the projected deposition of acidic compounds contributed by the Hat Creek Project to the surrounding aquatic ecosystems is thereby evaluated.

12.2 CASE STUDIES

To implement the study approach diagrammed in Figure I2-1, three study design elements had to be specified: areas potentially influenced by Hat Creek Project emissions, the meteorological conditions associated with impacts in these areas and the time scales of interest. Although the procedures listed in Figure I2-1 appear to follow a chronological sequence, these three design elements could not be chosen in advance, as they are, in fact, a part of the study results. Thus, the four study procedures were actually conducted concurrently, and were revised and refined as the study developed.

Three impact time scales of interest were selected for detailed analysis. The results are limited to some extent by availability of input information corresponding to these time scales. Most data obtained were in the form of annual averages, in some cases averages over several years. For this reason, greater confidence is placed in the results pertaining to long-term (annual) effects than in those for shorter averaging times.

Seasonal averaged wet and dry deposition rates, were also computed, and analysis of the meteorological data resulted in the definition of shortterm episodic cases. Of particular interest are events or combinations of events that lead to relatively high short-term contributions of acidic compounds at a particularly sensitive water body. Specific short-term cases of interest have been identified, including individual storms after stagnation episodes and surges of acidic compounds during spring melting of a snowpack.

I2-5

Case studies were designed to investigate particular water bodies and drainage areas of interest. Section I4.0 of this appendix describes in detail the choice of areas for these detailed studies. Selection criteria included water chemistry, biological, economic and recreational importance, drainage area buffering capacity, government and public interest and the frequency of meteorological conditions conducive to wet and dry deposition.

In addition to annual and short term precipitation events, a third time frame--the Project lifetime--is evaluated. The Hat Creek power plant is expected to operate for approximately 35 years. It is important to recognize that the effects on the exposed water bodies and ecosystems will not be simply additive over this period, since buffering agents as well as H⁺ions will continue to be added to the aquatic systems.

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Sensitivity analyses are provided to determine the significance of assumptions and variables chosen for key segments of the study. For most aspects of the study, a conservative bias was incorporated in the selection of inputs and procedures. Although this tends to represent conditions or factors not likely to occur, it provides a useful outside range of the potential effects. The results, therefore, are considered to represent overestimates of Project effects in most cases.

13.0 DIFFUSION MODELING

The air quality modeling methodology used to assess regional air quality effects of the proposed Hat Creek Project is described in Appendix B of the ERT report "Air Quality and Climatic Effects of the Proposed Hat Creek Project." These modeling techniques have been modified to include the effects of plume contaminant depletion due to precipitation scavenging, and to extend the model's applicability for simulations involving a variety of contaminant species. A discussion of these adjustments is provided in Section I3.1. Sections I3.2 and I3.3 describe parameterization of the relevant physical processes and selection of model input data.

The rates at which NO_x and SO_2 emissions from a power plant are transformed to the important acid plume constituents, NO_3^- and SO_4^- , depend on meteorological conditions and the other chemicals present in the plume. The natural removal of primary and secondary species through dry deposition at the earth's surface varies with the contaminant species and vegetation type. Natural removal is also achieved during precipitation through nucleation, in-cloud scavenging (rainout) and below-cloud scavenging (washout). The Hat Creek Source Depletion Model (HCSDM) has been developed to address these removal processes in an analytical manner in computing the patterns of ambient contaminant concentration and deposition due to the proposed power plant.

I3.1 THE HAT CREEK SOURCE DEFLETION MODEL (HCSDM)

The basic Gaussian plume model used to simulate the long-range air quality effects of the Hat Creek Project is described in Addendum A of Appendix B (Section A1.6). The methodology used to provide a preliminary estimate of Project effects on precipitation pH is also presented in Section B6.2 of the same Appendix. In that study only maximum changes in the acidity of the precipitation itself were addressed. No attempt was made to estimate the resulting effects on soils, water bodies, or biota. A modified modeling approach (the HCSDM) has been developed to facilitate a more realistic and detailed examination of potential acidification

in water bodies surrounding the Hat Creek Project site. This section deals with the model revisions designed to provide appropriate input information for the water quality calculations described in Section 16.0.

Chemical transformations and surface deposition are incorporated into the modeling by means of separate exponential depletion factors. Initially, ambient SO_2 , NO and TSP concentrations are calculated without consideration for depletion through chemical reactions or surface deposition. These concentrations are then multiplied by correction factors which are the ratios of the "effective emission rates" Q(I), and the actual emission rates Q(O), such that

$$x_{E} = \chi \cdot \frac{Q(I)}{Q(O)}$$
 (I3-1)

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where χ is the ambient concentration calculated without depletion mechanisms. Figure I3-1 indicates the depletion processes considered for each of the primary contaminants modeled in this study.

Q(I) are calculated in the following manner. The rate of change of the effective source strength for contaminant species "I" can be defined as:

$$\frac{\mathrm{dQ}(\mathrm{I})}{\mathrm{dt}} = -(\mathrm{A}(\mathrm{I}) + \mathrm{B}(\mathrm{I},\mathrm{J})) \mathrm{Q}(\mathrm{I})$$
(13-2)

where A(I) is the deposition rate (percent per hour) of species I and

B(I,J) is the chemical transformation of species I to species J (e.g., SO₂ to SO₄⁺ or NO to NO₃⁻) (percent per hour).

If the coefficients A(I) and B(I,J) do not vary with time, then the exact solution of Equation I3-2 is

$$Q(I) = Q_{exp} \{-[A(I) + B(I,J)]t\}$$
(I3-3)



where t is travel time from the source. However, the HCSDM was designed such that wet deposition rates and chemical transformation rates for NO and NO_3^- need not be constant either temporally or spatially. Contaminants in the plume are depleted or created continuously by atmospheric processes represented by the coefficients A(I) and B(I,J) along the plume trajectory. This is treated approximately by allowing the coefficients to vary discontinuously every 10 km or at each receptor location. Equation I3-2 was solved numerically for values of

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$$t_n = \frac{x_n}{u}$$

where n is the step number, u is always wind speed and X_n is the downwind distance at step n. To minimize the error introduced by solving Equation I3-2 numerically, the value $|X_{n+1} - X_n|$ must be reasonably small. Therefore, effective source strengths, Q(I), were calculated by Equation I3-2 every 2 km downwind until a distance of 2x* was reached [where $\sigma_z(x^*) \approx 0.47$ H, and H is the depth of the mixed layer]. Beyond this point, the contaminant plume is considered to be uniformly mixed in the vertical, and errors introduced by stepwise computations become smaller. Thus, beyond the distance of 2x*, effective source strengths were calculated every 10 km. For a chemically-reactive contaminant species I and a secondary contaminant J (e.g., I = SO₂ and J = SO₄²), the effective source strengths at the Nth downwind distance for each species are approximately:

$$Q_{N}(I) = \pi Q_{l-1}(I) \cdot \exp \left\{ \left[-(A_{2}(I) + B_{2}(I,J)) (t_{2} - t_{l-1}) \right] \right\} (I3-4)$$

and

$$Q_N(J) = \pi Q_{2-1}(J) \cdot \exp [-A_2(J) \cdot (t_2 - t_{2-1})] + 2 = 1$$

$$\frac{R(I,J) \cdot B_{N}(I,J) \cdot Q_{N-1}(I)}{B_{N}(I,J) + A_{N}(I) - A_{N}(J)} \cdot \left\{ \exp \left[-A_{N}(J) \cdot (t_{N} - t_{N-1}) \right] - \exp \left[-\left[A_{N}(I) + B_{N}(I,J) \right] \cdot (t_{N} - t_{N-1}) \right] \right\}$$
(I3-5)

 $\begin{array}{c} N \\ \pi \quad A_{\mathcal{L}} = A_{\mathcal{L}}^{A_{2}A_{3}} \cdots A_{N} \\ \mathcal{L}=1 \end{array}$

l is the number of downwind distance intervals to a receptor

R(I,J) is the molecular weight ratio of species J to species I, and the other parameters are the same as previously defined.

For a non-reactive species, K, such as TSP, Equation I3-4 simplifies to:

$$Q_{N}(K) = \frac{\pi}{l=1} Q_{l-1}(K) \cdot \exp\left(-A_{l}(K) \cdot (t_{l} - t_{l-1})\right)$$
(13-6)

As can be seen from Equations [3-4 through I3-6, the effective source strength at any given downwind distance is a function of the physical processes that occurred upwind of the receptor of interest. For example, contaminant washout due to varying precipitation rates upwind of a given point is accounted for in computing the effective source strength at that point.

13.2 CHEMICAL TRANSFORMATION RATES

Various chemical reactions are involved in the formation of sulfates and nitrates. As discussed in Appendix B, it has been determined that for the case of sulfur oxides, the literature supports a reaction rate of approximately 1% per hour for the transformation of SO_2 to SO_4^- in a plume in a rural location. This reaction rate value was used in this study for sulfur oxides. The sensitivity of the analysis results to changes in the assumed reaction rate is investigated in Section I6.8.

It is now known that the SO_2 oxidation rate exhibits a diurnal variation with a peak occurring during the midday hours (Mueller et al. 1980).⁷⁵ This is caused by the photochemically driven processes which oxidize SO_2 (e.g., by the OH radical, whose ambient concentration is influenced by sunlight intensity). The photochemical route may be superimposed on a base conversion rate due to heterogeneous oxidation processes, catalysis by metal ions, intradroplet reactions with H_2O_2 , O_3 , O_2 , etc. While

oxidation rates of 3 to 4% hr⁻¹ and higher may be observed during peak daylight hours, rates may drop to low levels at night. Assuming a constant 24-hour linear conversion rate of 1% hr⁻¹ appears a reasonable approach and may be conservative in possibly overestimating the conversion rate.

The rate of NO_3^- formation from NO in power plant plumes is not understood as well. Studies of NO_x chemistry have been performed in laboratory smog chambers and by means of mathematical modeling. However, only recently have field studies been designed to study NO_x behavior in power plant plumes.¹⁰

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In the local and regional NO_x modeling efforts described earlier (Appendix B, Section B6.4), the emphasis was placed on determining ambient concentrations and deposition patterns of NO and NO_2 . For that purpose, it was assumed that ground-level concentrations of these species could be realistically estimated with a nonreactive model, provided that initial NO_x emissions were apportioned properly between NO and NO_2 . For local modeling (within 25 km from the source), 50% of the NO_x emissions were considered to be in the form of NO_2 . This fraction was increased to 80% for applications beyond 20 km.

In the present study, ERT used the PHOtochemical KINetics (PHOKIN) model to infer an estimate of the transformation rate of NO to NO_3^- in the power plant plume. A technical description of this model is provided as Addendum 8 to this appendix. The PHOKIN model simultaneously solves the equations governing in-plume photochemical reactions and entrainment of clean air due to plume growth. Species concentrations are output as a function of plume travel time. The model simulates the chemical reactions resulting in the eventual conversion of NO to HNO_3 , nitric acid. It was assumed that the formation of HNO_3 was equivalent to $NO_3^$ formation. A pseudo-first order transformation rate of NO to NO_3^- was then calculated based on the time history of the species NO and $HNO_3^$ during the PHOKIN simulation. The PHOKIN calculations yielded a timedependent conversion rate (percent per hour) given by the approximate relationships:

 $R = 0.9 + 6.3 t - t \le 1 \text{ hour}$ R = 5.7 + 1.5 t t > 1 hour

The major processes assumed to drive NO to nftrate in the model are photochemically initiated. Thus, the nighttime conversion rates would be expected to approach zero. Daytime rates would maximize around midday. By assuming a constant conversion rate for 24 hours, an overestimate of the nitrate concentration is likely to result, at least in the near field. This fact should be considered upon interpreting the results.

13.3 WET AND DRY DEPOSITION RATES

The dry deposition of a contaminant onto the ground or vegetative surface depends upon its ground-level ambient concentration and the ability of the surface to retain that particular species. An artifact, the so-called "deposition velocity", is often employed as an empirical measure of this capability. Reactive gases such as SO_2 and NO_x , which may be readily ingested into groundwater and vegetation, have deposition velocities on the order 1 cm/sec (see Appendix B).

Deposition of airborne particulates results from mechanical impaction upon surface vegetation, other surface features and bodies of water. The size distribution and solubility of particles are contributing factors to the rate of dry deposition. Very large particles (diameter $>> 10 \ \mu\text{m}$; e.g., dust) can settle gravitationally. Particles with diameters exceeding 1 μm are able to impact upon vegetation because their inertia does not strictly follow the air flow. The trajectories of still smaller particles are controlled by eddy diffusion. However, in the presence of high relative humidity, droplets can form about the particles, and the effective size and deposition velocity are increased. In addition, the presence of a vegetation canopy has been shown to increase deposition by offering many impaction surfaces and producing small-scale turbulence that brings particles to the surface. An algorithm is incorporated into the HCSDM to take into account the dependence of deposition velocities

on particulate size distribution, wind speed and vegetation density. For sulfates and other small particulates, a representative value of deposition velocity is 0.1 cm/sec (see Appendix B, Modeling Methodology).

The removal of gaseous contaminants by precipitation is a complex process governed by such physical parameters as initial precipitation pH¹², background ambient contaminant concentration¹³, precipitation type and precipitation rate.¹⁴ The primary wet removal mechanism for gases is below-cloud washout. In the case of SO2, a rain droplet falling through a plume absorbs SO, until the equilibrium concentration of SO, in the droplet is reached. However, if the SO,-laden droplet subsequently falls below the plume into clean air, desorption takes place, and a fraction of the originally adsorbed SO₂ is returned to the atmosphere.¹³ On the basis of available precipitation chemistry data, empirical washout coefficients have been derived by various researchers with the intent of predicting the amount of gaseous contaminants that will be scavenged during below-cloud washout (the analogous mechanism during snowfall is called snowout).^{15,11} These washout coefficients are expressed in terms of ratios of gas concentrations in the precipitation to gas concentrations in the atmosphere. For the purposes of this study, the washout ratios recommended by Slinn¹¹ were used. It was also assumed that 90% of the contaminant mass deposited during periods of precipitation resulted from below-cloud washout. The model considers all SO, deposited by precipitation to be transformed to SO_4^{π} (also NO_{χ} to NO_{3}^{-}) during the wet scavenging process.

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The discussion in reference 14 on scavenging of gases by snow indicates that the scavenging efficiency of snowflakes for gases is much smaller than for raindrops. However, since a substantial portion of the study area's precipitation occurs in the form of snow, an algorithm was incorporated into the model to include contaminant scavenging by snowfall.

For particulate aerosols, both in-cloud and below-cloud scavenging may be important. A washout ratio developed for sulfates¹⁶ was adapted for TSP and NO_3^- removal in the model. In addition, the concentration of scavenged material is evaluated in the model at various stages of
hydrometeor growth. Scavenging efficiency is dependent on such factors as precipitation type, cloud type and in-cloud temperature. Washout ratios for particles decrease with decreasing precipitation rates¹⁴.

13.4 PRECIPITATION PATTERNS IN SOUTHERN BRITISH COLUMBIA

The washout ratios^{16,11} discussed in the preceding section are expressed in the HCSDM model as functions of the precipitation rate. In addition, the amount of contaminant mass scavenged is dependent on the precipitation type. Therefore, it was necessary to assemble representative precipitation data for the study area to provide the required input for the HCSDM.

Precipitation data for 34 relevant sites in southern British Columbia were available for this study. The data were primarily in the form of monthly and annual precipitation totals given in inches of water. Snowfall fraction, precipitation event frequency and thunderstorm frequency were also available for some stations. Table I3-1 lists the stations for which data could be obtained and indicates the types of data available for each station. The locations of the stations relative to the proposed project site and selected water sheds in the region are displayed in Figure I3-2.

As can be seen in Table I3-1, precipitation intensity statistics were available for only 9 of the 34 sites. For these 9 stations, curves of precipitation intensity versus duration were drawn for return times of 2, 5, 10, and 25 years. The average precipitation rate chosen for each station to characterize local scavenging efficiency was that corresponding to a two-year storm lasting 24 hours. Use of this value is considered conservative, (i.e., it will lead to an overestimate of material washed out) since a 24-hour storm with this average intensity occurs on the average only once per two years. This conservatism is offset somewhat by the portion of storms with greater intensities over shorter durations. For stations without intensity data, 24-hour intensity values were obtained by scaling from the intensity at the nearest of the 9 stations on the basis of annual (or seasonal) rainfall (or snowfall)

TABLE 13-1

PRECIPITATION DATA FOR SELECTED STATIONS IN SOUTHERN BRITISH COLUMBIA

	Total Precipitation	Totat Procipitation	Procipitation	Snowfall	Thunderstorm	Greatest 24 Hour Precipitation	Greatest	Greatost	Procipitation	Station
Station	<u>Annust</u>	Senson	Frequency	Fraction	Frequency	Total	<u>Aninfall</u>	Snowfall	Intensity	Humber
Analie i mi	*	ĸ	x	×		×	×	×		i .
Asheroft	*	*	×	×	¥	×		¥		2
Burriero	×	x	x	x		x	x	*		2
pratorno	×	×	x	×		×	x	x		4
bug Crook	×	*	. .	x	×	×	×	×		5
Hut Crook	×	*	x	×		x	x	×		6
Hedley	×	×	×	¥		x	¥	*		7
liolls Gato	×	x	x	X		x	x	×		
Hupo	×	x	×	×	¥	×	¥	¥	*	9
Hursofly Laka	×	x	×	x		*	÷.	*	*	10
Keetoobs	×	×	. x	x	x	×	×	¥	×	3.4
Kolowna	x	x	×	×		x	×	×	×	12
Alta Lako	×	x	x	x		×	x	*	x	13
1110001	×	*	×	Ŕ		1 x	*	×		14
lytten	×	x	×	×	· x	×	x	×		15
150 Hila Housa	×	×	x	×		×	*	x		16
Pontierton Hondows	×		×	×		*	×	x		17
Penticion	ĸ	x	x	×	x	x	×	x	×	18
Quanal	*	x	×	· 🗴		×	×	x		19
Salmon Arm	×	×	*	×		x	×	×	×	20
Vernon	×	×	×	x				×		21
Agussiz	×	*	×	x		x	×	×	×	22
Frincoton	*	*	×	x	×	x	×	×		23
Big Crook	*	*	×	x		¥	x	×		24
Scaver Lako	¥	×	×	×		, x	ж	x		25
Chuse	*	×	×	x			×	×		26
Blue River	×	×	×	x			×	x	x	27
Durfisid	×	×	×	×		×	ĸ	x		28
Horritt	×	×	×	*		x	x	x		29
Squantsh	×	×	×	x		×	×	×		30
Shuswap Falls	¥	×	ĸ	×		x	x	×		31
Aloxis Crock	×		×	¥		×	x	×		32
Boss Hountain	*	×		×						33
Houp Grook Clearwater	x	×		×						34

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per precipitation day. For example, the representative intensity at Pemberton Meadows was computed from the intensity of a 2-year storm of 24 hours at Alta Lake (0.075 inches/hour) times the ratio of rainfall per precipitation day at Pemberton Meadows (0.49 inches/day) to the corresponding value at Alta Lake (0.25 inches/day), i.e., 0.075 x 0.49/0.26 = 0.14 inches/hour at Pemberton Meadows. This method was used to estimate reasonable two-year storm and 24-hour precipitation intensities at all 34 stations. Values at individual model receptor locations were then obtained by interpolation.

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The resulting isopleth maps of precipitation intensity (inches/hour) for annual and seasonal periods comprise Figures I3-3 through I3-7. Contours indicating the number of seasonal and annual days with measurable precipitation are plotted in Figures I3-8 through I3-12. Figures I3-13 through I3-16 indicate the distribution of snowfall fraction [percentage of seasonal or annual precipitation (melted) occuring as snow]. There is no plot of snowfall fraction for the summer season. Maps of thunderstorm frequency (percent of total precipitation occuring during thunderstorms) are presented in Figures I3-17 and I3-18 for an average-annual period and for the summer season, respectively.

Subsequent to completion of the pH change calculations presented in this report, precipitation data from a substantially larger number of stations within the study area were obtained. The new data set represents measurements at 164 stations; precipitation intensity - duration statistics have been developed for 36 of these stations. Plots of the geographical distributions of the important precipitation parameters, i.e., representative 2-year/24-hour storm intensities, annual and seasonal days with precipitation, and snowfall fractions were constructed from the new data. These figures are presented in Addendum A to this appendix.

Statistical comparisons of the two precipitation data sets are also provided in Addendum A. In addition, a sample calculation, showing the effect of enlarging the data set on the pH change calculations for one of the selected B.C. water bodies is included. In some instances, the more refined analysis made possible by the incorporation of additional

data led to lower predicted pH changes in the selected water bodies. As described in Addendum A, the largest change in terms of increased pH change as computed with the expanded data set was about 0.32 pH units at Deadman River. Because the estimated pH changes obtained with the additional data were either similar to or smaller than those predicted with the original data, it was not considered necessary to repeat the entire modeling and water quality calculations to incorporate the new data.



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14.0 CRITICAL WATER RECEPTOR AREAS

Several criteria were considered important in evaluating the areas of concern in the vicinity of the proposed Hat Creek Project. Prevailing meteorological conditions, important biologically sensitive areas, and buffering capacity of soil and water were the major considerations in selection of the critical water receptor systems in terms of potential acid precipitation. These areas were largely defined geographically by a quadrant northeast (NE) of the proposed facility with additional consideration for a sector area to the southeast (SE). Predominant wind patterns would tend to transport project emissions directly NE with other important directions being directly toward the north (N) and SE.

ERT selected five areas in the NE quadrant and one area in the SE quadrant relative to the proposed site for detailed evaluation. These particular areas were chosen because of their recreational and economic importance and relatively limited buffering capacities. They are: 1) the Adams River watershed, 2) the immediate vicinity within 50 km of the Hat Creek power plant, 3) the Clearwater River system, 4) Boss and Hendrix Creeks, 5) Pennask Lake, and 6) Deadman River. All of these areas were reviewed in terms of potential acid precipitation effects due to operation of the Hat Creek power plant.

I4.1 BACKGROUND

Aquatic ecosystems, especially lakes and streams with low alkalinities, react more rapidly to pH changes than terrestrial ecosystems.¹⁷ In geographical regions where limestone or calcareous rock are prevalent, the natural buffering system will mitigate effects of acid precipitation. However, in Scandinavian countries and geological provinces such as the Canadian Shield where calcareous material is generally lacking, soils and water bodies are naturally low in buffering capacity and more susceptible to pH changes caused by acid precipitation. In mountainous areas or in northern latitudes where severe winters occur, effects of acid precipitation often fluctuate seasonally.

Water bodies near the proposed plant site are moderately or well-buffered, while waters further to the north and east are poorly buffered. The British Columbia Ministry of Recreation and Conservation (BCMRC) reviewed the available water quality data for 205 water bodies in the area of the proposed Hat Creek Project.⁹ The report identified 43 water systems considered potentially vulnerable to acidification. The present study involved a review of the BCMRC report and other available information to determine a set of aquatic systems best representing a cross-section of the areas of concern.

Of the 43 water bodies mentioned by the BCMRC, most have alkalinities of 50 mg/1 CaCO₃ or less. In addition, pH values were basic, generally 7.2 or higher. Only four lakes were identified with an average pH below 7 (range 6.5-6.9) and four between pH 7.0 and 7.2. Published water quality parameters (e.g., alkalinity and pH) are usually presented in terms of annual averages. The variability about such averages and the degree of uncertainty in such data is generally unknown. In addition, the reporting periods and consistency of the water quality measurement techniques are not specified.

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Soil buffering capacity, or base saturation, expresses the ability of a soil to resist pH reductions. A soil with a high proportion of calcium, magnesium, potassium and other basic cations among its exchangeable ions has a high base saturation. Such soils are usually neutral or alkaline and have high buffering capacities (i.e., they are relatively resistant to changes in pH). In specific studies, soils with a high buffering capacity have been shown to be capable of neutralizing 40 to over 90% of hydrogen ions added as a result of air pollution or acid precipitation.

A review of ionic budgets in terrestrial ecosystems is also required to evaluate the relative magnitude of any effects due to additional hydrogen ion deposition surrounding the Hat Creek Project. The behavior of hydrogen ions in terrestrial ecosystems is a major factor in determining stream water chemistry. Hydrogen ions may be viewed as the major factor in chemical weathering reactions in natural ecosystems.¹⁸ Therefore, weathering rates may be seen as the rate at which H⁺ is supplied to the system.

As H^{\dagger} is fixed in the terrestrial ecosystem, basic cations may be leached from the system. Thus, weathering rates and hydrogen ion fixation can be viewed in terms of cationic denudation rates.¹⁹

The hydrogen ion budget for a given terrestrial ecosystem is a function of climatological characteristics and various biological and chemical processes in soils. In an undisturbed system, cationic denudation rates should be balanced by the sum of the net external and net internal rates of supply of H⁺ ions. Studies of long-term cationic denudation in relation to atmospheric H⁺ inputs have been conducted at the Hubbard Brook Experimental Forest in New Hampshire, U.S.A. This collection of small mountain watershed is subject to an average precipitation pH of 4.1. Data suggests that under the prevailing biological and chemical conditions, external and internal sources have equal roles in H^{+} ion generation.¹⁸ A cationic denudation rate of 2.0 x 10^3 eg/ha/yr, typical of New England as a whole, is found in the mountainous New Hampshire watershed. In comparison, the cationic denudation for the Fraser River, British Columbia, has been estimated at 3.8 x 10^3 eg/ha/yr, which is equal to the rate for North America as a whole.^{19,20} The differences in weathering rates between watersheds or regions indicates the importance of recognizing hydrologic, geoclimatic and biogeochemical factors specific to an ecosystem when evaluating hydrogen ion movement.

The generalized weathering estimate for a large watershed such as the Fraser River system actually represents various input-output budgets within portions of the watershed. Studies in the Okanagan Valley of British Columbia have documented an elevation dependence on pH and cation content of soils and streams.²¹ Mountain streams east of Kelowna, British Columbia, had a pH gradient from 6.30-6.79 above 5,000 ft to 7.05-8.31 at 1,500 ft and below. The differences are attributable to climatic and soil development factors associated with elevation. At higher elevations there is heavier precipitation, lower transpiration, and often shallower soils; consequently, soils are more fully leached and streams contain less cations. Water quality and soil data collected by the Ministry of the Environment within 200 km of the Hat Creek site indicate similar cation count variations with elevation. Studies at

Carnation Creek, Vancouver Island, support the theory that watersheds with high annual rainfall, low evapotranspiration rates and shallow soils have generally lower ionic concentrations in streamflow.²² Sulfate is the dominant ion in precipitation at Carnation Creek, but it occurs at only one-third the concentrations observed in the northeastern United States. Bicarbonate and calcium are the principal anion and cation in the watershed streams.

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Soil orders as defined by the Canadian Soil Classification System provide a general indication of soil buffering capacity within the Hat Creek study area. The Luvisolic, Brunisolic, and Chernozemic soils that are found in the area of maximum predicted hydrogen deposition (within 50 km from the proposed project site) have moderate to high buffering capacities. The combination of alkaline parent materials, high cation exchange capacity, and moderate to high base saturation promotes neutralization of added protons. Soils belonging to the Podzolic orders have low buffering capacities; however, such acidic, well-drained soils are not common in the NE quadrant from the Hat Creek site until a distance of about 200 km. According to the modeling results (see Section I5.0), these areas will receive very low quantities of acid contaminants from deposition of Hat Creek emissions due to the highly dispersed nature of the emissions at this distance.

14.2 SELECTED CRITICAL WATER RECEPTOR AREAS

14.2.1 Adams River Watershed

Adams River and Adams Lake are located NE of the proposed Hat Creek power plant. The area includes a drainage system which provides approximately 50% of the salmon spawning stock to the Fraser River drainage basin. It is thus one of the most important salmon fishery streams in North America. Adams Lake and the upper and lower reaches of the Adams River above and below the lake extend from approximately 125 km to 250 km from the proposed Hat Creek Project.

The pH measurements reported for Adams River and Adams Lake range between 7.2 and 8.8. Annual average pH at the mouth of the Adams River

is 7.6; the corresponding value for Adams Lake is 7.7. Alkalinity and specific conductance reported for Adams River are 22.5 mg/l and 55.0 µmho/cm, respectively.⁹ Corresponding values for Adams Lake are 43.9 and 57.0. These characteristics indicate a soft water aquatic system with limited buffering capacity. No water quality or flow rate data were available for the upper Adams River, which is the principal area of concern in terms of salmon spawning. However, the upper Adams is farther from the plant site and in a narrower drainage basin than the lower Adams. Thus, effects in the upper Adams are expected to be similar to those predicted in this study, assuming similar buffering.

The upper Adams River system is a drainage basin with very low soil buffering capacity because of acidic, well-drained soils. These humoferric Podzolic soils have developed on coarse, noncalcareous materials and usually have a pH less than 5.5 throughout their depth. They generally support a coniferous forest. Chemical and biological transformations are rapid in the surface layer of organic matter and in the upper soil horitons. The soils are strongly leached by organic acids and large amounts of water pass down through the profile during the year. They contain few bases such as calcium or magnesium. Total exchangeable bases may be less than 2 meq/100 g of soil compared with 20 meq/100 g or more found in well-buffered soils.²³ The low cation exchange capacity of the podzols is dominated by hydrogen ions. Forest cover represents a primary source of hydrogen ion removal before deposition on these soils.

I4.2.2 Immediate Hat Creek Power Plant Environs (Thompson River, Loon Lake, Deadman River)

The area expected to receive the most intense deposition of H^{+} ions is the region to the east and northeast and within 50 km of the Hat Creek Project site. This region has several biologically important water systems for migratory as well as self-sufficient fish populations. Fortunately, this area also has soil and water buffering capacities considered moderate to high.

The most prominent water system in this area is the Thompson River. Its basin receives inputs from all of the medium and small watersheds in the

near (within 50 km) NE quadrant and constitutes the "water reservoir" with the highest expected deposition of proton donors due to the Hat Creek Project. In addition, it is the major migratory pathway for steelhead and salmon that spawn in the water systems throughout the NE quarter. As a result, adverse impacts to the Thompson River would affect fisheries throughout the region. Other important watersheds in this area include the Bonaparte River, Loon Lake, Tranquille River, Deadman River and others. Recreationally, the area is also one of the most important in British Columbia.

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Buffering capacities in water systems near the power plant site are an important factor in offsetting potential acidification. The water systems have ranges of alkalinity and specific conductance from 33.8 to 40.4 mg/l and 80.0 to 101.7 umho/cm, respectively. Reported pH values are generally about 7.5. These characteristics indicate a moderate buffering capacity, and, in combination with rather large water body volumes and flow rates, provide a large capacity for proton donor dilution.

Soils in the immediate power plant area (within 40 km) have moderate to high buffering capacities. Luvisolic and Brunisolic soil orders are most common throughout the area. Chernozenic soils are distributed along the Thompson River east of the plant site to Kamloops.

The Gray Luvisol soil of the study area is characterized by moderately acidic pH in the A and B (top) horizons and alkaline pH in the subsoil (C horizon). Soil buffering is provided by surface organic matter, clay accumulation in the B horizon and the alkaline subsoil. In addition, the soil profile has a high cation exchange capacity and moderate base saturation even in the leached surface mineral layer (A horizon). Brunisolic soils in the study area have little weathering because of climatic conditions. Although they are coarse-textured, Brunisolic soils have high base status throughout their soil depth as a result of their parent materials. Their pH is neutral to slightly acidic. Chernozemic soils occur where there is low rainfall and very low leaching. An accumulation of organic matter is found in the Chernozemic topsoil.

Such soils have high pH throughout the profile, high base saturation and high cation exchange capacity.²⁴ In general, these well-buffered soils maintain the alkaline stream conditions found in the area.

The combination of moderate water body buffering capacities and high soil buffering is indicative of water systems capable of short and longterm maintenance. Historic water quality information supports this because there has been very little change in most parameters over the years. It is expected that these conditions will prevail for a very long time with or without additional H^+ ion inputs from the Hat Creek Project. The specific water bodies in this area, for which pH effects were calculated, are the Thompson River, Loon Lake and Deadman River.

14.2.3 Clearwater River System

Another region of potential importance in terms of impacts due to the Hat Creek facilities also lies NE of the project site. The Wells Gray Provincial Park is approximately 200 km NE of the Project, and the Clear Water River System in Wells Gray Park is one of the most important in the Province in terms of recreational value.

The Clearwater River System, including Clearwater Lake, is similar to the Adams River System in that it has a relatively low buffering capacity due to surrounding soils which are generally acidic and moderate to low in buffering capacity. The system is utilized by salmon for spawning and, as its name implies, is characterized by very clear water with several recreationally important game fish populations.

In some respects, the Clearwater River System is also very similar to the Thompson River System. Average alkalinity and specific conductance values of 35.3 mg/l and 106.5 µmho/cm, respectively, have been reported. Although pH values were not found in the literature, other water bodies of the area have pH values generally in the range of 7.0 to 7.2. It is expected that similar values would be applicable for the Clearwater River System. The buffering capacities are therefore expected to be higher than the Adams River watershed but less than the Thompson River System.

The Clearwater River watershed has predominantly Podzolic soils, the same acidic and poorly buffered soils found in the upper Adams River watershed. Forest cover and surface organic matter are the principal buffering components in these soils. It is expected that the buffering capacity of the Clearwater River System is adequate to neutralize the relatively infrequent deposition of H^+ ions that would be transported to this area from the Hat Creek Project.

14.2.4 Boss and Hendrix Creeks

These creeks are located almost directly north of the proposed power plant site. These systems are much smaller in size than the rivers and lakes of the other systems. As such they were chosen as representative of water bodies with minimal dilution capabilities (low flow). Buffering capacities of the watersheds are low, and the pH ranges from 6.8 to 7.2. Alkalinity values are generally indicative of soft water, ranging from 22.8 to 28.3 mg/l. Specific conductance measurements have a much wider range, from 70.5 to 116.6 µmho/cm. Biologically, these aquatic systems are considered better than average fisheries with good resident gamefish populations.

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The Boss and Hendrix Creek watersheds are influenced by Podzolic and Luvisolic soil development. Coniferous forest is a key factor regulating hydrogen ion flow in these watersheds. Although horizon layers are probably of minimal depth, the coniferous forest development provides a rapid metabolic cycle for absorption of deposited protons. In addition the water bodies in these watersheds have sufficient pH and alkalinity for buffering small amounts of proton deposition.

I4.2.5 Pennask Lake

The fifth watershed selected for study is located in the SE quadrant from the proposed project area and is considered a major lake sport fisheries habitat. Biologically and recreationally this area receives a great deal of public and government attention. Wind frequency statistics indicate that this region will often be downwind from the power

plant. The lake is located less than 200 km from the proposed Hat Creek site and is within the area potentially affected by long-range transport of project emissions.

Water quality information for Pennask Lake is minimal, but average values for pH of 7.6 and alkalinity of 22.6 mg/l have been reported. Although the alkalinity is indicative of soft water, the pH measurements suggest a surrounding area capable of maintaining basic conditions. Pennask Lake has a moderate buffering capacity because of this latter characteristic.

The Pennask Lake watershed drains through Luvisolic and Brunisolic soils with moderate buffering capacities. Both major soil orders contain alkaline materials within the soil profile. It is largely these soil conditions in the watershed that enable Pennask Lake to maintain a moderate buffering capacity.

15.0 AIR QUALITY MODELING RESULTS

The methodology described in Section I3.0 was used to compute deposition fluxes $(grams/m^2/sec)$ for acidic species related to emissions from the proposed Hat Creek Project. Deposition fluxes were calculated for 256 receptors configured in a radial grid out to a distance of 200 km from the plant site. The contaminant species for which deposition fluxes were calculated are:

- SO₂ (wet and dry deposition)
- $SO_4^{=}$ (wet and dry deposition)
- NO_3^- (wet and dry deposition)
- TSP (wet and dry deposition)
- NO_x (dry deposition)

The computational model does not calculate wet NO_x deposition, but includes it with the wet NO_3^- deposition. Plume rise calculations for emissions from the proposed 366 (1200-ft) stack determined that the Hat Creek Plant plume would normally reach its equilibrium height at approximatly the 700 millibar (mb) level of the atmosphere. This result is based on the assumption of an average near-neutral stability. One year of radiosonde data (700 mb level) from Vernon, British Columbia, was used to provide meteorological input (wind speed and direction) for the modeling. For purposes of transport and dispersion modeling, the mixing depth (the depth of the atmosphere to which mixing of airborne material to the ground is possible) was set at 1500 m above the Hat Creek site elevation. This mixing depth was chosen so that the plume would always remain within the mixed layer and, therefore, affect concentrations at the surface.

15.1 CONTAMINANT DEPOSITION FLUXES

Isopleth maps of computed annual and seasonal average deposition fluxes for SO_2 , $SO_4^{=}$, NO_3^{-} , TSP, and NO_x are presented in this section. Wet and dry deposition patterns for SO_2 , $SO_4^{=}$, NO_3^{-} , and TSP are included; all

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wet NO_X (total of gaseous NO and NO₂) deposition was assumed to be in the form of NO₃. The following subsections describe the model results in terms of annual and seasonal variations. The effects of varying selected model input parameters on predicted deposition patterns and the resulting pH change in natural water bodies are discussed in Sections IS.3 and I6.6.

15.1.1 Annual Deposition Rates

The overall prevalence of southwesterly winds at the 700 mb level in Vernon is evidenced in the annual deposition patterns illustrated in Figures IS-1 through IS-9. The units corresponding to the plotted isopleths are g m⁻² sec⁻¹. Maximum wet and dry rates of deposition for all contaminants are predicted to occur to the NE of the proposed plant site. Secondary dry deposition maxima are also seen to the SE, reflecting a rather high frequency of northwesterly flow. The annual wind rose used in the calculations is found in Table A2-98 (Appendix A). The data indicate that certain wind directions are more likely to be associated with precipitation events than others. However, there are insufficient data to mathematically define the relationship. The peak mass deposition values may be ranked by contaminant in order of descending magnitude as follows:

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wet deposition - NO_3^- , SO_2^- , TSP, SO_4^{\pm} dry deposition - NO_x and SO_2^- , NO_3^- , TSP, SO_4^{\pm} .

Maximum depositions for primary contaminants (i.e., those directly emitted from the proposed power plant) occur nearer to the Hat Creek site than do secondary species. Thus maxima for wet and dry SO_2 are predicted between 50 and 70 km from the site, while peak SO_4^{-} values are expected further than 100 km downwind.

IS.1.2 Winter Deposition Rates

The winter wind rose for the 700 mb level is presented in Appendix A, Table A2-99. Winds from the southwest (SW) clockwise through northwest (NW) dominate during this season. This is reflected in Figures I5-10 through I5-18 which depict seasonal averaged deposition patterns for each species during the winter months. Much of the precipitation falling in the study area during winter is in the form of snow. The collection



Figure 15-1: Isopleths of Predicted Annual Wet SO₂ Deposition Rate Due to flat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-9}$)

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Figure 15-3. Isopleths of Predicted Annual Wet SO_4^{-} Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹x 10⁻¹²)

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Figure 15-6. Isopleths of Predicted Annual Dry NO₃ Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$). ENT ENTITE LA LA

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Figure 15-7. Isopleths of Predicted Annual Wet TSP Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).



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Figure 15-9. Isopleths of Predicted Annual Dry NO_X Deposition Rate Due to Hat Creek Project Emissions (g m⁻² sec⁻¹ x 10⁻⁹).

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Figure 15-10. Isopleths of Predicted Winter Wet SO₂ Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-9}$).

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Figure 15-13. Isopleths of Predicted Winter Dry SO_4^{-7} Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹ x 10⁻¹²).



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Figure 15-15. Isopleths of Predicted Winter Wet NO_3^- Deposition Rate Due to Hat Creek Project Emissions (g w⁻²sec⁻¹ x 10⁻⁹).



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Figure 15-17. Isopleths of Predicted Winter Dry TSP Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).

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efficiency of snow is considerably lower than that of rain; consequently it is not surprising to note that wet deposition peaks are smaller during this season than the annual maxima. Although the collection efficiency of snow is less, cumulative dry deposition of acidic components on a ground snow pack results in spring melt water of similar acidity to rain water droplets falling through the atmosphere. Dry deposition rate patterns exhibit maximum values comparable to those for the full year. Again, SO₂ and NO_x maxima are expected to occur nearer to the power plant site than those of the corresponding secondary contaminants, SO[#]₄ and NO^{*}₅ respectively. All the highest wet and dry winter deposition rates are predicted within the sector between NE and SE from the Hat Creek Project site.

15.1.3 Spring Deposition Rates

Figures 15-19 through 15-27 represent computed average deposition rates for the spring season. The magnitudes of maximum deposition rates are comparable to those presented for the annual averaging period. The wind rose for spring (Appendix A, Table A2-100) exhibits a more varied distribution of directional frequencies during this season than for winter. Correspondingly, the integrated mass deposition for spring is spread over a wider geographical area. Note that the patterns for some contaminants include non-negligible deposition rates on the western side of a line passing north-south through the Hat Creek site area. The highest values, however, are still found to the NE. In order of descending peak predicted mass deposition rates, the species considered may be ranked in approximately the same way as was indicated for the annual averaging period. Maximum wet and dry SO2 deposition rates are expected within 40 to 50 km from the site to the ENE and to the SW. Maximum wet deposition of sulfate is expected to occur much further from the source, just south of Wells Gray Park. The amount of SO_A^{-} deposited by dry removal processes is greater throughout the study area and the peak dry deposition rate is expected 60 to 80 km to the NE. Wet removal accounts for most of the nitrate deposited during spring, and generally high rates are expected over a wide range of distances -- roughly from the plant site to Adams Lake. As seen for the other seasons, wet and dry TSP deposition rates are relatively small throughout the area, reflecting the smaller projected emissions of this contaminant from the Hat Creek plant.



Figure 15-19. Isopleths of Predicted Spring Wet SO₂ Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-9}$).

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Figure 15-26. Isopleths of Predicted Spring Dry TSP Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).



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15.1.4 Summer Deposition Rates

Predicted seasonal average deposition patterns for the summer months in the study region are presented in Figures IS-28 through IS-36. The wind rose used in the model calculations for this season is included as Table A2-101 in Appendix A. Wet deposition maxima are at their highest values during the summer. This is partially attributable to the higher incidence of thunderstorm activity during these months, since deposition increases with increasing precipitation intensity. Maximum rates for both wet and dry deposition are predicted to occur between lines drawn from the Hat Creek site toward the NE and SE. Primary contaminants (SO₂, TSP, and NO_x) have maximum rates between 30 and 60 km downwind, while secondary contaminants are expected to exhibit maxima further from the source. Dry deposition is also highest during the summer in the areas where total precipitation is lowest for this season.

15.1.5 Autumn Deposition Rates

Patterns of seasonally averaged deposition for the autumn season are included in Figures I5-37 through I5-45. The fall wind rose used for these model applications is found in Appendix A, Table A2-102. As was noted in the spring, the Vernon 700 mb winds are distributed fairly uniformly during this transitional season, leading to a fairly broad spring deposition pattern. Differences between the distributions predicted for wet and dry depositions reflect the tendency of some directions to be preferentially associated with precipitation events.

In most of the figures, maximum rates are seen both near to and far from the Hat Creek site, often in the same downwind direction. In general, deposition rates for autumn are greater than the annual average values, and are exceeded only during the summer months.



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Figure 15-29. Isopleths of Predicted Summer Dry SO₂ Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹ x 10⁻⁹).





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Figure 15-31. Isopleths of Predicted Summer Dry SO_4^{\pm} Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹ x 10⁻¹²).



Figure 15-32. Isopleths of Predicted Summer Wet $NO_{\overline{3}}$ Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹ x 10⁻⁹).

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Figure 15-33. Isopleths of Predicted Summer Dry NO₃ Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).



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Figure 15-36. Isopleths of Predicted Summer Dry NO_x Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-9}$).

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Figure 15-37. Isopleths of Predicted Autumn Wet SO₂ Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-9}$).



Figure 15-38. Isopleths of Predicted Autumn Dry SO₂ Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹ x 10^{-9}).

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Figure 15-40. Isopleths of Predicted Autumn Dry $SO_{\overline{4}}$ Deposition Rate Due to Hat Creek Project Emissions (g m⁻¹sec⁻¹ x 10⁻¹²).

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Figure 15-42. Isopleths of Predicted Autumn Dry NO3 Deposition Rate Due to flat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).

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Figure 15-43. Isopleths of Predicted Autumn Wet TSP Deposition Rate Due to flat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).



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Figure 15-44. Isopleths of Predicted Autumn Dry TSP Deposition Rate Due to Hat Creek Project Emissions (g $m^{-2}sec^{-1} \times 10^{-12}$).

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Figure 15-45. Isopleths of Predicted Autumn Dry NO_x Deposition Rate Due to Hat Creek Project Emissions (g m⁻²sec⁻¹ x 10⁻⁹).

15.2 HYDROGEN ION DEPOSITION

For purposes of computing pH change due to Hat Creek Project emissions, the results of deposition rate calculations for individual plume species have been combined and figures prepared to indicate average net hydrogen ion deposition for each season and for an average year. The hydrogen ion isopleths represent the sum of contributions from the following atmospheric processes:

- dry SO, deposition
- dry SO^{*} deposition
- wet NO₃ deposition
- dry NO₂ deposition
- dry NO, deposition

Calculated wet SO₂ and SO₄^{*} deposition rates correspond to precipitation hydrogen ion concentrations which would be neutralized by even a low estimate for the ambient concentration of atmospheric ammonia found in temperate latitudes. For this reason only the dry deposition components for these species are considered capable of affecting pH in receiving water bodies. Conservatively, all SO₂ and SO₄^{*} reaching the surface are treated as pure sulfuric acid; similarly wet and dry NO₃^{*} and dry NO_x are assumed to have somehow completely oxidized to nitric acid. Clearly these assumptions may be expected to result in overestimates of the amount of H^{*} available to affect pH in the study area. Typical contributions to alkalinity in precipitation induced by dissolved flyash (TSP) in the plume were calculated and found to be negligible in terms of their effects on the chemistry of precipitation. Equivalent weights assumed for the species considered are listed below.

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Species	Equivalent Weight
so _z	32
so [#]	48
NO ⁻ 3	62
NOx	46 (assumes all NO
	converted to NO2)

Annual and seasonal plots of hydrogen ion deposition are presented in Figures I5-46 through IS-51. Seasonal variations in the observed patterns reflect the aggregate effects of meteorological and physical factors which influence the corresponding deposition patterns for the various species included. Units are $eq/m^2/sec$ calculated by dividing mass deposition rates by the respective equivalent weight of the important species. Figure I5-53 indicates the values of H⁺ deposition rate corresponding to a storm or 'episode' condition with a uniform precipitation rate of 0.35 inches per hour. For the purpose of illustration, the results for plumes following winds from the north clockwise through south are shown simultaneously, although in reality, the events affecting specific areas will occur at different times.

15.3 AIR QUALITY SENSITIVITY ANALYSIS

Sulfur and nitrogen oxide emissions from the proposed Hat Creek Project react chemically in the atmosphere to form sulfate and nitrate anions. These species are the primary sources of the acidic compounds $(H_2SO_4$ and $HNO_3)$ which could affect the pH of the precipitation and receiving waters in the Project vicinity. Because calculation of the ambient concentrations and surface deposition fluxes is important to the results of this study, it was deemed advisable to examine the changes in the ambient concentrations and deposition fluxes when selected model parameters are adjusted. The intent of the analysis was to examine the sensitivity of the various algorithms (depletion and chemical transformation mechanisms) in the HCSDM to the assumptions made in simulating these mechanisms.

A further motivation for performing the sensitivity analyses is provided by the particular geographical distribution of well-buffered and poorly buffered soils and aquatic systems in the study area. In most modeling applications, the use of high SO_2 to SO_4 conversion rate and high deposition velocities would be considered consistent with a conservative approach to estimating potential acid deposition impacts. However, since the area nearest the Hat Creek site is well buffered compared to the more distant regions of the study area, it is important to recognize

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Figure 15-46. Isopleths of Predicted Annual Hydrogen Ion Deposition Rate Due to Hat Creek Project Emissions (Eq/m²/sec x 10⁻⁹).

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Figure 15-47. Isopleths of Predicted Winter Hydrogen Ion Deposition Rate Due to Hat Creek Project Emissions (Eq/m² /sec x 10^{-11}).

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Figure 15-49. Isopleths of Predicted Summer Hydrogen Ion Deposition Rate Due to Hat Creek Project Emissions $(Eq/m^2/sec \times 10^{-11})$.



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Figure 15-51. Isopleths of Predicted Episode Hydrogen Ion Deposition Rate Due to Hat Creek Project Emissions (Eq/m²/sec x 10^{-10}).

that a range of values for the more important model parameters should be tested to ensure that the results of the pH change analyses indeed include "conservative" predictions.

Initially, the critical parameter in the modeling methodology is the transformation rate of a primary to a secondary contaminant (i.e., SO_2 to SO_4^{\ast} or NO to NO_3^{\ast}). In this study, the transformation rate of 1%/hr for SO_2 to SO_4^{\ast} was used. This rate was changed to 2%/hr and the results compared to the initial modeling results. It was determined that using a value of 2% would cause the wet and dry deposition fluxes of SO_4^{\ast} to increase by 98 and 93% respectively. At the same time, the wet and dry deposition flux of SO_2 would decrease by approximately 6%.

A further sensitivity test was performed to determine the effect of reducing the SO_2 to SO_4 transformation rate to 0.5% per hour. The results show that both wet and dry SO_4^{π} deposition fluxes change to 51% of the values computed for a 1.0% per hour conversion rate. The respective corresponding changes to wet and dry SO_2 deposition fluxes are 5% and 6% greater than the values for a 1.0% per hour conversion rate. These values (and all subsequent results discussed in this section) were computed for a representative distance of 100 km downwind from the proposed stack.

In this study, the assumed NO_3^-/NO_x washout ratio was approximately 0.3 at 100 km. This ratio was adjusted to 0.4, an increase of 33%, as part of the sensitivity analysis. As a result of this change, the wet deposition flux of nitrate increased by about 20%, while the dry deposition flux of NO_3^- and NO_x decreased by approximately 10 and 25%, respectively.

The effects of varying the magnitude of the assumed contaminant deposition velocities were also examined. During this study, the deposition velocity used for NO_x and SO₂ was 1.0 cm/sec. This parameter was adjusted to 2.0 cm/sec to assess the sensitivity to this assumption. As a result of this adjustment, the NO_x dry deposition flux at 100 km increased by 95% while the dry deposition flux for NO₃ decreased by only 4%. Correspondingly, the wet NO_x deposition flux decreased by about 10%.

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Particulate matter in the plume has a buffering effect on the acid species in the plume due to the basicity of the compounds composing the particulates in power plant emissions. Therefore, it was of interest to examine the effects on the computed ambient concentration and deposition fluxes of TSP due to a change in the assumed size distribution of the TSP. In the original modeling analysis, it was assumed that 30% of the particulates were greater than 1.0 µm in diameter. When this fraction was changed to 80%, the ambient concentration of TSP at 100 km decreased by slightly less than 1%, while the wet and dry deposition flux for TSP increased by 39% and 30%, respectively.

The results of the air quality sensitivity analyses are discussed in Section I6.8 in terms of potential changes in the pH values calculated for the water bodies of interest.

16.0 WATER QUALITY EFFECTS

16.1 TECHNICAL APPROACH

At present, no comprehensive model has been developed to relate proton deposition to changes in the pH of aquatic systems. Such a model would describe temporal variations in chemical composition, and would require input information about rainwater composition, atmospheric concentrations of acidic and alkaline species, efficiency of H^+ removal by specific vegetation types, chemical analysis of soils and groundwaters, weathering rates of rocks and minerals, buffering capacity of soils, size of drainage areas, volumes of water bodies, water quality data, precipitation rates and scavenging efficiencies, and a multitude of other data from which an accurate estimate of $\tilde{p}H$ effects in specific bodies might emerge.

In the absence of a comprehensive model, a much simpler approach to estimating changes in water quality from increased proton deposition is necessary. One approach is to make simplifying assumptions and approximations in a conservative manner, and to proceed using established chemical and physical principles when they are understood to be appropriate. In this section, a few simplified models are applied in the context of selected scenarios relating the deposition fields and the critical receptor areas (Sections I4.0 and I5.0) for annual, seasonal and shortterm "episode" cases in order to estimate changes in the pH of water bodies in the area surrounding the proposed Hat Creek Project. Model selection was based on the available type and quantity of information, the characteristics of the water bodies, and the time period of interest. These models are described briefly in Section I6.2.

16.2 MODELS FOR ESTIMATING CHANGES IN pH

Each of the models have several common elements, one of which is knowledge of the existing pH in the water bodies in the absence of the proposed power plant. The measured pH in all the lakes and streams studied ranged from 6.6 to 8.8 (in fact, both of these extreme values were measured in the Adams River near Squilax).⁹ A second element is the

average alkalinity for the season or year of interest. The buffering capacity of natural freshwaters in this pH range is dominated by the dissolved CO_2 system.²⁴ Under these conditions, the alkalinity is defined as

 $[Alk] = [HCD_{\tau}] + [CO_{\tau}^{2}] + [OH^{2}] - [H^{2}]$

where the brackets imply units of concentration, in this case taken to be microequivalents per liter (μ Eq/1). In water, having a pH of 7.0 and an alkalinity equal to 30 mg/l CaCO₃, the values of the respective concentrations would be:

 $[A1k] = 600 \ \mu Eq/1 \\ [HCO_3^-] \gtrsim 600 \ \mu Eq/1 \\ [CO_3^-] \gtrsim 0.02 \ \mu Eq/1 \\ [OH^-] = 0.1 \ \mu Eq/1 \\ [H^+] = 0.1 \ \mu Eq/1$

Thus, because of the negligible contribution of the last three species, the measured alkalinity of these waters may be equated to the bicarbonate ion concentration.²⁵

A third element is definition of a receptor area's size. For purposes of calculating pH effects, the published or estimated drainage area of a given water system is used as the potential deposition receptor area for the subject lake or river. A factor reflecting local soil types is applied as an estimate of the maximum fraction, f, of H^+ deposited in the area which is introduced to the water body. The remainder (1-f) is considered to be neutralized by buffering agents in the soil and vegetation. The estimated fraction, f, represents a fourth element. The basis for selecting such a fraction is discussed at length in the next several paragraphs. These calculations indicate the magnitude of increased proton additions to selected aquatic systems as a result of projected Hat Creek emissions. Watershed studies have shown that the chemical flux is minimally altered in undisturbed ecosystems.^{18,26} Although the final conclusions have not been drawn, there is some indication from studies at Hubbard Brook, New Hampshire,¹⁸ that acid precipitation (average pH 4.1) has apparently not altered the stream water chemistry. Recent analyses in soil water and groundwater samples in a subalpine coniferous forest in New Hampshire also indicate that sulfate anions supply 76% of the electrical charge balance in the soil leaching solution.²⁷ This implies that sulfuric acid in precipitation provides the dominant source of H⁺ ions for cation replacement and mobile anions for cation transport in the subalpine soils at the New Hampshire site. At the Thompson Research Center in Washington, precipitation sulfuric acid input was found to be small in comparison with sulfate and cation transfers within a Douglas-fir ecosystem.²⁸ Thus, present H⁺ ion inputs do not appear to have shortterm effects on leaching mechanisms.

The dispersion modeling presented in Section 15.2 indicates a rate of hydrogen ion input of $0.5-2.5 \times 10^{-9}$ Eg/m²/sec to the terrestrial ecosystem surrounding the proposed Hat Creek facility. This equals an annual hydrogen ion increase of 1.6 to 7.9 x 10^2 Eq/ha/yr. Assuming a present cationic demudation rate of 3.8 x 10^3 Eq/ha/yr for the Fraser River system, the increased input potentially represents 4% to 21% of present leaching mechanisms.¹³ However, a direct output from a slightly increased H⁺ input is not expected because of vegetation buffering mechanisms and the large concentration of hydrogen ions in soils. For example, predicted annual proton deposition rates range from 16 meq/m²/yr $(0.5 \times 10^{-9} \text{ Eq/m}^2/\text{sec})$ on the acidic soils in the Adams River watershed to 79 $meq/m^2/yr$ on Luvisolic and Brunisolic soils near the facility (see Figure 15-52). This possible exchange corresponds to a much smaller net H⁺ input since up to 90% of the hydrogen ions could be exchanged in vegetation.²⁹ Small proton inputs appear insignificant in Podzolic soils which have a high pH-dependent cation exchange capacity.³⁰

Several studies have shown the importance of forest canopies in removing incoming hydrogen ions through exchange processes. In the Cascade Mountains of Washington, second growth Douglas fir ecosystems had a throughfall pH of 5 during episodes of rainfall with pH 4 or less.²⁸ A precipitation input of 340 Eq/ha H⁺ ions per year resulted in a throughfall of 70 Eq/ha H⁺ ions per year. At Hubbard Brook, New Hampshire, 90% of the H⁺ ions remained in the northern hardwood forest canopy as precipitation passed through to the forest floor.²⁹ The removal of H⁺ ions by exchange in the canopy lessens the potential impact of acidic precipitation on forest soils.

The nature of the Hubbard Brook system suggests that it is suitable for establishing an input-output factor for sensitive soil types. This small headwater watershed with shallow acid soils is located in a region where acid precipitation prevails. Calculations based on ten years of - hydrogen ion input-output data indicates stream H⁺ output to be 0.08 to 0.18 times the input from the precipitation.¹⁸ Applying this factor to increased hydrogen ion inputs via precipitation would still be likely to provide an overestimation of potential stream increases because streamchemistry in Hubbard Brook remains at a steady state, despite continuing hydrogen ion inputs. For the Hat Creek area, soil conditions similar to those at Hubbard Brook are found at the long-range transport receptor areas. In the calculations of this section the conservative estimate of 20% precipitation penetration through the canopy (near the upper of the 8% to 18% range in the literature) was utilized for those receptor areas greater than 50 km from the proposed power plant site.

For soil types with higher organic composition, generally found within 50 km of the Hat Creek power plant, a precipitation throughfall of 20% would be a gross underestimation of the total buffering capacity of the terrestrial system. Buffering capacities of organic soils reduce to a large extent the remaining H⁺ ion contributions. Results of several studies indicate that generally less than 10% of the concentration of various leachates are labile (chemical or mechanically unstable) or dissolved in aqueous systems because of complexing with organic matter.²² Similar studies have also shown that the degree of organic matter as

well as other soil characteristics such as slope, moisture content and surface condition vary the effects from 12% to less than 1%.²² There is a pronounced relationship between organic matter and clay content such that soils generally classed in the brown or black groups have leachate of less than 2%. These characteristics are found largely in the Chernozemic and moderately in the Luvisolic soils which characterize the watershed areas in the immediate vicinity of the proposed Hat Creek power plant.

Another major soil type in the area is Brunisolic. These soils have small amounts of organic matter in the upper layer but a very high base status. This soil has a high buffering capacity as a result of this base content, rather than its slight organic matter. In all cases the buffering capacity of these soils is greater than the conservative estimate of 20% used for the far region soil types.

In the areas to the NE and SE of the proposed power plant site, the organic matter content of soil dominates buffering in the low-lying terrain of the tree-covered section of the Canadian Cordillera and stream lowlands. Streams and other water bodies are also commonly supplied by water from bogs, swamps and marshes. These sources have high organic content which, when combined with the silts and clays in the runoff, ensures a readily available molecular surface for cation exchange.

Perhaps the most important reaction of the metal-organic interaction is the chelation of trace elements with the polymeric organic compounds which comprise the humic matter.³¹ Studies have shown that these humic complexes of soluble and solid states are competitive in relation to hydrolytic and other precipitating reactions, as well as very strong in cation exchange properties.²⁵ As a result, trace elements are removed from solution and deposited in solid phase in the sediment. Of the organic species involved, humic and fulvic acids and humins are the major components of the heterogeneous polymer system formed. Humic matter is an efficient acidity buffer.²² As a result, this organic matter would play a large role in the absorption of the proton deposition to the system as well as complexing with metallic ions.

The use of a single factor for the fraction of new protons unneutralized by buffering agents in the soil-and vegetation for all of the Hat Creek area would be an oversimplification of the natural systems. A 20% factor is considered to provide a very conservative estimate for the long-range transport areas and the associated soil types 50 to 200 km NE of the Hat Creek Project site. In the near field area (within 50 km from the power plant site), a factor of 2% is considered realistic, but calculations using 10% were also made to provide for consideration of the full range indicated in the literature. Both factors were used for all modeling efforts on water bodies in the near vicinity of the Hat Creek Project.

Estimates of atmospheric concentrations and the solubility of ammonia in rainwater are available in the literature. Ambient measurements of ammonia concentrations range from about 1 $\mu g/m^3$ to over 100 $\mu g/m^3$ in temperate zones.³² "Background" concentrations over land average approximately 3 µg/m^{3} . Typical partition coefficients (expressed as ammonia concentration in water divided by that in the gas phase) are around 10,000 for pure water and higher by many orders of magnitude in pure water to which small amounts of mineral acid have been added. However, when carbon dioxide is dissolved in water, the solubility of ammonia is diminished.^{32a} Thus, in precipitation, the increased solubility of NH_ due to decreased pH is somewhat offset by the apparent decrease in solubility due to CO2. Since the pH effect is expected to dominate the dissolved CO, effect, 32a the minimum concentration of dissolved ammonia in precipitation in the study area may be calculated from the following expression for dissolution in pure water: molarity of total dissolved ammonia = $H[NH_{\tau}(g)] + \sqrt{K_{h}H_{N}H_{\tau}(g)}$ where,

 $[NH_{3}(g)]$ is the molar concentration of gas phase ammonia K_{0} is the dissociation constant for the equilibrium

 $[NH_{3}(g)] \approx [NH_{4}^{+}] + [OH^{-}]$ and is equal to 1.374 x 10⁻⁵ at 0°C

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H is Henry's law constant given by 32

 $\log H = \frac{1477.8}{T} - 1.6937$

and T is the water temperature, °K.

Conservatively assuming the ambient ammonia concentration in the study area to average 2 μ g/m³, less than the 3 μ g/m³ usually assumed for background over land areas, and substituting this value into the above expression yields, at 0°C, a normality in precipitation of 3.5×10^{-6} equivalents per liter. The resulting concentration estimate for dissolved ammonia in the rainwater is essentially equal to the sum of dissolved ("wet") SO₂ and SO^{*}₄ predicted by the dispersion/deposition model for distances greater than 100 km from the proposed power plant. Therefore, these sulfur species (in their acid form) are considered to be neutralized by dissolved ammonia in the following calculations of pH change presented in this report:

- Model using annual averages for deposition, water quality and hydrology. (Models I6.2a, b below).
- The autumn contribution to the snow pack in the spring snowmelt model (I6.2c).
- The cumulative effect of 35 years of Hat Creek Project deposition.

All other potentially acidic species considered in these models are assumed to deposit in their acid form, i.e., wet, and dry NO_3^- and NO_X as HNO_3^- , dry SO_2^- and SO_4^- as $H_2SO_4^-$. No neutralization by ammonia was included in Models I6.2d or e and in the winter and spring contributions to Model I6.2c.

All neutralization pathways other than those considered above (alkalinity of lake or stream as bicarbonate ion, soil/vegetation buffering, and ambient ammonia combination) are neglected in most of the models which follow. Some of the other possible pathways are:

• Alkaline flyash emitted by the power plant (the mass of particulate matter emitted is projected to be about 7% of the sum of emissions for SO_2 and NO_2).

• Ammonia emitted by the power plant (the projected mass rate of NH, emissions is approximately equal to that of the particulate matter).

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- Species more basic than HCO_ present in the water bodies. For example, the measured sum_of OH, HPO, H_PO, NH, (aq) and CO, is equal to 8.5 x 10⁻⁷ N (equivalents per liter) near the mouth of the Adams River.
- Neutralization in the snow pack. Studies at Hubbard Brook have involved measurement of the [H⁺] of the snow pack.³¹
 Measurements indicate averages less than half that of the incident precipitation. This pathway is included only in the winter season model and the spring snow melt model.

Failure to consider these components and their effects on precipitation pH contributes toward overestimation in predicted pH changes by the models described below. Furthermore, the maximum predicted deposition rates within a receptor area (the drainage area of the water body under consideration) are used to represent the deposition rate over the entire area.

Additional conservatism in predicted pH changes is introduced by the assumption that all SO_2 and SO_4^{π} deposited in the study area by dry removal mechanisms reach the ground and are in the form of sulfuric acid. Reynolds and Johnson¹⁹ found that within 100 km of the Inco stack, less than 10% of the plume sulfur was in the form of sulfate on most occasions. Near the stack the percentage of sulfate in the plume was normally between 1.2% and 1.5%. Measurements for sulfuric acid indicated that about 70% of the water soluble sulfate (approximately 0.90% of the total plume sulfur) was in the form of sulfuric acid.

(a) <u>Model Treating Annually or Seasonally Averaged Statistics</u> for Rivers or River-Lake Systems

In addition to the common elements discussed above, this model uses computed annually or seasonally-averaged deposition rates, water quality data, and hydrological data (primarily water body discharge rates). It is assumed that the discharge rate at the mouth of the water body is equal to the total inflow and, furthermore, that the total volume (flow) of water available for dilution of input hydrogen ions is equal to this

discharge rate. This steady-state approach overestimates the hydrogen ion concentration, $[H^+]$, since the actual effective dilutional volume is usually greater. For example, the total annual-average discharge from the Adams River is 4.6 x $10^7 m^3$, whereas the volume of Adams Lake alone is approximately 2.3 x $10^{10} m^3$. This approach was chosen for its conservatism, its avoidance of complexities associated with treating thermally and compositionally stratified lakes, and the availability of data which yield a reasonable estimate of the hydrogen ion $[H^+]$ concentration, in eq l^{-1} , by:

$$[H^+] = f (R_d A/F) \times 10^{-3} m^3 \ell^{-1}$$

where,

- f is the fraction of deposited H⁺ remaining after neutralization by the forest canopy and contact with the soil
- R_d is the sum of the deposition rates (in equivalents m⁻²S⁻¹) for wet and dry NO₃; dry SO₂, SO₄ and NO_x.
- A is the drainage area $(in m^2)$
- F is the discharge rate (in $m^3 S^{-1}$).

(b) Model Treating Annual Statistics for Lake Only

This model includes all the assumptions discussed above with the following exceptions. The dilutional volume used to calculate $[H^+]$ is taken as the measured or estimated lake volume. No provision is made for input of buffering agents over the course of the year beyond those initially present in the lake. Thorough mixing of the hydrogen ions in the lake volume is assumed. Thus,

$$[H^{\dagger}] = f (R_{d}At/V) \times 10^{-3} m^{3} l^{-1}$$

where,

f, Rd, A are as defined above t = 3.15×10^7 seconds (per year) V = lake volume (in m³).

(c) Spring Snowmelt Model

The approach represented by this model was chosen to account not only for the hydrogen ions that will be collected by falling snow or will deposit on a snow pack during autumn, winter and spring, but also for the known high acidity of initial snowmelt (approximately 3.4 times the average acidity of the bulk snow)^{32b} and for the leaching of acidic components caused by rainfall on a snow pack. The technique used is to calculate an effective peak deposition rate for spring which contains contributions from the previous two seasons and is representative of the initial snowmelt conditions.

Let the "effective" seasonal depositions for fall, winter and spring represent the hydrogen ions deposited during the respective seasons which remain in the snow to contribute to a "spring surge" of acidity during the initial snowmelt. For purposes of this computation, the following assumptions were made:

- 50% neutralization of [H⁻] in the snowpack;
- no neutralization by the vegetation canopy or soil ("sheet" runoff over frozen ground);
- NH_ neutralization of wet SO₂ and SO₄[±] deposition is assumed only during the fall; the temperature dependence of atmospheric ammonia concentrations makes this assumption questionable during the colder season;

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• the full spring [H^T] deposition is included in the calculations, i.e., the snowmelt comes at the end of the spring season.

The "effective" fall deposition is the sum of the total wet and dry deposition in the falling snow and on the snowpack minus the fractions of these quantities removed, or leached out by rain. If it is assumed that 1) the fraction of wet deposition remaining in the snowpack can be estimated as the total wet deposition times the fraction of seasonal precipitation occurring as snow, 2) that the scavenging efficiency of snow is one-tenth that of rain, and 3) that the dry deposition remaining in the snow pack is the total dry deposition times the fraction of precipitation occurring as snow, then the effective fall deposition is approximated by

$$R_{d_{fall}}^{(eff)} = \left[(R_{fall}^{dry}) (S_{fall}) + (R_{fall}^{wet}) (\frac{0.1 \text{ x snowfall}}{\text{rainfall} + 0.1 \text{ x snowfall}}) \right]$$
$$x (1-f_{fall}^{L})$$

where:

Similarly, the effective deposition rates for winter and spring are given by:

$$R_{d_{winter}}^{(eff)} = \begin{bmatrix} R_{d_{fall}}^{(eff)} + (R_{winter}^{dry}) (S_{winter}) \\ + (R_{winter}^{wet}) (\frac{0.1 \times \text{snowfall}}{\text{rainfall} + 0.1 \times \text{snowfall}}) \end{bmatrix}$$
$$\times (1 - f_{winter}^{L})$$

and

$$R_{d}^{(eff)} = 0.5 \left[R_{c}^{(eff)} + (R_{spring}^{dry}) (S_{spring}) + (R_{spring}^{wet}) (\frac{0.1 \times snowfall}{rainfall + 0.1 \times snowfall}) \right]$$
$$x (1 - f_{spring}^{L}) (3.4$$

where 0.5 is the fraction of the H^+ not neutralized during its residence in the snow pack. The 3.4 factor represents the expected peak H^+ concentration (compared to that in the bulk snow) in the meltwater for a sudden and continuous snow melt.^{32b} Thus,

$$[H^+] = (R_{spring}^{(eff)} A/F) \times 10^{-3} m^3 l^{-1}$$

where

F is the average spring discharge rate (in $m^3 s^{-1}$).

(d) (1) Precipitation Episode Model

This model shares the common elements discussed above. However, the dispersion/deposition model calculates the deposition rates differently from all other cases. The centerline of the plume is held constant in one direction from the stack to a distance of 200 km. Precipitation commences at a distance of 100 km from the stack and continues uniformly to 200 km at a rate of 0.35 inches per hour. Thus, for an hour during the precipitation episode, deposition rates increase over their annual or seasonal averages. However, the dilutional volume of water in this model is large. It is estimated as the total volume of rain occurring during the hour on the drainage area plus 1% of the volume of the water body (a small surface volume).

Although no actual measurements of stratification for individual water bodies were utilized, the 1% of the lake volume estimate is considered very conservative for several reasons. Thermal stratification in the water bodies generally results in an upper layer (the epilimnion) of the lake with a depth of 6 to 10 feet. During storm events of the type assumed for the precipitation episode (one-hour), prevailing meteorological conditions are indicative of strong winds and a consequent wellmixed and well-circulated epilimnion. As a result, the storm precipitation will be expected to be diluted and mixed with epilimnion waters quite rapidly. For the case of Loon Lake in this study, the one-hour precipitation event has a rainfall volume of approximately 2.7 x $10^7 m^3$, and the lake approximately 2.6 x $10^3 m^3$. Precipitation volume is approximately 10% of

the Loon Lake volume. Calculations assuming a factor for lake volume mixing of 1% are, therefore, considered an underestimate of expected dilutional capabilities for precipitation episodes.

The hydrogen ion calculation proceeds as follows:

$$[H^+] = f [R_dAt/(V_p + 0.01V)] \times 10^{-3} m^3 \ell^{-1}$$

where,

- f = fraction of H⁺ unneutralized by vegetation and soil after throughfall and runoff
- t = 3600 seconds per hour
- $V_p = \text{total volume of precipitation on drainage area in an hour}$ (in m³)
- V = 1 ake volume (in m³).

(d)(2) <u>Precipitation Episode Following Prolonged Stagnation</u> Condition

A second episode model was developed to evaluate the effects of acid deposition during a one-hour precipitation event following a prolonged period of atmospheric stagnation. Such a condition is considered typical of a frontal passage through the study area at the end of a stationary high pressure condition. During the period of stagnation, pollutant emissions are assumed to be confined to a constant volume of air, resulting in elevated ambient concentrations. The buildup of pollutant concentrations within this restricted volume was estimated by means of a simple box model. The wet deposition of acidic compounds during a one-hour rainfall event through this volume of elevated concentrations was calculated next, and the resulting input of hydrogen ions to the water body of concern was estimated in the same manner as was used in the preceding precipitation episode model. The following assumptions were made in computing the concentrations of pollutants during the stagnation condition:

- All emissions over a seven-day period from the Hat Creek project and other major sources within the study area (see Industrial Emissions Inventory, Section A.3.4, Appendix A) are assumed to be well mixed through a constant volume.
- The restricted volume is defined as a 67.5° wedge between lines drawn to a distance of 200 km from the Hat Creek site toward the northeast and the east-southeast and to a height of 1,000 meters.
- Sulfur dioxide is assumed to be transformed to sulfate at a rate of 1.0 percent per hour.
- SO₂ and NO₂ are assumed to be deposited with a deposition rate of 1.0 cm/sec and SO₄ with a deposition rate of 0.1 cm/sec. During a given hour these deposition rates are assumed to apply only in the lowest 50 meters of the volume for SO₂ and NO₂ and the lowest 10 meters of the volume for SO₄.
- To account for local effects such as mountain drainage flows 10% of the pollutant mass is assumed to be flushed from the volume at the end of each 24-hour period.

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The resulting predicted concentrations at the end of seven days are:

$$[SO_2] = 45.1 \ \mu g/m^3; \ [SO_4^*] = 59.8 \ \mu g/m^3; \ [NO_2] = 61.4 \ \mu g/m^3$$

The assumptions incorporated in this calculation are extremely conservative and the results indicate ambient contaminant concentration buildups far in excess of any that would ever occur in practice. First, the winds under such stagnation periods are typically highly variable rather than, as assumed here, confined to a narrow directional range. In addition, the horizontal length of the trapping volume used here is smaller than would actually be experienced by the Hat Creek plume. For example, if a net unidirectional wind of only 1.0 ms⁻¹ occurred throughout the episode period, the Hat Creek emissions would be transported as far as 605 km in seven days.

(e) Winter Season Model

The minimum discharge from rivers in the study area occurs during the winter season. Use of the approach described in Section I6.2(a), where the deposition rate is divided by the discharge rate to calculate $[H^+]$, should therefore yield a much higher $[H^+]$. However, offsetting this effect is the entrapment of much of the acidic deposition and neutralization in the snowpack. Thus, this model allows only a fraction of the

net deposition after neutralization in the snowpack to reach the water body. This fraction is estimated as the ratio of rainfall amount to snowfall amount and can be visualized as leaching of the snow pack by the rainfall.

$$[H^{+}] = f_{winter}^{L} (0.5 R_{d}^{A/F}_{winter}) \times 10^{-3} m^{3} \ell^{-1}$$

where,

No neutralization as a result of contact with soils is assumed in this model (i.e., soils are considered frozen during winter).

16.3 GENERAL CALCULATION PROCEDURE FOR CHANGE IN pH (Δ pH)

The initial step in computing ΔpH for a subject water body as a result of the deposition of acidic species is to determine the H⁺ deposition rate over the entire associated drainage area:

$$R_{d} = \begin{pmatrix} n \\ \Sigma \\ i=1 \end{pmatrix} \times A$$

where,

 $R_i = deposition rate for i_{th} species (g m⁻² s⁻¹)$ A = drainage area (m²)EW_i = equivalent weight of i_{th} species (g Eq⁻¹)

Species	EW
so ₂	32
so4	48
NO ²	62
NOx	46 (Assumes all NO converted to

The H^+ concentration, $[H^+]$, input to the water body is calculated as:

where,

 NO_2)

f = unneutralized fraction of deposited H⁺ reaching the water body

F = discharge rate at outlet of drainage area $(m^3 s^{-1})$.

From the measured alkalinity, [Alk] original, the new alkalinity as a result of the proposed project is calculated

[Alk]_{new} = [Alk]_{original} -[H^{*}]_{input}

At the observed pH range of the natural waters in the study area (6.6 to 8.8), the dissolved CO_2 system dominates the buffering chemistry. Therefore, the original sum of H_2CO_3 and CO_2 (aq), $[H_2CO_3^*]$, may be computed if the original pH and acidity constant are known from the expression:

$$pH = pK_1 + log \frac{[HCO_5]}{[H_2CO_5]}$$

where:

 $[HCO_{3}^{-}] \text{ is equated to } [Alk]_{\text{original}}$ $\log K_{1}^{-} = -\frac{3404.71}{T(^{\circ}K)} + 14.8435 - 0.032786 T(^{\circ}K) \qquad (Ref. 74)$

and:

$$K_1 = \frac{[H^*] [HCO_3]}{[H_2CO_3^*]}$$

Before proceeding, it should be noted that two limiting cases were considered for calculation of estimated pH changes:

- 1. A closed system where $C_T = [HCO_3^-] + [H_2CO_3^+] + [CO_3^-]$ is held constant.* This assumption results in a maximum predicted negative pH change pH for a given addition of H^+ ions.
- 2. An open system where, P_{CO_2} , the partial pressure of CO_2 , is assumed constant and the water is well mixed and in equilbrium with the CO_2 . In this case,

$$[A1k] = [HCO_3^{-}] = \frac{[K_1]}{[H^+]} K_H P_{CO_2} - [H^+]$$

where

$$P_{CO_2} \approx 10^{-5.5} \text{atm}$$

K_H, Henry's law constant = $10^{-1.5}$ mole l^{-1} atm⁻¹ @ 298°K

For the range of alkalinities reported in the data for the study area, the second approach yields unrealistic pH values, higher than the actual measurements. For example, the Adams River is predicted to have a pH of 8.3 under conditions where the actual pH is 7.6. Because the addition of H^+ ions cannot increase pH using this limiting case, the actual situation for the natural waters in the study area is assumed to be that pH changes will be allowed to vary from none at all to those predicted by limiting case 1, above.

Proceeding with the assumption that C_{T} is constant, i.e.,

 $[HCO_3]_{original} + [H_2CO_3^*]_{original} = [HCO_3]_{new} + [H_2CO_3^*]_{new},$

^{*}In subsequent calculations $[CO_3^{-7}]$ is neglected since it represents less than 2.5% of C_T at the highest pH considered here, 8.7 at Loon Lake, and less than 0.5% of C_T at pH <8.0.

the new $[H_2CO_2^*]$ after addition of $[H^+]$ will simply be

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Using the acidity constant expression, the new pH is

$$pH_{new} = pK_1 + \log \frac{[Alk]_{new}}{[H_2CO_3^*]}$$

and

 $\Delta pH = pH_{new} - pH_{original}$

16.4 SUMMARY OF APH CALCULATIONS BY CASE

In the case study calculations presented in the following subsections, certain physical parameters for the watersheds discussed are described as "known quantities." The sources for these data include:

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- Alkalinity, water temperature and pH^{33,34}
- Drainage areas and discharge rates ^{35, 36, 37} from Loon Lake³⁸
- Adams and Pennask Lakes 39
- (a) <u>Case 1</u>, Adams River at Mouth, Annually-Averaged Statistics, Model I6.2(a)

The known quantities are as follows:

- $A = 3 \times 10^9 \text{ m}^2$
- $F = 71 \text{ m}^3 \text{ s}^{-1}$
- pH = 7.6 (high 8.8, low 6.6)

• Water temperature = 285°K

^{*}The water quality and flow data required for these calculations were available only for Adams Lake and between the lake and the mouth where the river empties into the south Thompson. However, as described in Section I4.2.1, it is reasonable to expect that ApH effects in the upper Adams, where concern for salmon is greatest, will be somwhat smaller than those predicted here for the mouth of the river.

$$[Alk]_{river} = 4.5 \times 10^{-4} \text{ Eq } \ell^{-1}$$

$$[Alk]_{lake} = 8.8 \times 10^{-4} \text{ Eq } \ell^{-1}$$

$$[Alk]_{av} = 7.36 \times 10^{-4} \text{ Eq } \ell^{-1}, \text{ where the weighted average}$$

$$alkalinity \text{ is calculated by conservatively}$$

$$estimating the lake volume to be twice that of$$

$$the river.$$

The total deposition rate of acidic species predicted by the deposition model (corrected for soil and vegetation buffering by multiplying by the factor f = 0.2) is 0.159 neq m⁻² s⁻¹ as H⁺.

 $[H^+]_{input} = 6.74 \times 10^{-6} \text{ Eq } l^{-1}$, new pH = 7.544, thus $\Delta pH = -0.056$, the estimated annual average pH reduction as a result of the Hat Creek Project.

 (b) <u>Case 2</u>, Adams River at Mouth, Spring Statistics, Model I6.2(c) (Spring Snowmelt Model)

The known quantities are as follows:

- $A = 3 \times 10^9 \text{ m}^2$
- $F = 117.2 \text{ m}^3 \text{ s}^{-1}$
- pH = 7.7 (high 8.8, low 7.2)
- Water temperature = 281°K
- [A1k] , as in Case 1
- Precipitation statistics for Blue River used for Adams River drainage basin:

	Summer	Fall	Winter	Spring
Rain, cm	26.1	23.2	4.6	14.8
Snow, cm as liquid	0	8.2	30.6	5.3
Fraction of total preci- pitation as snow, %	0.	26.2	85.8	26.5

The assumed quantities are:

- Deposition rate in snow = 0.1 x (deposition rate in rain)
- Fraction of [H⁺] neutralized in snow pack = 0.5
The effective H[•] deposition rate is 0.859 neq m⁻² s⁻¹. $[H^+]_{input} = 2.20 \times 10^{-5} \text{ Eq } \ell^{-1}$ $\Delta pH = -0.186$, the estimated maximum pH reduction in Spring as a result of the Hat Creek Project.

(c) <u>Case 3</u>, Adams River at Mouth, Winter Statistics, Model 16.2(e) The known quantities are as follows:

- $A = 3 \times 10^9 \text{ m}^2$ • $F = 18.9 \text{ m}^3 \text{ s}^{-1};$
- pH = 7.5 (high 8.2, low 7.0)
- Water temperature = 276°K
- $[Alk]_{av} = 7.36 \times 10^{-4} \text{ Eq } l^{-1}$, as in Case 1

The assumed variable is:

• $f = 0.5 (f_{winter}^{L}) = 0.17$

where

0.5 = unneutralized fraction of H⁺ in snow pack f^L_{winter} = fraction of H⁺ in snow pack leached out by rain and snowmelt into runoff.

The deposition rate is 0.698 n Eq m^{-2} s⁻¹ as H⁺.

 $[H^{\bullet}]_{input} = 1.88 \times 10^{-5}$ Eq l^{-1} , the new pH = 7.398, thus, $\Delta pH = -0.102$, the estimated seasonal average pH reduction during Winter as a result of the Hat Creek Project.

(d) (1) <u>Case 4A</u>, Adams River at Mouth, One-hour Precipitation Episode in Spring, Model 16.2(d) (1)

The following quantities are known:

- $A = 3 \times 10^9 \text{ m}^2$
- pH = 7.7
- Water temperature = 231 °K

- [A1k]_{av}, as in Case 1
- $V_{1ake} = 2.32 \times 10^{10} m^3$

Other quantities assumed or derived:

- Rainfall rate = 2.47 x 10⁻⁶ m s⁻¹ (0.35 inches per hour)
 No neutralization of wet SO₂ and SO₄⁼ is assumed. The H⁺ deposition rate is 113 neq m⁻² s⁻¹. [H⁺] = 9.42 x 10⁻⁷ Eq l⁻¹, and ApH = -0.010, the estimated one-hour precipitation episode
 - in Spring as a result of the Hat Creek Project.

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(d) (2) <u>Case 4B</u>, Adams River at Mouth, One-Hour Precipitation Episode Following Prolonged Stagnation Conditions, Model I6.2(d) (2)

The following quantities are known:

- $A = 3 \times 10^9 m^2$
- ← pH = 7.7
- Water temperature = 281°K
- [Alk] ar; as in Case 1
- $V_{Lake} = 2.32 \times 10^{10} \text{ m}^3$

Other quantities assumed or derived:

- Rainfall rate = $2.47 \times 10^{-6} \text{m s}^{-1}$ (0.35 inches per hour)
- No neutralization of wet SO_2 and SO_4^{-} by atmospheric ammonia is assumed

The H^+ deposition rate is 605 n Eq m⁻²s⁻¹

 $[H^+] = 2.52 \times 10^{-5}$ eq l^{-1} and the new pH = 7.401, thus,

ΔpH = -0.199

(e) <u>Case 5</u>, Boss Creek Above Hendrix Creek, Annual Statistics, Model I6.2(a) The known quantities are:

- $\lambda = 7.6 \times 10^7 \text{ m}^2$
- $F = 2.28 \text{ m}^3 \text{ s}^{-1}$
- pH = 7.1
- Water temperature = 277.7°K
- [Alk] = 5.6 x 10^{-4} Eq 2^{-1}

The deposition rate is 0.339 meq $m^{-2} s^{-1}$ as H^+ .

 $[H^+]_{input} = 2.26 \times 10^{-6} \text{ Eq } 2^{-1},$

new pH = 7.092, thus,

ApH = -0.008, the estimated annual average pH reduction as a result of the Hat Creek Project.

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(f) <u>Case 6</u>, Pennask Lake, Annual Statistics, Models I6.2(a) and I6.2(b)

Two sets of assumptions with differing degrees of conservatism were used for purposes of estimating upper and lower bounds to the annual average water volume available to dilute incremental H⁺ ions deposited in Pennask Lake:

- 1. The discharge rate of Pennask Creek into Pennask Lake is the only water available for H⁺ dilution (more conservative).
- The entire volume of the lake is available for dilution but no H⁺ is allowed to flow from the lake, and no buffering agents are allowed to enter the lake (less conservative).

The known quantitites are as follows:

- A (Pennask Creek) = $5.4 \times 10^7 \text{ m}^2$
- F (Pennask Creek) = $0.43 \text{ m}^3 \text{ s}^{-1}$
- pH = 7.6
- Water temperature, estimated = 278°K
- [Alk] = 4.32×10^{-4} Eq 2^{-1}
- $V_{lake} = 7.8 \times 10^7 \text{ m}^3$

The H⁺ deposition rate is 0.250 n Eq m⁻² s⁻¹

Subcase 6.1

$$[H^+]_{input} = 6.28 \times 10^{-6} \text{ Eq } \ell^{-1},$$

new pH = 7.527, thus,
 $\Delta pH = -0.073$, the estimated annual average pH reduction
as a result of the Hat Creek Project.

Subcase 6.2

 $[H^+]_{input} = 1.05 \times 10^{-6} \text{ Eq } l^{-1}$, and

 $\Delta pH = -0.012$, the estimated annual average pH reduction as a result of the Hat Creek Project.

(g) Case 7, Loon Lake, Annual Statistics, Model 16.2(b)

This lake coincides with the location of maximum predicted annual deposition of H^+ ions as computed by the dispersion/deposition model. The soils around Loon Lake are more alkaline (i.e., higher buffering capacity) than those in the Adams River watershed. Thus, it may be assumed that a smaller fraction (f) of deposited H^+ ions will remain unneutralized in the runoff than the value of 0.20 assumed for the Adams River watershed. Two values for f were examined: 0.1 and 0.02. In addition, to bound the range of possible pH reductions, separate calculations were made for different assumed dilution volumes for Loon Lake. For one set of cases, the volume of the lake itself was used; in the other, only the discharge rate for Loon Creek was assumed available to dilute the deposited H^+ ions.

The known quantities are:

- $A = 4.79 \times 10^8 \text{ m}^2$
- F (Loon Creek) = $0.535 \text{ m}^3 \text{ s}^{-1}$
- pH = 8.7
- Water temperature, estimated = 283°K
- [Alk] = 5.86×10^{-3} Eq ℓ^{-1}
- $V_{lake} = 2.63 \times 10^8 m^3$

I6-23

The deposition rate is 2.5 neq m^{-2} s⁻¹ For dilutional volume = V lake: Subcase 7.1 f = 0.1 $[H^{+}]_{input} = 1.434 \times 10^{-5} Eq \ l^{-1}$ ApH = -0.153, the estimated annual average pH reduction as a result of the Hat Creek Project. Subcase 7.2 f = 0.02 $[H^+]_{input} = 2.87 \times 10^{-6} Eq \ell^{-1}$ ApH = -0.035, the estimated annual average pH reduction as a result of the Hat Creek Project. It must be emphasized that Model I6.2(b) allows no inputs of buffering agents during the year and no neutralization pathways beyond the initially present alkalinity in the lake (e.g., H⁺ removal by interaction with detrius or sediment at the lake bottom). Compare with results using Model 16.2(a): For dilutional volume = F Subcase 7.3 f = 0.1 $[H^{\dagger}]_{input} = 2.236 \times 10^{-4} Eq l^{-1}$ ApH = -0.894, the estimated annual average pH reduction as a result of the Hat Creek Project. Subcase 7.4 f = 0.02 $[H^+]_{input} = 4.473 \times 10^{-5} Eq l^{-1}$ ApH = -0.367, the estimated annual average pH reduction as a result of the Hat Creek Project.

Clearly, the pH change predicted is very sensitive to the choice of models used to make the estimate. Since both of the above models contain elements of conservatism, we feel that Subcases 7.1 and 7.2 approach the real situation more closely than Subcases 7.3 and 7.4.

(h) <u>Case 8</u>, Loon Lake, Spring Snowmelt Model, I6.2(c)
 The known quantities are:

- $A = 4.79 \times 10^8 \text{ m}^2$
- $F = 0.763 \text{ m}^3 \text{ s}^{-1}$
- pH = 8.7
- Lake elevation = 2822 ft.
- Water temperature, estimated = 283°K
- [A1k] = $5.86 \times 10^{-3} \text{ Eq } \text{ l}^{-1}$
- Precipitation statistics for 150 Mile House (2,900 ft.), which is at nearly the same elevation as Loon Lake, were used.

	Fall	Winter	Spring
Rain, cm	7.06	1.07	5.08
Snow, cm as liquid	2.54	9.63	2.08
Fraction as snow, %	26	90	29

The assumed quantities are as in Case 2, yielding an effective deposition rate, as H^+ , of 1.89 $n \text{ Egm}^{-2} \text{ s}^{-1}$.

[H⁺] input = 1.18 x 10⁻³ Eq 2⁻¹ ΔpH = -1.651, the estimated seasonal average pH reduction in spring as a result of the Hat Creek Project.

(i) <u>Case 9</u>, Loon Lake, Winter Statistics, Model I6.2(e)

The known quantities are:

- $A = 4.79 \times 10^8 m^2$
- F_{winter} (Loon Creek) = 0.217 m³ s⁻¹;

- pH = 8.7
- Water temperature, estimated = 276°K
- [Alk] = 5.86 x 10^{-3} Eq 2^{-1}

No neutralization due to soils or vegetation is assumed. However, 50% of the H⁺ is assumed to be neutralized during its residence in the snow pack and 25% of the remaining H⁺ is assumed to be leached out by winter rains. Thus,

. f = 0.115

The deposition rate, R_d , is 1.03 n m⁻² s⁻¹ as H⁺.

 $[H^+]_{input} = 2.62 \times 10^{-4} \text{ Eq } l^{-1},$

new pH = 7.809

ApH = -0.891, the estimated seasonal average pH reduction during Winter as a result of the Hat Creek Project.

The simple model used for the above calculations includes the assumption that only the water volume represented by the runoff (equal to outflow) is available for dilution with no dilution due to the much larger volume of the lake. It is therefore considered to lead to substantial overprediction of the pH effects.

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(j) <u>Case 10</u>, Thompson River, Annual Statistics, Model I6.2(a) The following are the known quantities:

- pH = 7.56 (at Kamloops)
- Water temperature = 285°K
- $[AIk] = 6.76 \times 10^{-4} \text{ Em } l^{-1}$

The remaining quantities are derived or estimated:

A = area inscribed by 1.5 n Eqm⁻² s⁻¹ isopleth from annual H^T deposition field (see Figure I3-46).
 = 3.3 x 10⁹ m²

F = 594 m³ s⁻¹, estimated as twice the flow rate of the South Thompson at Monte Creek. (Thompson River discharge rates through the area of consideration were not available.)

Subcase 10.1 f = 0.1

 $[H^+]_{input} = 1.11 \times 10^{-6} Eq l^{-1}$

ApH = -0.008, the estimated annual average pH reduction as a result of the Hat Creek Project.

Subcase 10.2 f = 0.02

 $[H^+]_{input} = 2.22 \times 10^{-7} \text{ Eq } \ell^{-1}$

- ΔpH = -0.002, the estimated annual average pH reduction as a result of the Hat Creek Project.
- (k) <u>Case 11</u>, Clearwater River in Wells Gray Park, Annually-Averaged Statistics, Model 16.2(a)

The known quantities are as follows:

- A = 2.95 x $10^9 m^2$ (at Clearwater Lake outlet)
- $F = 141.5 \text{ m}^{3} \text{ s}^{-1}$ (at Clearwater Lake outlet)
- pH = 7.56 (at Clearwater; high 8.8, low 6.8)
- Water temperature = 281.6°K
- $[Alk] = 6.855 \times 10^{-4} \text{ Eq } l^{-1} (\text{at Clearwater})$

The annual average deposition rate, as H^+ , is 0.0706 nEq $m^{-2}s^{-1}$, corrected for 80% neutralization by soils and vegetation (f = 0.2).

TABLE 16-1

HYDROGEN TON CONCENTRATION OF SNOW MELT WATER*

Fraction Metted (%)** f	_5	10	<u>15</u>	20	<u>25</u>	<u>30</u>	<u>35</u>	<u>40</u>	45	<u>50</u>	<u>55</u>	<u>60</u>
Fraction leached, f_L^{+}	0.078	0.23	0.34	0.42	0.49	0.56	0.61	0.68	0.72	0.75	0.78	0.81
$c_i/c_b^{\dagger \dagger}$	1.7	3.4	2.3	1.75	1.6	1.4	1.3	1.25	1.0	0.7	0.6	0.55

* The values appearing in this table were taken from Figure 2 of Ref. 32b.

** \$ snowpack melted.

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† Fraction of the total available ion in the snow pack before melting commences which appears in the meltwater.

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It Ratio of ionic concentration in the meltwater to that in the bulk snow.

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 <u>Case 12</u>, Deadman River above Criss Creek, Annually-Averaged Statistics, Model 16.2(a)

The following are the known quantities:

- $A = 8.62 \times 10^8 m^2$
- $F = 1.70 \text{ m}^3 \text{s}^{-1}$ (1977 statistics for comparison, 1977 stream flow for Criss Creek was only 74% of the preceding 23-year average)
- pH = 8.2
- Water temperature = 282°K (estimated from Tranquille River temperature readings)
- [A1k] = 3.02×10^{-3} Eq ℓ^{-1}

The annual average deposition rate, as H^+ , is 1.44 neq $m^{-2}s^{-1}$.

Subcase 12.1 f = 0.1 $[H^+]_{input} = 7.32 \times 10^{-5} \text{ Eq } l^{-1}$, new pH = 7.831 $\Delta pH = -0.369$ the estimated annual average pH reduction as a result of the Hat Creek Project

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Subcase 12.2 f = 0.02
[H<sup>+</sup>] input = 1.46 x 10<sup>-5</sup> Eq 2<sup>-1</sup>,
new pH = 8.099
ApH = -0.101, the estimated annual average pH reduction as a
result of the Hat Creek Project
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 (m) <u>Case 13</u>, Deadman River above Criss Creek, Winter Statistics, Model I6.2(e)

The known quantities are:

- $A = 8.62 \times 10^8 m^2$
- $F_{winter} = 0.50 \text{ m}^3 \text{s}^{-1}$

- pH = 8.2 (annual average pH used since seasonally segregated data not available)
- Water temperature = 274 °K (estimated from Tranquille River temperature readings)
- [Alk] = 3.02×10^{-3} Eq 2^{-1}

No neutralization due to soils or vegetation is assumed. However, 50% neutralization is assumed during the H⁺ residence in the snow pack and 34% of the remaining H⁺ is assumed to have been leached out by winter rains. Thus,

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	 £ = 0.17.
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The deposition rate, R_d , is 0.783 nEq m⁻²s⁻¹ as H⁺

- [H⁺] input = 2.29 x 10⁻⁴ Eq 2⁻¹, new pH is 7.535, thus, ApH = -0.665, the estimated seasonal average pH reduction during winter as a result of the Hat Creek Project
 - (n) <u>Case 14</u>, Deadman River above Criss Creek, Spring Snowmelt Model, I6.2(c)

The known quantities are:

- $A = 8.62 \times 10^{8} m^{2}$
- $F = 4.88 \text{ m}^3 \text{ s}^{-1}$
- pH = 8.2
- Water temperature = 280.6°K (estimated from Tranquille River temperature readings)
- [Alk] = 3.02×10^{-3} Eq 2^{-1}
- Precipitation statistics for Kamloops were used.

	Fall	Winter	Spring
Rain, cm	5.31	1.18	3,99
Snow, cm as liquid	0.81	6,68	0.15
Fraction as snow, %	13.0	85.0	

The assumed quantities are as in Case 2, yielding an effective deposition rate, as H^+ , of 0.742 nEq m⁻²s⁻¹.

 $[H^+]_{input} = 1.31 \times 10^{-4} \text{ Eq } l^{-1}$, yielding a new pH of 7.672. Thus,

 $\Delta pH = -0.528$, the estimated seasonal average pH reduction in spring as a result of the Hat Creek Project.

16.5 ESTIMATE OF pH IN PRECIPITATION

In this section, the effects of power plant emissions on the pH of precipitation are computed for several short and long-term situations. These estimates are compared with predictions described in the summary volume to which this report is an appendix. It should be emphasized that the pH reductions expected in the precipitation during short "episodes" translate to much less severe effects within receiving bodies of water, as seen in the examples given in Section 16.4.

- (a) <u>Case 15</u>, Annual Precipitation and Deposition Statistics (choose "hot spot" deposition rate, i.e., those from 40 km NE of the plant):
- $R_d = Wet SO_2 + Wet SO_4^2 + Wet NO_3^2 = 2.278 \times 10^{-9} Eq m^{-2} s^{-1}$ as H^+

• Annual rainfall intensity from Fig. 13-3: 0.02 in $hr^{-1} = 1.4$ $x 10^{-7} m s^{-1}$ $[H^+]_{input} = 1.627 \times 10^{-5} Eq \ell^{-1}$ $[H^+]_{net} = 1.072 \times 10^{-5} Eq \ell^{-1}$ (assumes equilibration with atmospheric CO₂ and no other naturally occurring alkaline ions present)

- pH = 4.97, the estimated annual average pH of precipitation in the near-field area as a result of the Hat Creek Project.⁴⁰
- (b) <u>Case 16</u>, Estimate of Annual pH of Precipitation in Adams River Drainage Basin (approximately 200 km NE of proposed plant site).
 - $R_{d} = SO_{2 wet} + SO_{4 wet} + NO_{3 wet}$ = 0.32 + 0.0008 • 0.37 nEq m⁻² s⁻¹ = 0.691 neq m⁻² s⁻¹

Annual rainfall intensity from Figure 13-3 = 0.05 in. hr^{-1} (Blue River statistics) = 3.35 x 10⁻⁷ m s⁻¹

f# [*] 1	=	6.91×10^{-10} Eq. m ⁻² s ⁻¹
" input to rain	L -	$3.53 \times 10^{-7} \text{ m s}^{-1}$
	3	$1.96 \times 10^{-3} \text{ Eq m}^{-3}$
	z .	$1.96 \times 10^{-6} \text{ Eq } 2^{-1}$

$$[H^*]_{net} = 2.799 \times 10^{-6} Eq l^{-1}$$

pH = 5.55, the estimated annual average pH of precipitation in the far-field area as a result of the Hat Creek Project.

Note that in case 15, the $[H^+]$ input is buffered by the dissolved CO_2 system, whereas in case 16 the $[H^+]$ input is smaller than the equilibrium concentration of $[H^+]$ for the $H_2CO_3^* \pm H^+ + HCO_3^-$ system and has a very small effect on the pH.

16.6 DISCUSSION OF PREDICTED pH CHANGES IN THE HAT CREEK AREA

Table 16-2 is a summary of the 16 cases treated in detail for acid precipitation and water body pH. As can be seen from the table, calculated pH changes (ApH) for the water bodies of concern have a total range of -0.002 to -1.65. The predicted annual pH decreases have a smaller 22

TABLE 16-2

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RESULTS OF MODEL CALCULATIONS OF pH CHANGES FROM ANNUAL AND EPISODIC EVENTS IN SELECTED WATER BODIES OF THE HAT CREEK PROJECT AREA

Case Number	Location	Average pil	Soil & Vegetation Buffering Factor	Change of pil	Description
1	Adams River	7.6	0.2	-0.056	Annual, at mouth
2	Adams River	7.7	0.5*	-0,186	Autumn, winter, and spring effective deposition run- off, at mouth
3	Adams River	7.5	0.5*	-0.102	Winter deposition, at mouth
4.1	Adams River	7.7	0.2	-0.010	Spring precipitation event, at mouth
4,2	Adams River	7.7	0.2	-0.199	Precipitation event after 7-day stagnation
5	Boss Creek	7.1	0.2	-0.008	Annual, at mouth
6.1	Pennask Lake	7.6	0.2	-0.073	Annual, in lake, dilution from Pennask Creek
6.2	Pennask Lake	7.6	0.2	-0.012	Annual, in lake volume # dilution
7.1	Loon Lake	8.7	0.1	-0.153	Annual, in lake, no buffer input, annual 0.911 ⁴ neutral- ized, lake volume dilution
7.2	Loon Lake	8.7	0.02	-0.035	Annual, in lake, no buffer input, annual 0.98H* neutral- ized, lake volume dilution
7.3	Loon Lake	8.7	0.1	-0.894	Annual, annual 0.94 ⁺ neutral+ ized loon Creek dilution
7.4	Loon Lake	8.7	0.02	-0.367	Annual, annual 0.9811 ⁺ neu- tralized Loon Creek dilution

Table 16-2 c	ontinued
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Case Number		Average pll	Soil & Vegetation Buffering Action	Change of pll	Description
8	Loon Lake	8.7	0.5*	-1.651	Autumn, winter and spring effective deposition run- off, at mouth
9	Loon Lake	8.7	0.5*	-0.891	Winter deposition, at mouth, assumes 50% snowpack neutral- ization
10.1	Thompson River	7.56	0.1	-0.008	Annual, in river
10.2	Thompson River	7.56	0.02	-0.002	Annual, in river
11	Clearwater River	7.56	0.20	-0.012	Annual, in river
12.1	Deadman River	8.2	0.1	-0.369	Annual, above Criss Creek
12.2	Deadman River	8.2	0.02	-0.101	Annual, above Criss Creek
13	Deadman River	8.2	0.5*	-0.665	Winter deposition above Criss Creek
14	Deadman River	8.2	0.5*	-0.528	Autumn, winter and spring effective deposition runoff, above Criss Creek
15	Precipitation pH Power Plant vicinity (<50 km)	4.97			Annual, short-range transport
16	Precipitation pH Adams River Watershed	5.55		· · ·	Annual, long-range transport

* Fraction unneutralized in snowpack only.

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range, from -0.002° to -0.894. The computed values for ΔpH for seasonal and episodic events indicate a range from -0.010 to -1.651 for pH decrease in the receiving water bodies. Calculated pH changes for the water bodies of the Hat Creek area are thus generally quite low. Only the conservatively estimated maximum effective deposition cases for episodic events (spring snowmelt) indicate values at the upper end of the ΔpH range. In fact, for the cases examined, only Loon Lake in the vicinity of the proposed power plant facilities had pH changes predicted greater than 1 pH unit and that was as a result of acidic inputs during a spring snowmelt.

The pH change calculations are overestimated because of the assumptions incorporated into the calculations by the choice of data. The water quality models only incorporate the buffering capacities of the water body bicarbonate system and those of the local soils and associated vegetation in the estimated receptor area. A conservative use of buffering capabilities was also incorporated into the calculations (for example, the bicarbonate system is biased toward the high range or an overestimate of the expected pH change). Similarly, although the literature presents data for soil and vegetation neutralization of acidic inputs in the range of 82% to 92%, the models used generally had a factor of 80%. Neutralization factors reported in the literature for highly organic soils are generally greater than 90% and, in many cases, reflect essentially total adsorption. The pH change models of this study assumed both 90% and 98% neutralization for soils of high organic content. Further, the maximum computed H^+ deposition rate in a given receptor area was assumed to represent deposition over the entire area. No weathering or other inputs of materials with buffering capabilities were assumed to reach the water body. These assumptions, while highly conservative, are necessary because of the incompleteness of the available information. and contribute to substantial overestimation of expected pH changes.

None of the additional buffering mechanisms available for neutralization of protons from the Hat Creek Project were accounted for. Some of these factors were mentioned briefly earlier in this chapter. For example, power plant emissions contain alkaline particulates, ammonia, and other basic chemical compounds. The combined Hat Creek particulate and ammonia emissions have been estimated at approximately 14% of the combined SO₂ and NO_x emissions. A major portion of these materials would provide additional buffering capability. Similarly, increased neutralization due to the presence of other basic compounds and interaction with the sediments in the water bodies, neutralization in the snowpack, dilution by runoff from other water sources outside the assumed receptor area, the reduced mixing volumes assumed for the water bodies, and conservative estimates of lake volumes as only twice the value of the parent river, correspond to buffering capabilities which in nature would greatly reduce the potential effects of the predicted H⁺ additions.

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If all factors are considered, it is apparent that both the H^{+} ion calculations and the predicted water body pH changes would be expected to be much greater than would ever be likely to occur. The estimated pH changes for the water bodies after H^{+} ion neutralization range from virtually undetectable in the annual cases of the Thompson River (7.56 -0.002 = 7.56) and the Adams River (7.6-0.056 = 7.544), to noticeable in the case of spring snowmelt into Loon Lake (8.7 - 1.65 = 7.05). In fact, the buffering capabilities of Loon Lake are so large, as shown by its high pH of 8.7, that it is unlikely that a pH as low as 7.05 would be measured in the field even following a spring snowmelt. A pH value of 7.05 is, in any case, capable of supporting economically important species of fish, as presented in the reference literature. $^{36, 37, 38}$

In view of the conservative bias incorporated in the modeling of water quality effects, it is expected that the worst case, Loon Lake, including its seasonal and episodic events, will have the buffering capabilities to absorb any of the projected additional proton depositions to its watershed. This is certainly true for the other water bodies of concern examined in this study.

Another result of the modeling conducted in this study was to calculate the expected annual average pH of the <u>precipitation</u> in the near and farfield areas of the Hat Creek Project. The values, also presented in Table I6-2, are 4.95 and 5.55 for the near and far-field, respectively, and include no dissolved alkaline species. Precipitation pH values in this range are widely represented in the literature. Hutchinson⁴¹ and several other authors^{18,26,27} have reported precipitation pH between 4.6 and 5.6, with the low values generally representing regions with proton addition and the high values representing precipitation pH levels of precipitation not having a net excess of acidic over basic dissolved ions.

Studies in Europe and North America also indicate that precipitation pH values lower than those calculated for the Hat Creek area have had no effect on the surrounding watersheds. Although sufficient baseline data for Hubbard Brook, New Hampshire may not be available for conclusive statements, rainwater pH measurements have averaged 4.1 with no apparent resulting effects on the stream water chemistry.¹⁸ Results reported in the literature as well as the calculations of this study indicate that predicted precipitation pH changes will have little effect on the pH values of the receiving water bodies found in the Hat Creek area.

16.7 PREDICTED CUMULATIVE EFFECTS

The assumption that the predicted pH changes calculated for the Hat Creek Project would occur consistently over the projected 35-year life of the power plant is not realistic since the water bodies are not in general capable of storing acidity. Summing the increments of hydrogen ions deposited over the life of the project would grossly overpredict the cumulative or long-term water body pH changes particularly for the smaller water bodies such as Deadman River. The major error of this approach is that the conservative assumptions in the calculations are multiplied by the length of the long-term period such that the cumulative predictions become largely unrealistic. Since it is expected that the buffering capacities of the watersheds in the Hat Creek area are sufficient to absorb most of the projected proton depositions for annual, seasonal

and episodic events, cumulative estimates based on summing misrepresent the actual physical, chemical and biological processes occurring in the ecosystem.

This can be examined further with the following example of a representative soil system of the study area. Consider Podzolic soils of a type low in buffering capacity compared to the other soil types of the Hat Creek area. The Adams River watershed, for example, is considered to have low capabilities for all of the possible proton neutralization mechanisms other than the carbonate system. With this background, the cumulative effects of the H⁺ inputs for the assumed life of the Hat Creek Project can be evaluated in terms of potential base saturation and pH changes in the Podzolic soils. A square meter of the A horizon soils (top 10 cm) with a cation exhange capacity of 6-8 mEq/100g would contain 780-1040 meq. For example, in the Upper Adams River watershed the hydrogen ion input to the Podzolic soils is expected to average 2-4 $mEq/m^2/yr$, assuming vegetation removal of 75% to 90% of the proton deposition inputs. This corresponds to an A horizon increased H⁺ ion input of 70-140 meg over 35 years. This would represent only a 7% to 18% decrease in the base saturation of the A horizon.

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Base saturation in a humo-ferric Podzolic has been estimated at approximately 15%, so that in 35 years the A horizon could be depleted by the increased H^+ ion inputs. However, this effect is also mitigated by several factors. They include: 1) the entire soil depth (A, B, and C horizons) probably represents 6-10 times the buffering capacity found in the A horizon alone, 2) other cation inputs would counteract the slight H^+ increase, and 3) weathering would supply additional basic cations. As a result, the minimal projected annual increase in H^+ ions would be easily balanced each year because of the steady-state biogeochemical processes. Again, this example considers only the soil, and similar cases can be presented for the other buffering capabilities of ecosystems in the study region. For purposes of discussion, if cumulative effects are estimated on the assumption of additive effects, most of the predicted pH changes for the water bodies of the Hat Creek area can be dismissed as having no appreciable effects. For example, the annual predicted pH change for the Thompson River (f = 0.1) is -0.008. Assuming the same H⁺ input to be constant over 35 years, the simple arithmetic sum of the H⁺ inputs would yield an estimated pH change in the river of 0.26 from 7.56 to 7.30. This pH change would be difficult to distinguish from natural variations and no adverse environmental effects would result.

For some of the other water bodies such an overly conservative analysis leads to incorrect conclusions on the long-term effects of the Hat Creek Project. For this reason a separate calculation of long term (35-year accumulation) has been made which calculates the change in neutralization capacity of the soils for each year and thus modifies the factor f in the previous modeling treatment.

This model starts with the input of an estimate of the cation exchange capacity (CEC) of the soil in the impacted water shed. Over the 35-year period, a constant annual average input of H^+ is assumed. It is further assumed that 40% of the input H^+ is neutralized during throughfall by the forest canopy. The remaining 60% of input H^+ is then allowed to leach the soil of its CEC in yearly increments. For instance, for the Adams River water shed, a vegetation and soil neutralization factor of 80% (F=0.2) has been assumed for the calculations in Section 16.4. Thus, one-third of the H^+ deposited after throughfall remains unneutralized by the soil by the time it is input to the water body the initial year

> $f_{combined} = f_{veg} \times f_{soil},$ 0.2 = 0.6 x 0.333

where f is the unneutralized fraction of H⁺ passing the barrier of interest.

In subsequent years, the neutralization ability of the soil is steadily diminished and is reflected in a reduction in its CEC equivalent to the H deposition below the forest canopy. Note the conservatism of this approach in that no rejuvenation of the CEC, due to biogeochemical processes such as weathering or decomposition of organic materials, is allowed. Mathematically, the model takes the form:

$$[H^+]_{input}^{35-yT} = [H^+]_o \left\{ 0.6 \left[1 - \left(1 - \frac{f_o}{0.6} \right) \left(\frac{CEC_o - 35D}{CEC_o} \right) \right] \right\}$$

where,

f

- [H⁺]^{35-yr} is the H⁺ concentration input to the water body in the 35th year due to the Hat Creek Project;
- [H⁺] is the hypothetical H⁺ concentration added to the water body with no neutralization pathways;
- 0.6 is the unneutralized fraction of H⁺ passing the forest canopy;
- CEC is the initial cation exchange capacity (meq m⁻²);
 D is the yearly deposition per m² under the forest
 canopy
 - = 3.15×10^7 s yr⁻¹ x 0.6 x (annual average deposition flux, meq m⁻² s⁻¹)
 - is the initial fraction (before CEC depletion) of H^T deposition which is left unneutralized by the time it reaches the water body.

In the case where $33 \text{ D} \geq \text{CEC}_0$, only H⁺ removal by the forest canopy is taken into account (i.e., the CEC is considered to be completely depleted). The values of the above variables, which were used for calculating the cumulative change in pH for 35 years of acidic deposition for the water systems of interest, are given in Table 16-3.

Using this technique, long-term pH changes are calculated to be -0.15, -0.45, -0.70, -0.03, -0.02, -0.02, and -0.10 for Adams River, Loon Lake, Deadman

TABLE 16-3

DATA INPUTS TO 35-YEAR ACCUMULATION MODEL AND PREDICTED CUMULATIVE PH CHANGES

fu ⁺ } cee	*	[411]	
Case Water System Eq/L mEq/	$m^2 \frac{mEq/m^2}{mEq/m^2} \frac{f^0}{soil}$	$\frac{\text{pH}}{\text{o}}$ $\frac{[\text{ATK}]}{\text{Eq/L}}$	PH35 ApH
1 Adams River 3.37x10 ⁻⁵ 260	14.9 0.333	7.6 7.4x10 ⁻⁴	7.45 -0.15
7.1 Loon Lake 1.44x10 ⁻⁴ 2600	47.3 0.167	8.7 5.9x10 ⁻³	8.26 -0445
12.1 Deadman River 6.48x10 ⁻⁴ 2600	26.8 0.167	8.2 3.0×10^{-3}	7.50 -0.698
10.1 Thompson River 1.11x10 ⁻⁵ 2600	37.8 0.167	7.56 6.8x10 ⁻⁴	7.53 -0.033
11 Clearwater River 7.3x10 ⁻⁶ 52(6.6 0.333	7.56 6.9x10 ⁻⁴	7.54 -0.023
5 Boss & Hendrix 1.13x10 ⁻⁵ 260	6.0 0.333	7.1 5.6×10^{-4}	7.08 -0.023

*Estimated from representative soil types in watershed.

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River, Thompson River, Clearwater River, Boss Creek and Pennask Lake, respectively. Resultant long-term potential pH for the water bodies are given in Table 16-3. These values reflect a high degree of conservatism and are all well within the range capable of supporting existing aquatic systems.

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As stated earlier, the estimated cumulative pH changes for the Hat Creek area water bodies are further biased because of the conservatism included in the assumed initial buffering capacity and other neutralization factor estimates. It is expected that the projected pH changes are so small as to assure almost total absorption of each year's proton deposition contributions. As a result, annual contributions are, in reality, expected to be non-accumulative.

16.8 EFFECTS OF FLUE GAS DESULFURIZATION ON ESTIMATED PH CHANGES

An additional set of calculations was performed to evaluate the potential effects of equipping the Hat Creek power plant with a flue gas desulfurization system (FGD) in terms of reducing potential pH changes in precipitation and water bodies in the study area. Four FGD (scrubber) systems with SO_x removal efficiencies of 48%, 54%, 86% and 90% were examined in this context. These removal efficiencies yield respective SO₂ emission rates at the stack of 170, 150, 44 and 32 megagrams per day. As in the analyses presented in the report, <u>Air Quality Effects and</u> <u>Climatic Effects of the Proposed Hat Creek Project</u> to which this document is an appendix, only sulfur oxide emissions are assumed to be reduced by the FGD systems, although emissions of other contaminants will be affected to some degree as well.

Three types of analyses were performed for both assumed FGD removal efficiencies:

(1) Calculation of annual average hydrogen ion deposition patterns throughout the study area.

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- (2) Calculation of pH reduction in rainfall for the near and far fields.
- (3) Long term cumulative pH reductions in water bodies of the study area.

The results presented in this section should be viewed as semiquantitative estimates, since they are not based on complete new diffusion/deposition modeling analyses. Rather, the predicted effects for sulfur oxides without FGD were scaled to reflect scrubber removal efficiencies and the results recombined with the NO_x and TSP effects to provide new estimates of overall impacts. The reduction in plume rise normally associated with FGD is not accounted for. Thus, the impacts computed for the FGD cases are probably slightly less conservative than those reported for the uncontrolled plant.

Figures 16-1 and 16-2 indicate the estimated geographical distributions of annual average hydrogen ion deposition for the 54% and 90% removal efficiencies, respectively. For the 54% removal case, values above 1.5 x 10^{-9} Eq/m²/sec are restricted to relatively small areas between 25 and 50 km to the northeast of the Hat Creek site and between 20 and 40 km to the east and southeast. The additional effect of increasing scrubber efficiency to 90% is seen in Figure 16-2 with the shrinking of the contours for 0.5 and 1.0 x 10^{-9} Eq/m²/sec and elimination of the 1.5 x 10^{-9} Eq/m²/sec contour.

Near and far field calculations of pH in precipitation (cases 15 and 16 in Section 16.5, respectively) were performed to estimate the effects of the four assumed scrubber systems. The results of these calculations are summarized below.

	Precipitation	pH at Spec	ified Perc	ent SO, Re	: SO ₂ Removal		
	No Control	48%	54%	<u>86 %</u>	90%		
Near Field	4.97	5.05	5.06	5.13	5.14		
Far Field	5.55	5.58	5.58	5.60	5.60		

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Figure 16-1. Isopleths of annual-average hydrogen ion deposition in Eq. $m^{-2} \sec^{-1} v_{10}^{-9}$ for the 54% is the set of the s

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Figure 16-2. Isopleths of annual-average hydrogen ion deposition in EQ m⁻²sec⁻¹x10⁻⁹ for the 90% Scrubber Case.

These results may be compared with the predicted values given in Section I6.5 for uncontrolled power plant emissions. Near and far field annual average pH values of 4.97 and 5.35 were obtained for the case without FGD.

Annual average pH changes predicted for the seven water bodies discussed in Section I6.5 are given in Table I6-4 for the case without scrubbers as well as for the 48%, 54%, 86% and 90% removal efficiencies. Cumulative pH changes for an assumed 35-year project lifetime are indicated in Table I6-5. Overall the changes in pH attributable to the addition of scrubbers are small. But then, the pH changes without FGD were predicted to be relatively small. This analysis should be viewed as only a rough indication of scrubber effects, since NO_x emissions are assumed to be the same as for the uncontrolled plant.

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16.9 SENSITIVITY ANALYSIS

A determination of the effects of varying the magnitudes of some input variables on the calculated values of pH has been presented earlier in this section. For example, in the limiting case of holding $C_{\rm T}$ constant in water body buffering capacity, the results overestimate the reduction in pH from the addition of H ions to a water body. Similarly, proton deposition adsorption by soil and vegetation is conservatively estimated at 80% for low organic matter conditions and from 90% to 98% for soils of higher organic matter content with calcareous bedrock. For the latter soil conditions, it is plausible that the organic matter found in the predominant soil types would absorb all of the proton deposition. Similarly the highly base-saturated soils of the areas within 50 km of the Hat Creek site would probably totally absorb the deposition of H ions from the power plant. The estimates utilized in the calculations probably represent a conservative bias of 50% to 100%. It is, therefore, highly unlikely that any cumulative effects would occur. The cases presented below also show the additional conservative bias incorporated for the specific cases in calculations of pH change.

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TABLE 16-4

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ESTIMATED ANNUAL AVERAGE PH REDUCTIONS FOR ALTERNATE POWER PLANT EMISSION CONTROL SYSTEMS

∎······	Dilution		Existing	pil Change Without	pil Change at Specified Percent SO, Removal				
Case	Mode*	Water Body	pH	Scrubbers	488	551	86%	90%	
1	D	Adams River	7,6	-0.056	-0.047	-0.046	-0.040	-0.039	
5	Ð	Boss Creek	7,1	-0.008	-0.008	-0.008	-0,007	-0.007	
6.1	Ð	Pennask Lake	7.6	-0.073	-0.057	-0.054	-0.042	-0.041	
6.2	L	Pennask Lake	7.6	-0.012	-0.010	-0.010	-0.008	-0,007	
7.1	L	Loon Lake	8,7	-0.153	-0.132	-0.129	-0.114	-0.112	
7.2	L	Loon Lake	8.7	-0.035	-0.030	-0.029	-0.025	-0,025	
7,3	D	Loon Lake	8.7	-0.894	-0.829	-0.817	-0.763	-0,757	
7.4	Q	Loon Lake	8.7	-0.367	-0.325	-0,319	-0.287	-0,284	
10.1	Ð	Thompson River	7.56	-0.008	-0.008	-0,008	-0.007	-0,007	
10.2	a	Thompson River	7.56	-0,002	-0.002	-0.002	-0.001	-0.001	
n	Ð	Clearwater River	7.56	-0,012	-0.010	-0,010	-0.009	-0.009	
12,1	Ð	Deadman River	8.2	-0,369	-0.312	-0.304	-0,259	-0,254	
12.2	Ð	Deadman River	8.2	-0,101	-0.082	-0.079	-0.065	-0,063	

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*D = discharge rate

l. = lake volume

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TABLE 16-5

ESTIMATED 35-YEAR ACCUMULATED DI REDUCTION POR ALTERNATE POWER PLANT EMISSION CONTROL SYSTEMS

Case Water						pH (Perc			
	Water Body	Pilution Model*	Initial f**	Existing 	NO Control	485	54%	865	904
1	Adams River	ß	0.2	7.6	-0.150	-0.129	-0.126	~0.111	-0.110
s	Boss Creek	Ð	0.2	7.1	-0.023	-0.020	-0,019	~0.017	-0.017
6.1	Pennask Lake	Ð	0.2	7.6	-0.096	-0.070	-0.067	~0.049	-0.048
6.2	Pennask Lake	Ł	0.2	7.6	-0,018	-0.013	-0.012	-0.009	-0.009
7.1	Loon Lake	I.	0.1	8.7	-0.445	-0.363	-0.353	-0,296	-0,290
7.2	ioon lake	E.	0.02	8.7	-0.425	-0.337	-0.326	-0.266	-0.259
7.3	loon lake	ą.	0.1	8.7	-1,529	-1.380	-1.359	-1.246	-1.233
7.4	Loon Lake	Ø	0.02	8.7	-1.493	-1.330	-1.307	-1.181	-1.167
10.1	Thompson River	A	0.1	7.56	-0.033	-0.025	-0.024	-0.020	-0.019
10.2	Thompson River	Ø	0.02	7.56	-0.029	-0.022	-0.021	-0.016	-0.016
11	Clearwater Rive	or Ø	0.2	7.56	-0.023	-0.019	-0.018	-0.016	-0.015
12.1	Deadman River	D	0.1	8.2	-0.698	-0.562	-9.544	-0.443	-0.431
12.2	Deadman River	a	0.02	8.2	-0.626	-0.478	-0.459	-0.351	-0.339

* D = discharge rate

L = lake volume

** $f = fraction of H^{\dagger}$ deposition input to water body

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For instance, in developing Case 5 for Pennask Lake, two subcases involving alternative methods for estimating dilutional volume were considered. If the discharge rate of Pennask Creek into Pennask Lake is taken as the dilutional volume, the $[H^+]$ concentration change due to acid deposition is 15% higher than if the lake volume is chosen as the volume available for dilution.

Case 7 for Loon Lake serves as an example of the effect of holding all other variables constant and varying the neutralizing efficiency of the soil by a factor of five. The equilibrium $[H^+]$ of the lake is increased by 31% as the H^+ input is increased by a factor of 5. The effects of varying still other variables from the values chosen in Cases 1 through 14 are discussed below.

(a) <u>Neglect Neutralization of Acidic Species by Atmospheric Ammonia</u> Arguments were presented earlier to support the assumption that dissolution of atmospheric ammonia in rainwater would neutralize at least the amount of H⁺ present in precipitation equivalent to the wet SO₂ and SO^{$\frac{3}{4}$} predicted by the dispersion/deposition model. If this neutralization pathway is neglected, the H⁺ deposition rate is increased by 40% on an annual-average basis for the Adams River watershed. The effect upon the pH change of including wet SO₂ and SO^{$\frac{3}{4}$} depositions would be to increase the predicted ΔpH in Adams River from -0.056, as originally calculated, to -0.076.

(b) Increase Plume Conversion Rate of SO₂ to SO₄⁻¹ from 1% hr⁻¹ to $\frac{2\%}{2\%}$ hr⁻¹

Again taking the Adams River watershed as an example, the original and new (2% hr⁻¹ rate of SO_2 to SO_4^{\pm} conversion) annual H⁺ deposition rates used to calculate ΔpH are, in nEq m⁻² s⁻¹,

, . +		(1% hr ⁻¹) R _i	(2% hr ⁻¹) R _i
	15:		
Dry	so ₂	0.25	0,24
Dry	s0 <mark>=</mark>	0.003	0.006
Wet	NO ⁻ 3	0.371	0.371
Dry	N0-	0.029	0.029
Dry	NOx	0.141	0.141
Sum		0.804	0.787

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The predicted change in the pH would be reduced from -0.056, using the 1% hr⁻¹ conversion rate, to -0.055 using the 2% hr⁻¹ value. In this case, the Δ pH values do not change appreciably in response to small changes in the SO₂ to SO₄² conversion rate.

Similarly the effects on annual H^{+} deposition rates of reducing the SO_2 to SO_4^{-1} conversion rate from 1.0 to 0.5 percent per hour are shown below. Again, units are nEq m⁻² s⁻¹, and again these results are for Adams River.

<u>H⁺as:</u>	(1% hr ⁻¹) R_i	(0.5% hr ⁻¹)
Dry SO2	0.26	0.276
Dry SO4	0.003	0.002
Wet NO ₃	0.371	0.371
Dry NO3	0.029	0 .029
Dry NO _x	0.141	0.141
Sum .	0.804	0.819

The predicted annual average pH change for the 0.5 percent per hour conversion rate is -0.057 compared with -0.056 for the 1.0 percent per hour case. Thus, the results in the far field from the Hat Creek site are quite insensitive to changes in the SO₂ to SO₄ coversion rate.

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(c) Increase NO Dry Deposition Velocity from 1 cm s⁻¹ to 2 cm s⁻¹

Increasing the deposition velocity for NO_x by a factor of two increases the deposition rate (flux) for NO_x by 95%, and decreases the deposition rates for wet and dry NO₃ by 10% and 4%, respectively. To examine the effect upon ΔpH of these changes, the Spring Snowmelt Model will be considered using Adams River statistics. Because this model assumes entrapment of dry deposition for part or all of three seasons in the snow pack followed by its release in the Spring, the effect of increasing the dry NO_x deposition rate should be greatest in this model.

When this change is made to the spring snowmelt model calculations, the resulting change in pH is only 0.01 greater than predicted previously.

(d) Increase NO_3^2/NO_x Washout Ratio from 0.3 to 0.4.

Using Adam River annual statistics to examine the effect of the above increase, the following original and new H^+ deposition rates, in neq m⁻² s⁻¹, and ΔpH result:

	(ratio = 0.3) ^R i	(ratio = 0.4) R_i
Dry SO ₂	0.26	0.26
Dry $SO_4^=$	0.003	0.003
Wet NO_3^-	0.371	0.445
Dry NO3	0.029	0.026
Dry NO _x	0.141	0.104
Sum	0.804	0.838
∆pH	-0.056	-0.058

Thus, a 33% increase in the NO_3^-/NO_x washout ratio has a negligible effect on the ΔpH calculated using the resulting deposition rates. In summary, the factors whose variability most importantly influences the ΔpH calculation are the estimated mixing volume of water and the neutralization efficiency of the soils and vegetation. Because of the assumption

that all sulfur and nitrogen oxides are deposited in their acid form, variations in individual deposition rates, washout ratios, and chemical transformation rates do not have a large effect on pH changes. Only when the total amount of acidic species input to the water systems is varied by a large amount do noticeable variations occur in the ApH calculations. The conservative assumption for soil and vegetation additive proton absorption is also likely to result in overestimates in the predicted values of pH changes.

16.10 UNCERTAINTIES IN THE ANALYSIS

The technical approach described in this Appendix probably represents the first published attempt to develop quantitative estimates of pH reduction in precipitation and in lakes and streams due to emissions from a proposed source. In the absence of any verified methodology, and in view of the importance of British Columbia's waterways in the economic and recreational life of the Province, it has been necessary to adopt procedures that are: (1) based on established physical principles; and (2) designed and implemented in a manner which ensures that errors in the analysis will be in the direction of overestimating the effects of the project on water chemistry in the surrounding area. This conservatism has been incorporated in the formulation of the simulation procedures themselves, as well as the selection of input data for the various phases of the analysis to compensate for the substantial uncertainties inherent in the application of new technologies. The following paragraphs indicate the important aspects of uncertainty in the air quality and water quality analyses. The procedures adopted to ensure conservatism in the air quality and water quality calculations have been identified in the technical discussions in Sections 13.0 through 16.5, and the sensitivity of results to variations in analysis parameters was discussed in Sections 15.3 and 16.9.

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The air quality tasks (see Sections I3.0 through I6.5) include: the formulation and application of diffusion/deposition modeling to estimate ambient concentrations and deposition patterns for primary and secondary plume contaminants within 200 kilometers from the Hat Creek Project site. The principal areas of uncertainty in this regard include:

- Parameterization of a point source diffusion/deposition algorithm for regional-scale applications with limited meteorological data.
- Selection of appropriate wind data.
- Selection of appropriate atmospheric conversion rates.
- Selection of appropriate dry deposition velocities for individual plume species.
- Characterization of appropriate values for scavenging efficiencies for different contaminants and precipitation types.
- Interpretation of available precipitation data for extrapolation throughout the study area.

Water quality tasks (see Sections I6.0 through I6.6) include the formulation and application of techniques to infer values of long and shortterm pH change in selected waterways as a result of the deposition of acidic species from the power plant plume. Principal areas of uncertainty in this process include:

- Identification of the plume constituents capable of affecting acidity in precipitation and receiving bodies of water.
- Understanding the mechanisms for neutralization of acidity in a power plant plume.
- Determination of the role of alkaline species in the soil in neutralizing acid deposition and the pathways by which unneutralized hydrogen ions reach receiving waters.
- Estimation of the volume available in lakes and streams for dilution of deposited H⁺ ions.

• Interpretation of available physical data for receiving waters and extrapolation of such data to areas where the required information is unavailable.

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To compensate for such uncertainties, it has been necessary to choose parameterizations and input data in such a way as to avoid underestimating potential impacts of the Project on surrounding waterways. For example, when several values for a relevant parameter are cited in the technical literature, a range of values was chosen for use in the present analysis including the one which ultimately leads to the largest pH reduction estimate. Additionally, in cases where required data are missing, a range of approximations were used, including those expected to result in overestimated impacts. Important examples include the fraction of H^+ neutralized in the soils near the case study areas, and the volumes of water available for dilution of the unneutralized acid in lakes and streams.

As discussed in Appendix 3, the type of analytical diffusion/deposition model used in this study is not ideal for applications involving regionalscale transport distances. However, the available data is insufficient to warrant selection of a sophisticated numerical modeling approach. Consequently, the HCSDM was used with inputs selected to ensure conservative concentration and deposition predictions. For example, all model receptors were assigned elevations at least as high as the Hat Creek site, whether or not the actual topography was lower, in order to minimize the "miss distance" between the plume and the ground.

Wind speed/wind direction statistics were developed from the record of twice-daily upper air observations at Vernon, British Columbia. While hourly values would be preferable, they are not available at the heights above ground where the Hat Creek plume is expected to reside. The 700 mb wind roses at Vernon and Prince George (the nearest other upper-wind station) are sufficiently similar (see Appendix A) that no significant change in the pH reduction predictions would be expected for an analysis based on Prince George data.

No quantitative estimate of the actual uncertainty in calculated pH changes is possible, since, as noted, this study represents the first known attempt to perform an analysis of this type for an unbuilt source. Furthermore, even with extremely conservative techniques and assumptions incorporated, the results indicate the influence of the proposed Project on acidity in natural water bodies will almost certainly be below the level of significance in terms of effects on the biological communities . of the study area.
17.0 BIOLOGICAL EFFECTS IN AQUATIC ECOSYSTEMS

Biological effects of surface water acidification were first documented in lakes and rivers of Scandinavia.⁴⁵ Comparable changes in aquatic fauna and flora have also been verified in the Sudbury region of Ontario^{8,42} and in the Adirondack Mountains of New York, U.S.A.^{46,47} A great deal of research has been conducted to determine the specific effects of increased acidity on freshwater organisms, with particular emphasis on fish populations.

The range of pH tolerance varies widely among fish species, but all are adversely affected by sufficiently low pH values. Eggs and larvae are more susceptible to acid conditions, and spawning physiology is also affected at pH levels below the tolerance limit for adult fish. Thus, reproduction is curtailed as acidity increases, and the population becomes moribund. Further increases in acidity cause direct adult mortality, and entire populations can disappear rapidly.

Other portions of the freshwater community are similarly affected by acid conditions. Phytoplankton, zooplankton and aquatic macrophytes have distinct changes in species composition and productivity as pH decreases. Fish food organisms are often more tolerant to acidity than fish, so these changes generally have no major effect on the fish populations. The microbial decomposition of organic material in the sediments is also reduced under acid conditions, affecting the accumulation of bottom sediments and the biological recycling of nutrients. In extreme cases, acid conditions may lead to almost complete sterilization of surface water bodies.

Some secondary effects of acidification have also been implicated from damage to freshwater organisms. The biological effects of many toxic substances are known to be enhanced under acid conditions because of increased solubilization. In particular, many trace metals are more soluble at low pH, and thus more available to cause direct physiological damage. The biomethylation of highly toxic mercury compounds is also

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sharply increased at low pH. However, it appears that, in general, these processes have no major effect on freshwater organisms under conditions produced by acid precipitation. These changes mainly occur at pH levels less than 4.5, generally below those which produce direct effects from acidity alone.⁴³

The results of the modeling program provide a conservative basis for assessing the biological effects of acid precipitation in the Hat Creek study area. This section considers the anticipated effects on all major groups of freshwater organisms as a result of increased acidity. In ' addition, the implications of enhancing the biological activity of heavy metals will be addressed.

I7.1 FISH

Fish populations in lakes and streams have been shown to be adversely affected by acid precipitation in water bodies in Norway, 45 Canada, 8,42 and New York.U.S.A. 46,47 Similar effects are also documented for streams receiving acid mine drainage. 48,49 Tolerance to acid conditions varies widely, depending upon the species of fish and its age, size, acclimation history, genetic constitution, and other aspects of the water chemistry to which it is exposed. Effects range from complete extinction of populations to changes in density, structure, growth rates and reproductive physiology. 47

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Tolerance levels of adult fish of many species extend to the 4.5 to 5.0 pH range. ^{48,50,51} In the absence of other adverse conditions, most fish are capable of tolerating a fairly wide range of pH. The tolerance levels are also a function of the stage of the life cycle at which the fish is exposed. Emerging larvae (e.g., salmon alevins) are generally the most susceptible to damage from acid conditions, and adults the most tolerant. Various sources have suggested water quality criteria in the range of pH 5.0 to 6.5 as a minimum, with a maximum of 9.0 to 9.5, as being suitable for the maintenance of viable freshwater fish populations.

It is questionable whether the lower limits in the range of 5.0 to 6.0 are suitable for reproduction of sensitive species, although fully developed young and adults of many species can withstand even lower pH levels.⁵³ Beamish noted that most species ceased reproducing at pH levels higher than those which cause direct fish kills.⁴³ Reproductive failure occurred as females failed to release ova. This phenomenon was related to abnormal calcium metabolism resulting from the increased acidity of the water. Lockhart and Lutz also indicated that calcium dynamics were significant in fishery declines.⁵⁷ Acid waters inhibit the absorption of calcium at the exchange surfaces, and limit the normal ovarian development prior to spawning. Without recruitment the fish populations will ultimately decline and disappear.

Emerging larvae (e.g., salmon alevins) are also vulnerable to acid conditions, and substantial mortality can occur if the hatching period coincides with peak acidification during the spring snowmelt.⁵¹ Other physiological effects are related to the direct toxicity of acid waters. Freshwater fish absorb ions in an active (energy-requiring) process across the gill epithelium. Sodium ions are exchanged for hydrogen ions, and chloride for bicarbonate. Brown trout have been shown to lose their ability to regulate plasma sodium and chloride concentrations in acid water as the increased hydrogen ion activity in the surrounding medium impedes the active uptake of sodium.⁵⁸ Low ion concentration in the receiving water tends to increase the severity of salt imbalances, and thus decrease the tolerance to low pH.⁴⁵ Experimental evidence suggests the possibility of increasing fish survival by applying salts or limestone to low pH lakes with soft water.^{45,59} However, these results cannot yet be extrapolated over a variety of lake conditions.

Sudden changes of pH are also important in influencing the toxicity of acid waters. "Acid shocks" can lead to severe stresses of non-acclimated fishes.^{51,60} However, most evidence of this effect concerns pH decreases of 0.7 units or more, occurring in waters of already low pH (5.5 to 4.3). Under less acid conditions, many fishes appear to tolerate even larger changes in pH with no adverse effects. For example, Weibs.⁶¹

found that largemouth bass fingerlings tolerated rapid changes of pH from 8.1 to 6.0, and 9.2 to 6.1. Harrison⁴⁹ concluded that stream biota in general tolerated brief decreases of pH from 7.0 or 6.0 into the 6.0 to 5.0 range. Huet⁵⁴ also indicated that temporarily higher or lower pH can be tolerated reasonably well by freshwater fishes. It should also be noted that natural surface waters exhibit wide diel fluctuations in pH, related to photosynthetic activity and other factors.⁶²

The fish species of concern in the Hat Creek region include several species which are relatively intolerant of acid conditions (e.g. whitefish, salmon and trout). For these species, the larvae, eggs and reproductive females are the most susceptible to lowered pH. Therefore, the peak episode of acid input to surface waters during spring snowmelt is likely to be the most important for the maintenance of a viable fishery. Other precipitation episodes could affect spawning females, but the levels of change indicated in the modeling program suggest no basis for concern. The projected pH changes of the water bodies of the Hat Creek area is well within the tolerance range for adults of all the species.

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Acid runoff in streams will mix quickly throughout the water column, thus markedly reducing the effective pH decrease. Normal pH values in the selected streams are in the 7.7 to 7.1 range, and maximum pH decreases are projected to be less than 0.199 unit under worst conditions (precipitation event after 7-day stagnation, Table I6-2). These changes in stream chemistry will have no perceptible effect on eggs, larvae, juveniles or adult fishes within the study area.

Demersal eggs of the fishes which reproduce within the lakes will, of course, be on the bottom; juveniles and adults may concentrate at the surface during spring runoff because food is most abundant. The modeling considered only this upper layer when calculating pH changes (upper 1%) so that values calculated should be representative of the worst-case impacts the fish will experience. The model calculations for lakes indicate pH decreases on the order of 0.894 to 0.073 units, with one case (Loon Lake) decreasing by 1.65 units (Table I6-2). Given the respective baseline pH values of 7.6 and 8.7 for Pennask and Loon Lakes, these

changes would not be expected to produce any impact on fish, as populations of these lakes. The resulting pH levels are well above the lower tolerance limits of the species in the region, with respect to hatching, reproduction and normal growth.

Decreases in pH of this magnitude will not stress the resident fishes, even if they occur rather rapidly. Considering the conservative nature of the model, fairly substantial deviations from the expected acid input to the system could still be accommodated with no impacts on the fishery resource.

17.2 PRIMARY PRODUCERS AND DECOMPOSERS

Acid waters influence phytoplankton populations directly and indirectly. Many species of algae, particularly diatoms and green algae, are sensitive to changes in pH. During acidification, a succession of different species and species groups occur, each finding suitable conditions within a particular pH range. Under strongly acidic conditions, the diversity of flora becomes very restricted; biomass may decrease or remain at previous levels, depending upon other ecological factors. ^{51,59,63} Algae may also be adversely affected by acid-induced oligotrophication of water bodies (see below) which limits the nutrients available for photosynthesis and growth.

Species composition of macrophyte communities is altered by acidification, leading to a reduction in species number. Under some circumstances, <u>Sphagnum or similar species dominate the macrophyte community</u>. Large mats of <u>Sphagnum bind calcium and other ions needed for biological</u> production.⁶⁴ Acid also decreases the rate of decomposition of organic material in the sediments by retarding the microbiological processes. Acid-intolerant bacterial decomposers are functionally replaced by less efficient fungi.⁶⁴ Organic matter then accumulates, and recycling of nutrients is inhibited.

Changes in the primary producers and decomposer populations as a result of acid precipitation in the Hat Creek Project area are expected to be undetectable. Variations in surface water pH as a result of predicted

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precipitation pH and pH changes will be less than the normal background fluctuations during the growing season. The projected pH values are well within the range supporting a diverse and balanced community of phytoplankton and macrophytes. For the decomposers, changes in metabolic activity would not be expected until pH declined to approximately 6.0.⁵¹ Since pH decreases in the study area will not even approach this value, no changes are expected in biogeochemical cycling rates.

17.3 ZOOPLANKTON AND BENTHOS

Effects of acid precipitation on zooplankton and benthic organisms include direct lethal effects, delayed moulting and changes in species composition. In food chain relationships, these animals will also be affected by changes in their food sources (phytoplankton, bacteria and detritus); in turn, changes in the macrofauna will affect the fish which utilize these organisms for food.

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The most consistent response of aquatic invertebrates to increasing acidity is a general reduction in species diversity and changes in composition of the resident species. 45, 51, 65, 66 Total biomass may also be decreased, although other ecological interactions can affect this pattern. Hendrey et. al. described a variety of changes in zooplankton and benthos in Scandinavian lakes subjected to acid precipitation.⁵¹ The number of invertebrate species generally decreased with pH: most of these changes occurred beginning at pH of 6.0 to 5.0. However, tolerance varies among species and according to the stage of the life cycle. Gastropods and mayflies seem to be particularly sensitive to acid conditions, generally decreasing below of 6.6 to 5.8. In Canada and Norway, several tooplankton species important as fish food organisms are absent in lakes below pH 6.0. 45,51 Aquatic insects are particularly sensitive to acid conditions during emergence. Thus, acid shocks may be of greatest significance to spring-emerging insects that encounter strong acid from snowmelt runoff.⁵¹ Mortality and delayed moulting have also been observed for some crustaceans at pH 5.5, especially in soft waters.45

With respect to trophic interactions, zooplankton and benthic populations can be affected by reductions in their food supply. Large reductions in phytoplankton and bacterial populations may limit invertebrates, although the direct detrimental effects of acidification may act simultaneously on both levels. Hendrey et. al. concluded that the insect prey organisms may disappear before direct effects occur in fishes. ⁵¹ This is probably true for some preferred food organisms such as <u>Gammarus lacustris</u>. However, as a group, aquatic insects may be more tolerant of acid conditions. ⁴⁸ It is possible that even qualitative changes in fish food populations do not occur before reproductive failure and population decline occur in the fishes.

Available evidence suggests that no changes should occur in aquatic invertebrate populations at pH levels above 6.6 (or even lower). The modeling results indicate a large margin of safety for even the most sensitive species. Further, the spatial and temporal aspects of acidification episodes associated with snowmelt runoff assure that the zooplankton and benthos will be effectively shielded to a large degree from contact with acid waters. During other seasons, pH changes will be within the normal range of fluctuation, except perhaps for very brief periods within a short distance from the air-water interface. No adverse effects are expected on the aquatic invertebrate populations in the Hat Creek Project area, or on their quality as food for higher organisms.

17.4 HEAVY METALS

Toxic substances in surface waters are derived from both anthropogenic and natural background sources. In relation to the biological effects of acid precipitation, heavy metals are the primary substances of concern. In areas of substantial atmospheric emissions of heavy metals (e.g., smelters in Sudbury, Ontario), direct additions of metals to the water bodies is believed to be a major factor affecting aquatic organisms. At lower levels of heavy metal emissions, the principal concerns are related to increased solubilization and biological transformations which increase the biological activity of these compounds under acidic conditions.

Direct toxicity of heavy metals is unlikely to exert major biological effects on water bodies subject to acid precipitation. Although solubility of many metals is increased at low pH, significant increases in biologically active forms do not occur within the pH range required for successful propagation of fish and normal invertebrate populations.^{41,45,67}

Beamish considered the possibility of heavy metal toxicity contributing to the ecological effects of acid precipitation in lakes near Sudbury, Ontario.⁴³ Metal concentrations were generally below levels considered 'safe' for a variety of freshwater organisms, but zinc was present at marginal concentrations for some species. In contrast to the lack of cause-effect relationships between heavy metal concentrations and laboratory studies of fish response, the correlation between pH and fish response was very good. He concluded acidity was the primary factor in reducing fish populations, but synergistic effects of heavy metals at lowered pH may further stress these populations.

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Metals are also known to affect fish orientation processes. For example, zinc and copper can induce an avoidance reaction by Atlantic salmon which could affect spawning migrations.⁶⁸ However, there is no evidence that these effects would occur as a result of mild or moderate acidification of normal water bodies from acid precipitation inputs.

(a) Mercury

Of special concern is the fate of elemental mercury and its related compounds. Worldwide attention has arisen in response to mercurial poisonings such as the Minamata Bay deaths of 46 individuals following prolonged ingestion of methylmercuric-contaminated fish. Mercury contaminations have also been found in other major food resources such as tuna and swordfish.⁶⁸ Scientific investigations of toxic mercury entry into the human food chain have resulted in an understanding of the dynamics and existing levels of mercury in nature. These studies include determination of the indirect sources of mercury, the extent of biological influence within aquatic and terrestrial ecosystems, and the continuation of efforts characterizing mercury's biogeochemical cycle.

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Evidence from this research has prompted governmental agencies in the United States, Canada and Sweden to ensure cessation of direct mercurial pollution of aquatic ecosystems. The problems of mercury toxicity within the environment continue to receive the emphasis of major scientific and legislative activities.

(b) Abundance and Distribution of Mercury

Quantitative determinations of elemental mercury concentrations within the environment have been extensively reported. Nearly all of the data available have been obtained during the past 30 years, the majority of which has centered on the results of investigative efforts occurring during the last 10 years.⁶⁹

As a naturally occurring element, mercury is ubiquitous, being found in minerals, rocks, soil, water, air, plants and animals. Of particular importance is its concentration in aquatic systems which represent the dominant dispersal component of its biogeochemical cycle. Background mercury levels vary widely in unpolluted fresh water lakes, streams, and rivers due in part to the complex ions occurring naturally in these waters. Parameters affecting the movement of mercury include pH, reduction-oxidation potential, temperature, alkalinity and existence of chelating agents (chemical entities capable of binding mercuric ions). Representative mercury concentrations in aqueous forms range from 0.05-0.48 ppb in rainfall, 0.01-0.1 ppb in normal stream, river and lake waters, and 0.01-0.10 ppb in normal ground waters.⁷⁰ In comparison, stream and river waters near mercuric mineral deposits range in concentration from 0.5-100 ppb.

This natural occurrence of mercury in aquatic systems is related to the release of mercurial compounds in soils and bedrock during surface water runoff. Average soils contain approximately 100 ppb of mercury, but the input to water bodies through runoff depends upon the erosion, leaching and dispersion characteristics of rainfall events. Erosion and leaching of mercury due to rainfall and surface runoff have, until recently, been considered the major source of mercury into the environment. Several

major indirect sources of mercury introduction have, however, been identified. Indirect sources of major concern include the disposal of mercury-containing industrial waste and consumer products, and perhaps more importantly, the loss of large quantities of mercury through the burning of fossil fuels and ore smelting operations.

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(c) Biomethylation

The mere presence of elemental mercury is, in itself, not threatening to the environment. It is the fate of chemically reactive ionic mercury, particularly its availability to biomethylation processes and the formation of organic and inorganic compounds, to which so much attention is directed.

The formation of toxic mercuric compounds is largely a result of its chemical behavior in aqueous media, the major transport component of its geochemical cycle. Assuming usual conditions of temperature and pressure for surface water bodies, mercury can be present in as many as three different oxidation states: the metal liquid form normally associated with Hg; the mercurous ion Hg_2^{+2} ; and a mercuric ion Hg^{+2} . The mercuric ion predominates as the stable form in oxidizing conditions and at low pH. In addition, the inorganic divalent mercuric ion is usually required for the biological methylation reaction to methylmercury to proceed.

An indirect source of mercury entry into the environment, fossil fuel combustion, provides an example of the type of chemical equilibria required for biomethylation processes to occur. The combustion of Hgcontaining coal may result in the precipitation of mercury oxide from the atmosphere into an aquatic environment. If the pH value of the system is alkaline or neutral, the mercury will primarily remain in the insoluble oxide form. If, however, the pH of the aquatic system is acidic, the mercury oxide will dissociate resulting in the formation of divalent mercury ions, which would then be available for the process of methylation. Methylation may occur in an aquatic system as the result of enzymatic micro-activity (biomethylation) in bottom sediments, but

has also been shown to occur via alky1-B₁ compounds which serve as alkalating agents to convert inorganic mercury into mono- and dimethyl-mercury.

The existing pH values also play an important role in the dissipation of mercury from an aquatic system. If the pH of an aquatic system remains acidic, an equilibrium between the formation of mono- and dimethylmercury exists, favoring the formation of monomethylmercury. An alkaline or neutral state will favor the formation of dimethylmercury which has a significantly lower vaporization pressure than the monomethyl form of the mercury complex. The decreased vaporization pressure of dimethylmercury results in the dissipition of mercury from the aquatic environment through vaporization.

17.5 ENVIRONMENTAL EFFECTS OF ACID PRECIPITATION AND HEAVY METALS

This chapter has presented a brief overview of the concerns attributed to acid precipitation on biological organisms and the relationships to heavy metal effects. The literature presents many cases which indicate a cause for concern. However, most reports are indicative of environmental conditions much worse than those predicted for the Hat Creek Project. The results of this study suggest that neither direct acid precipitation nor heavy metal related effects from additional proton deposition will occur. Values calculated from the modeling indicate no environmental effects directly or indirectly to the aquatic organisms related to acid precipitation or heavy metals, especially mercury.

Water quality criteria with a pH range from 5.0 to 9.0 have been suggested by several sources to support viable freshwater aquatic systems.^{1,42,43} Results in this study (see Section I6) indicate acid precipitation pH changes well in the middle segment of the above pH range. In fact, all predicted calculations indicate resultant annual and episodic pH values above 7.0 such that productive and viable aquatic systems are maintained. It is generally expected that pH changes in the water bodies of the Hat Creek area will be essentially negligible.

Another potential effect expected of the H⁺ ion contributions from the Hat Creek Project has been the direct acidity of the rainwater. Modeling calculations in this study indicate acid precipitation levels of 5.55 and 4.97 for the long and short-range areas downwind of the Hat Creek facility. These values are higher than most reported in the literature with documentation of no effect on the surrounding aquatic ecosystems. Similarly the pH of precipitation from the Hat Creek Project should have no deleterious effects on the water bodies of the area. Biological effects as a result of these proton contributions will be immeasurably small.

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Finally, the possibility of enhanced heavy metal (especially mercury) availability because of greater solubilities at acid pH levels is also not a problem. As presented earlier and in Section I6, pH levels even for the lowest predicted values will not approach concentrations which will alter the heavy metal loadings. In fact, as several authors have indicated, lowered pH will have greater environmental effects than that resulting from release of heavy metals.^{53,54} By the time pH levels decrease to concentrations affecting heavy metal levels, the biological populations would largely be eliminated. The pH values predicted for the Hat Creek area as a result of proton deposition will not produce changes of a magnitude to alter heavy metal concentrations in the water bodies. As a consequence, there will be no biological effects attributed to heavy metals, including mercury, because of any proton depositions from the Hat Creek Project.

18.0 SUMMARY AND CONCLUSIONS

ERT was requested by B.C. Hydro to undertake a study to determine the potential importance of proton deposition (H⁺ ions) which might result from air emissions of the Hat Creek Project. The major concern regarding the effects of reduced pH precipitation was its ultimate distribution to the aquatic ecosystems of the Hat Creek area. Emphasis was focused on several critical water body receptors and the biological communities within them. Results of this study indicate that the effects of air emissions diffusing and reacting in the atmosphere and eventually reaching surfaces by wet or dry deposition will be negligible near and far from the Hat Creek Project. Further, no adverse effects are expected to occur in the aquatic systems and their biological communities. Detailed conclusions of the study are summarized below.

- Proton donor deposition concentrations will primarily occur in the northeast quadrant from the Hat Creek Project area.
- Maximum deposition rates will be within 50 km of the proposed power plant site.
- Long-range deposition will extend beyond 200 km from the power plant location but will be of very small magnitude.
- Model calculations indicate that precipitation pH levels in the study area may be reduced, at most, to values in the range 4.97 to 5.55. Considerable uncertainty is associated with this result, since many assumptions regarding precipitation chemistry were necessary in the absence of detailed data.
- Small annual and episodic pH changes in the water bodies of concern are predicted; however, these changes will be indistinguishable from natural variations.
- Estimated pH changes will have no effect on the maintenance of viable fishery populations, including reproduction, growth and survival of sensitive species.

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- No adverse effects from the predicted pH changes are predicted for the eggs, larvae, juvenile, and ichthyoplankton segments of the animal populations.
- Net productivity and species composition of the phytoplankton, zooplankton, benthic and aquatic macrophyte communities will not be affected by the expected pH changes.
- Biological effects of trace metals, including mercury, will not be enhanced by any form of deposition from the Hat Creek Project. Synergistic effects of acid and heavy metals will not change from those levels which may presently be occurring in the aquatic systems of the area.

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ADDENDUM A . ANALYSIS OF EXPANDED PRECIPITATION DATA BASE

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(A).1 INTRODUCTION

This addendum presents analyses of precipitation data for a network of 164 precipitation measurement stations in the Hat Creek Project study area. The modeling work described in the main text of Appendix I was based on the use of a substantially smaller data set (34 stations). Furthermore, data in the form of precipitation intensity-duration curves were originally available for only 9 stations, while the new data set incorporates this information for 36 stations. In view of the importance of precipitation statistics in terms of computing deposition patterns for acidic species of the Hat Creek plume, an investigation into possible differences in predicted effects for the two input data sets was considered essential.

Table (A)-1 lists the 164 precipitation and snowfall stations comprising the revised data set. The 36 precipitation intensity stations are listed in Table (A)-2. Figures (A)-1 and (A)-2 are respectively maps indicating the precipitation and intensity stations.

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Another source of precipitation data was examined to determine its possible usefulness in the context of computing pH change effects. A computer plot of estimated annual-average total precipitation for the entire province of British Columbia is presented in a report by Shawinigan Engineering Co., Ltd. (Report S019-1-70, November 1970). No seasonal data and no information regarding intensity, precipitation days, or snowfall fraction, the most important parameters in terms of the present study are provided. Any attempt to derive such statistics from the information provided in the Shawinigan Report was considered highly speculative and generally less appropriate than the analyses of actual measurement data. Consequently, these data are not incorporated.

The remainder of this addendum is organized as follows: Section (A).2 presents plots of annual- and seasonal-average precipitation intensity, number of days with measurable precipitation and fraction of precipitation occurring as snowfall. Section (A).3 provides statistical comparisons of

(A) -2

TABLE (A)-1

LOCATIONS OF 164 PRECIPITATION AND SNOWFALL STATIONS

1. Adams Lake/Skwaam Bay 2. Agassiz 3. Albreda 4. Alexis CK Tautri Ck 5. Allison Pass 6. Alouette Lake 7. Alta Lake 8. Arawana 9. Armstrong 10. Armstrong North 11. Avola 12. Bankier Chain Lake 13. Barkerville 14. Barriere North 15. Beaverdell 55. 16. Blue River 17. Blue River North 18. Boss Mountain 19. Boston Bar 20. Bowron Lake 21. Bralorne 22. Buntzen Lake 23. Chief Lake (not shown) 24. Chilliwack 25. Chilliwack Gibson Rd. 26. Chilliwak R Centre Ck 27. Chilliwak R. Foley Ck. 28. Chilliwack R Mt. Thurston 29. Chilliwack Yale Rd. East 30. Christian Valley 31. Coquitlam Como Lake Ave 32. Coquitlam Lake 33. Cultus Lake 34. Daisy Lake Dam 35. Dome Creek (not shown) 36. Dunster 37. Eagle Bay 38. Enderby 39. Enderby Ashton Ck 40. Falkland Salmon River

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41. Falkland Spanish Lake 42. Garibaldi 43. Gates Station 44. Gillis Crossing 45. Haney Corrl Instn. 46. Haney East 47. Haney UBC RF Admin. 48. Hatzic Prairie 49. Heffley Creek 50. Hells Gate 51. Hemp Ck Clearwater 52. Highland Valley BCCL 53. Highland Valley Lornex 54. Hixon Hixon BCFS 56. Hope A 57. Hope Kawkawa Lake 58. Hope Slide 59. Horsefly BCFS 60. Huntingdon VYE Road 61. Jesmond 62. Joe Rich Ck. 63. Kamloops 64. Kamloops A 65. Kamloops CDA 66. Kamloops Cherry Ck 267. Kamloops Valley View68. Kelowna 69. Kelowna A 70. Kelowna PCC 71. Keremeos 72. Kersley 73. Kettle Valley BCFS 74. Lac Des Roches 75. La Joie Dam 76. Likely
 77. Lillooet 78. Lillooet Cedar Falls 79. Lillooet Seton BCHPA 80. Little Fort

TABLE (A) -1 (Continued)

81. Logan Lake 121. Puntchesakut Lake 82. Loon Lake 122. Puntzi Mountain 83. Lumby Sigalet Rd 123. Quesnel 124. Quesnel A 84. Lytton 125. Quesnel Moose Heights 85. Mabel Lake 86. McBride 4SE 126. Red Lake 87. McBride North 127. Red Pass Mt.Robson Park 88. McCulloch 128. Revelstoke A 129. Richland 89. McGregor 90. McLeese Lake Granite Mtn. 130. Rosedale 131. Salmon Arm 91. McLure 92. Merrit Craigmont Mines 132. Salmon Arm 2 93. Mica Dam 133. Salmon Val Erickson Rd. (not shown) 134. Sardis 94. Mission 95. Mission West Abbey 135. 70 Mile House 96.Monte Lake Paxton Valley136.Seymour Arm97.Mt. Kobau Observatory137.Shalalth98.Mt. Lolo Kamloops138.Sicamous99.Nazko139.Similkameen 99. Nazko 139. Similkameen Mine 100. Nemaih Valley Chilko Lake 140. Sorrento 101. Ochiltree 141. Sorrento East 102. Okanagan Centre 142. Squamish FMC Chem 143. Squamish St. Davids 144. Stave Falls 103. Okanagan Falls 104. Okanagan Mission 105. Oliver 145. Sumas Canal 106. Oliver STP 146. Sumas Prairie 107. 100 Mile House 147. Summerland CDA 148. Summit Lake BCFS (not shown) 149. Tatelkuz Lake 108. Osoyoos 109. Osoyoos West 110. Oyama 150. Tatla Lake BCFS 111. Paradise Valley151. Tatlayoko Lake112. Perchland152. Valemount 112. Peachland 152. Valemount 112. Peachland Brenda Mines 152. Valemount BCFS 114. Pemberton BCFS 154. Valemount North 115. Pemberton Meadows 155. Vavenby 116. Penticton A 156. Vernon 117. Porcupine 157. Vernon Coldstream Ranch 118. Prince George A (not shown) 158. Vernon South 119. Prince George Westwood (not 159. Westwold 120. Princeton 8NE shown) 160. Whistler Roundhouse 161. Williams Lake A 162. Williams Lake Glendale 163. Wineglass Ranch 164. Winfield

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TABLE (A)-2

LOCATIONS OF 36 RAINFALL INTENSITY STATIONS

$\frac{1}{2}$	Agassiz Alouette Lake	21.	Lillooet Seton BCHPA
3.	Alta Lake	23.	McBride 4SE
4.	Barkerville	24.	Mission Abbey West
5.	Blue River	25.	Oliver STP
6.	Buntzen Lake	26.	Pemberton BCFS
7.	Chilliwack	27.	Penticton A
8.	Coquitlam Lake	28.	Prince George A
9.	Daisy Lake Dam	29.	Revelstoke A
10.	Hâney UBC RF Admin	30.	Salmon Arm
11.	Hells Gate	31.	Squamish St. Davids
12.	Hixon	32.	Stave Falls
13.	Hope A	33.	Summerland CDA
14.	Horsefly BCFS	34.	Tatlayoko Lake
15.	Huntingdon VYE Road	35.	Valemount BCFS
16.	Kamloops A	36.	Vernon
17.	Kelowna A		
18.	Kelowna PCC		
19.	Kettle Valley BCFS		
20.	La Joie Dam		

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the values for each parameter interpolated to the HCSDM model receptor locations for the original and expanded data sets. A sample calculation indicating the ultimate effect of using the larger data base, in terms of estimated pH change in one of the sensitive water bodies, is also included.

(A).2 ANALYSIS OF KEY PRECIPITATION PARAMETERS BASED ON THE EXPANDED DATA SET

Figures (A)-3 through (A)-7 show maps of annual and seasonal distributions of precipitation intensity based on the 36-station network in Table (A)-2. The plotted values represent the intensities of 2-year storm events with 24-hour duration. Unlike the analyses of this type prepared on the basis of only 9 stations, the contours representing the 36 stations are not augmented by extrapolation of data for inches per precipitation day, since the expanded intensity data set provides sufficient coverage of the area to allow construction of isopleths without resorting to such approximations.

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Figures (A)-8 through (A)-12 are plots of the annual- and seasonalgeographical distributions of the number of days with measurable (0.01inch or greater) precipitation. Figures (A)-13 through (A)-16 are the annual and seasonal plots of snowfall fraction, i.e., the percent of precipitation as water that occurs as snow. There is no plot of snowfall fraction for the summer season.

The information presented in Figures (A)-3 through (A)-16 was used to estimate precipitation input parameters to the diffusion/deposition model at each of the 256 specific locations chosen as model receptors. These receptors are deployed along 16 radials extending to a distance of 200 km from the Hat Creek site in the 16 wind directions. Section (A).3 provides direct comparisons of these model inputs as derived from the original data analysis in Section I3.4 and from the figures in this section.



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(A).3 COMPARISON OF ORIGINAL AND EXPANDED PRECIPITATION DATA SETS FOR DEVELOPING MODEL INPUTS

Since the original and revised data sets are of different sizes, none of the standard statistical analyses of comparison (e.g., linear regressions) were attempted with the raw measurements. Instead, the annual and seasonal plots of the geographical distributions for both data sets were analyzed to estimate values of the key precipitation parameters at specific locations (receptors) for which the diffusion/deposition model computed wet and dry deposition rates. Regressions statistics were developed for rainfall intensity, precipitation days and snowfall fraction at each model receptor based on the original and revised data sets. Table (A)-3 shows the results of these calculations.

In general, correlation coefficients between the values obtained from the two data sets are fairly consistent between 0.6 and 0.8. Only limited significance should be attached to these statistics, since the analyses based on the enlarged data set caused precipitation parameter values to increase relative to the original analysis at some locations and to decrease at others.

Of perhaps more interest is the effect of changing data sets on the critical precipitation parameters at the specific water bodies chosen for detailed analysis, since the major conclusions resulting from this study are based on calculations for these sensitive locations. Table (A)-4 compares the local values of the three precipitation parameters at these water bodies for the original and expanded data sets. Wet deposition of acidic compounds is expected to increase at locations where the representative rainfall intensity increases and where the number of days with appreciable precipitation increases. Less deposition is expected for locations where the snowfall fraction increases due to the reduced scavenging efficiency of snow related to that of rain on dry deposition patterns.

(A) -23

TABLE (A)-3

REGRESSION STATISTICS COMPARING PRECIPITATION PARAMETERS FOR ORIGINAL AND EXPANDED DATA SETS AT 256 MODEL RECEPTOR LOCATIONS

Parameter	Time Period	Correlation Coefficient
Rainfall Intensity	Winter	0.661
	Soring	0.804
	Summer	0.842
	Fall	0.796
	Annual	0.651
Days of Measurable .		
Precipitation	Winter	0.631
•	Spring	0.593
	Summer	0.369
	Fall	0.686
	Annual	0.625
Snowfall Fraction	Winter	Q.874
	Spring	0.345
	Fall	0.419
	Annual	0.608
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TABLE A-4

A COMPARISON OF THE KEY PRECIPITATION VALUES AT THE CRITICAL WATER BODIES USED IN THE ORIGINAL AND EXPANDED DATA SETS (ANNUAL VALUES ONLY)

	R Inten	ainfall sity (in/m)	Days o Precip	of Meas. Ditation	Snowfa Fractic	11 n (%)
Water Body	Orig.	Expanded	<u>Orig</u> .	Expanded	<u>Orig.</u>	Expanded
Adams River	0.05	0.04	150	135	30	40
Boss Creek	0.10	0.05	150	150	50	60
Pennask Lake	0.01	0.025	75	75	35	40
Loon Lake	0.03	0.04	100	100	30	45
Thompson River	0.05	0.04	125	125	30	35
Clearwater River	0.11	0.05	150	. 150	60	55
Deadman River	0.03	0.03	110	125	30	60

(A) - 25

Examination of Table (A)-4 shows that local precipitation parameters obtained from the new data generally remained near their original values. An incorrect data point in the northeastern part of the study area caused erroneously high precipitation intensity and precipitation day estimates for this area in the original analysis. Thus, the values at Boss Creek and Clearwater Lake decreased in the revised analysis. On the other hand, the addition of more stations caused slight increases at Loon Lake and Deadman River. On a percentage basis, the location where the revised analysis would change projected impacts upward most dramatically appears to be Deadman River.

A sample calculation was performed to demonstrate the ultimate effect of expanding the precipitation data base in terms of computed ΔpH in a water body. Because the effect is expected to be greater at Deadman River, the annual average pH change for this water body was recalculated with the new precipitation inputs. The computation is otherwise identical to that shown for Case 12 in Section I6.4. Using the new information, the computed pH changes for assumed 90% and 98% neutralization (f = 0.1 and 0.02) are -0.458 and -0.135, respectively. These may be compared with corresponding values obtained with the original data of -0.369 and -0.101. Thus, even where the effects are expected to be greatest, the expansion of the precipitation data set will cause only minor revisions to the original ΔpH values. ADDENDUM B DESCRIPTION OF THE ERT PHOTOCHEMICAL KINETICS MODEL

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DISCUSSION OF THE PHOKIN CODE AND ITS APPLICATION

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The PHOKIN (Photochemistry and <u>Kinetics</u>) trajectory model was used to complete the conversion of nitrogen oxide emissions to nitrate in the power plant plume. PHOKIN is a single-cell variable volume photochemical trajectory model. PHOKIN accepts large chemical mechanisms, yet is relatively inexpensive to run. The mechanism used for this study is shown in Table B-1. This shows the involvement of the nitrogen oxides with different classes of hydrocarbons to produce ozone, NO₂ and other products.

Features of the PHOKIN model include:

- Dilution of the air parcel according to a user-specified schedule of mixing heights.
- Entrainment of pollutants aloft as the mixing height grows. Pollutants are entrained using a combination of user-specified and steady-state concentrations. PHOKIN accepts a diurnal schedule of user-specified pollutant concentrations aloft.
- Flexible specification of chemical rate constants. Rate constants can be specified as temperature dependent in the form

 $k = AT^n e^{(B/T)}$

where temperatures (T) are updated from a user's-specified temporal schedule. Photolytic rate constants can be specified with an explicit temporal schedule or as proportional to rate constants with schedules.

- Reaction mechanisms with variable (functional) stoichiometric coefficients. This feature is a powerful technique to minimize the number of species (and computational expense) without using the pseudo-steady-state approximations.
- Surface deposition effects on selected species. PHOKIN allows user specification of surface deposition velocities. These are assumed to apply only to the volume of pollutants in a 10meter thick surface layer. These effects are approximate because the average concentration in the mixed layer is employed

(B) - 1

TABLE (B)-1

	Rate Constant
Reactions	(generally ppm min) at 305 K and 1 Atmosphere
	3 20E 01
	5.202-01
$0 + 0_2 + M = 0_3 + M$	4.12E+06
$0_3 + N0 = N0_2 + 0_2$	2.50E+01
$NO + NO_2 + H_2O = 2HONO$	2.20E-09
$2HONO = NO + NO_2 + H_2O$	1.40E-03
HONO + hv = OH + NO	8.96E-02
OH + NO + M = HONO + M	1.44E+04
$OH + NO_2 + M = HNO_3 + M$	1.44E+04
$OH + CO = HO_2 + CO_2$	4.40E+02
$HO_2 + NO = NO_2 OH$	1.20E+04
$HO_2 + NO_2 = HNO_4$	1.71E+03
$HNO_4 = HO_2 + NO_2$	1.26E+01
$2HO_2 = H_2O_2 + O_2$	3.61E+03
$NO_2 + O_3 = NO_3 + O_2$	5.00E-02
$NO_3 + NO = 2NO_2$	2.70E+04
$NO_3 + NO_2 = N_2O_5$	9.30E+02
$N_2O_5 + H_2O = 2HNO_3$	1.00 E-06
$N_2 O_5 = NO_3 + NO_2$	3.09E+01
$OH + ALKE = AO_2$	8.26E+04
$OH + C_2H_4 = AO_2$	1.20E+04
$AO_{2} + NO = NO_{2} + AO$	2.90E+04

GENERALIZED REACTION MECHANISM

(8)-2

TABLE (B)-1 (Continued)

		Rate Constant
		(generally ppm ⁻¹ min ⁻¹) at
	Reactions	305 K and 1 Atmosphere
22	$AO + O_2 = .5RCHO + 1.5HCHO + HO_2$	4.10E+05
23	0^{2} .3EPOX + .3RCHO	
	$+ 4HO_2 + .4RO_2$	4.28E+04
24	$0 + C_2 H_4 = 2.3 EPOX + .3 RCHO$	
	+ $.4HO_2$ + $.4RO_2$ + $.4CO$	1.10E+03
25	$0_3 \div ALKE = .5HCHO \div .5RCHO$	
	+ .4HD + .4RD $+ .1RO_{2} + 0.3HO_{2}$	
	+ 0.2C0 ₂	3.18E-01
26	$0_3 - C_2 H_4 = HCHO + .8HD$	
	+ $.4HO_2$ + $.2CO_2$	2.50E-03
27	$HD + NO = HCHO + NO_2$	2.90E+04
28	$RD + NO = RCHO + NO_2$	2.90E+04
29	$HD + NO_2 = HCHO + NO_3$	1.90E+04
30	$RD + NO_2 = RCHO + NO_3$	1.90E+04
31	HD + HCHO = OZID	1.00E+01
32	HD + RCHO = OZID	1.00E+01
33	RD + HCHO = OZID	1.00E+01
34	RD - RCHO = OZID	1.00E+01
35	$OH - PA = H_2O + PAO_2$	3.80E+03
36	$PAO_2 + NO = NO_2 + .85PAO + .15RO_2$	2.90E+04
37	$PAO_2 + NO = NTRA$	2.60E+03
38	$PAO = RO_2 + .5HCHO + .5RCHO$	1.40E+05

(B) - 3

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	~~	Rate Constant
		(generally ppm ⁻¹ min ⁻¹) at
	Reactions	305 K and 1 Atmosphere
39	$RO_2 + NO = NO_2 + PAO$	2.90E+04
40	$PAO + O_2 = RCHO + HO_2$	6.70E+04
41	PAO + NO ₂ = .85NTRA + .15RCHO + .15HONO	2.30E+03
42	$OH + RCHO = RCO_3 + H_2O$	2.20E+04
43	$RCHO + hv = RO_2 + HO_2 + CO$	1.40E-04
44	$RCO_3 + NO = CO_2 + NO_2 + RO_2$	2.90E+04
45	$RCO_3 + NO_2 = PAN$	1.70E+04
46	$PAN = RCO_3 + NO_2$	6.88E-02
	0_	
47	$HCHO + hv = 2.HO_2 + CO$	4.60E-04
48	$HCHO + OH = H_2O + HO_2 + CO$	1.60E+04
49	$RO_2 + HO_2 = RO_2 H \bullet O_2$	4.20E+03
50	0 ₃ + WALL = LOSS OF 0 ₃ *	3.12E-04
51	$OH + AR = HO_2 + AC$	1.67E+04
52	OH + AR = ARO	3.33E+03
53	$OH + AC = ARP + HO_2$	4.90E+04
54	$ARO + NO = NO_2 + ARIN$	2.90E+04
55	$ARO + NO_2 = ANO_2$	1.90E+04
56	$ARO \bullet HO_2 = AC + H_2O_2$	1.80E+03
57	ARIN = RO ₂ + HO ₂	1.00E-01
58	WALL + $hv = OH^*$	1.00E-04

TABLE (B)-1 (Continued)

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(3)-4

		Rate Constant (generally ppm ⁻¹ min ⁻¹) at
	Reactions	305 K and 1 Atmosphere
59	$AR + OH = H_2O + ABO$	5.00E+03
60	$ABO + NO = NO_2 + HO_2 + ACHO$	2.90E+04

*Used only in simulation of smog chamber data

TABLE (B)-2

CHEMICAL SPECIES SYMBOL DEFINITIONS

Species	Symbol Designation
94	Alkoxy radical equivalent of A02
10 ₂	Product of OH addition to olefin in the presence of O ₂
AR	Aromatic hydrocarbons
AC	Product of OH addition to aromatic hydrocarbon followed by H atom abstraction by O_2 .
ARO	Product of addition of OH to an aromatic in the presence of O_2
ARP	Product of OH addition to AC followed by H atom abstraction by 0_2 .
ABO	Product of H-abstraction from side chain alkyl group on benzene ring followed by addition of O ₂ to radical formed
ARIN	Intermediate formed from reaction of ARO with NO, forming NO ₂
ACHO	Aromatic aldehyde
ANO ₂	Aromatic nitro compound
OZID	Ozonide
CO	Carbon monoxide
co _z	Carbon dioxide
HD	Criegee intermediate (HCHO ₂)
RD	Criegee intermediate (RCHO ₂)
EPOX	Epoxide formed from 0 atom addition to olefin
HCHO	Formaldehyde
HONO	Nitrous acid
HNO	Nitric acid

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Species	Symbol Designation
hno ₄	Pernitric acid, HO2NO2
HO2	Hydroperoxyl radical
н ₂ 0	Water
H ₂ 0 ₂	Hydrogen peroxide
hu	Photon
м	Any third body, such as N_2 or O_2
NO	Nitric oxide '
NO2	Nitrogen dioxide
NO3	Nitrate radical
N203	Dinitrogen pentoxide
NTRA	Organic nitrate
0	Oxygen atom (ground state)
0 ₂	Oxygen
03	Ozone
OH	Hydroxyl radical
C ₂ H ₄	Ethylene
ALKE	Alkenes (olefins) other than ethylene
PA	Alkanes (paraffinic hydrocarbons)
PAN	Peroxyacetyl Nitrate
PAO	Alkoxy radical formed by PA
PAO ₂	Alkyl peroxy radical from the O ₂ addition to the radical formed by H-abstraction from a paraffinic hydrocarbon
R	Generalized alkyl group (e.g., C ₂ H ₅ , C ₃ H ₇ , etc.)
RCHO	Aldehydes other than formaldehyde

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TABLE (B)--2 (Continued)

Species	Symbol Designation			
RCO3	Acyl peroxy radical			
RO	Alkoxyl radical			
RO2	Alkyl peroxy radical			
ro ₂ h	Product of disproportionation between HO_2 and RO_2			

and the deposition velocities are constant (i.e., not functions of wind speed, surface roughness, soil/vegetation type, etc.).

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- Emission schedule for up to 15 chemical species.
- Efficient numerical integration of the equation with a Geartype algorithm.

These features account for the major phenomena influencing pollutant concentrations in a varying air parcel. PHOKIN's conceptual formulation does not account for wind shear, lateral diffusion or vertical concentration gradients.

For the B.C. Hydro acid precipitation study, several modifications were made to tailor the model to the specific application. These modifications are:

• The chemical mechanism was substantially shortened and all the hydrocarbon reactions neglected. This assumption is justified on the basis of the very low hydrocarbon loading in the geographic area under consideration. The list of chemical reactions and rate constants used are shown in Table 8-3. There is no entrainment of ozone or other pollutants. Ammonia (NH_3) is shown to react with the free nitric acid to form nitrate

 $NH_3 + HNO_3 + NH_4 NO_3$

This reaction is assumed to be rapid and is not rate determining. Thus, the conversion rate used is for NO, to HNO_2 .

 Dilution of the plume was simulated assuming a typical wind speed of 5 m/s. In the calculations, various dilution factors were employed for different time scales. These are summarized in Table B-4.

Upon exit from the stack, the plume is predicted to undergo the greatest rate of dilution with a subsequent rapid decrease in the rate with downwind distance. This is typical behavior for a plume from a point source. These dilution rates were computed for various downwind travel times on the basis of cross sections for Gaussian plumes emanating from a point source and spreading at a rate corresponding to neutral stability.

(B)-9

TABLE (B)-3

CHEMICAL REACTIONS USED IN PHOKIN CODE TO CALCULATE NO \div NO⁻₃ CONVERSION RATES

	Reactions	Rate Constant (ppm ⁻¹ min ⁻¹)
1	$NO_2 + hv = 0 + NO$	3.20E-01
2	$0 + 0_2 + M = 0_3 + M$	4.12E+06
3	$0_3 + N0 = N0_2 + 0_2$	2.50E+01
4	NO \bullet NO ₂ \bullet H ₂ O. = 2HONO	3.17E-05
5	$2HONO = NO + NO_2 + H_2O$	1.40E-03
6	HONO + $hv = OH + NO$	8.96E-02
7	OH + NO + M = HONO + M	1.44E-03
8	$OH + NO_2 + M = HNO_3 + M$	1.44E-03
9	$OH \leftarrow CO = HO_2 + CO_2$	4.40E-05
10	$HO_2 + NO = NO_2 + OH$	1.20E-02
11	$HO_2 + NO_2 = HNO_4$	1.71 E-03
12	$NO_2 + O_5 = NO_3 + O_2$	5.00E-02
13	$NO_3 + NO = 2NO_2$	2.70E+04
14	$NO_3 + NO_2 = N_2O_3$	5.60E+03
15	$N_2 O_5 + H_2 O = 2HNO_3$	1.44E-02
16	$N_2O_5 = NO_3 + NO_2$	2.76E+01
17	$HNO_4 = HO_2 + NO_2$	1.12E+01
18	NH ₃ + HNO ₃ = NTRA	1.00E+05

TABLE (B)-4

Dilution Factor (% hr ⁻¹)	Time Segment	Total Time (min.)
15,840	1.8	1.8
1,044	15.0	16.8
397	17.0	. 33.8
115	50.0	83.8
58	50.0	133.8
32	34.0	167.8

DILUTION FACTORS FOR SELECTED DOWNWIND TRAVEL TIMES

• The photolysis rate constants are kept constant. The constant value chosen for the NO₂ photolysis rate of 0.32 min⁻¹ is just over half of that for a typical cloudless mid-summer day in the Vancouver area.

An initial NO concentration of 600 ppm was assumed for the first phase of the plume calculation. Other key concentrations (in ppm) were NO_2 , 60; CO, 58; H₂O, 1.39 x 10⁵; NH₃, 186. All other concentrations were less than 10⁻⁴ ppm. For each segment of the plume shown in Table B-4, the calculation was carried out using the dilution rate specified in Table B-5. The calculation was expected for each segment using a different distribution rate and the last computed concentrations were used as initial inputs to the subsequent calculation. From these calculations, a relationship was found between NO and HNO₃ formation such that an approximate first order conversion rate of NO and HNO₃ could be deduced. This was found to fall in line with regimes as given in the main text, i.e.

> $R = 0.9 + 6.3 \tau$ $\tau \le 1$ hour $R = 5.7 + 1.5 \tau$ $\tau \ge 1$ hour

where R is the rate of conversion of NO to HNO_3 in $% hr^{-1}$ and t is in hours.